Doctoral Thesis

Catalytic alcohol dehydrogenations with rhodium(I) amino olefin complexes using $O_2$, $N_2O$ and nitrosoarenes as hydrogen acceptors

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Catalytic Alcohol Dehydrogenations with Rhodium(I) Amino Olefin Complexes using O$_2$, N$_2$O and Nitrosoarenes as Hydrogen Acceptors

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Falls Gott die Welt geschaffen hat, war seine Hauptsorge sicher nicht, sie so zu machen, dass wir sie verstehen können.

(Albert Einstein)
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Abstract

This work addresses the problem of the deactivation of the successful transfer hydrogenation catalyst [Rh(trop₂N)(ax-PPh₃)] 1 (trop=5-H-dibenzo[a,d]cyclohepten-5-yl). In order to prevent isomerisation of the amino hydride complex [Rh(eq-H)(trop₂NH)(ax-PPh₃)] 2, which is intermediately formed in the catalytic cycle, two tetradeptate ligands, 3 and 4 (Scheme 1), which has the phosphane donor bound to the bis-olefin amine moiety, were produced. The successful synthesis of 3 and 4 from easily accessible starting material is achieved by several standard organic reactions, which were generally performed in high to excellent yields.

Scheme 1: Synthesised tetradeptate ligands, 3 and 4, and their coordination to rhodium. Reagents: a) [RhCl(COD)]₂; b) AgOTf.

The rhodium complexes of both ligands were used as catalysts for transfer hydrogenation reactions and dehydrogenative coupling reactions. [Rh(tropNHStilbPPh₂)]OTf 5 showed a high initial rate of conversion but was deactivated during the course of the catalytic reaction. [Rh(tropNHtropPhPPh₂)]OTf 6 proved to be a stable catalyst and achieved turn over numbers (TON) up to 9·10⁵ in the transfer hydrogenation of acetophenone.
Transfer hydrogenation catalysts of the type [Rh(trop₂NH)(L₆)]OTf (L₆ = axial ligand) also catalyse the dehydrogenative coupling reaction of primary alcohols with water, methanol and amines to carboxylic acids, methyl esters and amides respectively. The flaw of these reactions is a low atom efficiency caused by the need of an excess of hydrogen acceptor, such as cyclohexanone or methyl methacrylate (MMA). Molecular oxygen was successfully applied as an alternative hydrogen acceptor. In order to prevent contact between the air sensitive catalyst 1 and oxygen, the reaction was performed in the two separated compartments of a fuel cell. The advantages of this system are the production of electric energy and the physical separation of the oxidation of the amino hydride complex 2 to the amido complex 1 and to protons and the reduction of oxygen to water. The molecular catalyst was deposited on carbon black and served as anode catalyst.

Power densities up to 24 mW cm⁻² were obtained at 60 °C using an ethanol (10%), KOH (2 M) solution as fuel. However the performance of the fuel cell decreased rapidly. The reason for the activity loss was found to be the formation of crystalline [Rh(OAc)(trop₂N)(PPh₃)] 7 which is still an active catalyst but the formation of crystals up to 1 µm in diameter decreased the catalytically active surface. The formation of crystalline complexes deposited on the carbon support was suppressed by exchanging the phosphane ligand PPh₃ with P(p-BuPh)₃ (P(p-BuPh)₃ = tris(4-butylphenyl)phosphane) and using a carbon support with a fivefold higher surface.

The improved fuel cell showed a much better recyclability (only 14% activity loss over 3 cycles) and the catalyst loading could be reduced to 0.1 mg cm⁻². Specific activities up to 10⁴ A g⁻¹ (Rh) were measured, which is the highest value ever reported for ethanol electrooxidation.

Beside the successful application of molecular oxygen as hydrogen acceptor in a fuel cell, O₂ from air was also applied as hydrogen acceptor in homogeneous catalysis using the oxygen tolerant catalyst [Rh(trop₂NH)(TMIY)]OTf 8. A series of primary alcohols were dehydrogenatively coupled with water in the presence of 8 to the carboxylic acids. It was found that one oxygen atom from O₂ is converted to water while the other one is transferred to DMSO, which served both; as oxygen acceptor and solvent, to yield Me₂SO₂. Hence, the following net reaction was found for this dehydrogenative coupling reaction (Eq. 1),

\[
R-\text{CH}_2\text{OH} + 2 \text{O}_2 + 2 \text{DMSO} \rightarrow R-\text{COOH} + 2 \text{Me}_2\text{SO}_2 + \text{H}_2\text{O}
\] (Eq. 1)
As described above, O₂ required an oxygen acceptor in order to be successfully applied as hydrogen acceptor. As alternative to oxygen, nitrous oxide (N₂O) was used, which was cleanly converted to molecular nitrogen and water when used as hydrogen acceptor. The formed water could be removed with molecular sieves from the reaction mixture. Under these conditions two primary alcohols were coupled together to esters (Eq. 2). If the reaction was run without molecular sieves but with 1 equivalent of base, primary alcohols were converted to the corresponding carboxylates (Eq. 3).

\[
2 \text{R-CH}_2\text{OH} + 2 \text{N}_2\text{O} \rightarrow \text{R-C(O)O-CH}_2\text{-R} + 2 \text{H}_2\text{O} + 2 \text{N}_2 \quad \text{(Eq. 2)}
\]

\[
\text{R-CH}_2\text{OH} + 2 \text{N}_2\text{O} + \text{t-BuOK} \rightarrow \text{R-C(O)OK} + \text{H}_2\text{O} + 2 \text{N}_2 + \text{t-BuOH} \quad \text{(Eq. 3)}
\]

Various primary alcohols were used as substrates for both catalytic protocols. The corresponding esters and carboxylates were isolated in yields up to 98%.

So far, acids, esters and amides have to date been the only obtained products from the dehydrogenation of primary alcohols with [Rh(trop₂N)(L₄)] type complexes. However, using 2 equivalents of nitrosobenzene as a hydrogen acceptor, the aldehydes could be isolated in up to 96% yield with substrate to catalyst ratio of up to 1000. Nitrosobenzene was found to be reductively coupled to azoxybenzene under the reaction conditions (Eq. 4).

\[
\text{R-CH}_2\text{OH} + 2 \text{PhNO} \rightarrow \text{R-CHO} + \text{PhN=N(O)Ph} + \text{H}_2\text{O} \quad \text{(Eq. 4)}
\]

With ethanol as hydrogen donor, several nitrosobenzene derivates were coupled to the symmetrically substituted azoxybenzene derivatives which were isolated in generally high yields after 2 to 4 hours reaction time using a low catalyst loading.
Zusammenfassung

Diese Arbeit befasst sich mit dem Problem der Deaktivierung des ansonsten sehr erfolgreichen Transferhydrierungskatalysators \([\text{Rh(trop}_2\text{N})(\text{ax-PPh}_3)]\) 1 (trop=5-H-dibenzo[a,d]cyclohepten-5yl). Um die Isomerisierung des Amino Hydrid Komplexes \([\text{Rh(eq-H)(trop}_2\text{NH})(\text{ax-PPh}_3)]\) 2, welcher Teil des katalytischen Zyklus ist, zu verhindern, wurden zwei tetradentate Liganden 3 und 4 (Schema 1), in welchen der Phosphan Donor an den bis-Olefin Amin Teil gebunden ist, hergestellt. Die erfolgreiche Synthese von 3 und 4 aus einfachen Ausgangsstoffen wurde durch mehrere organische Standardreaktionen, welche generell mit exzellenten Ausbeuten durchgeführt wurden, erreicht.

 Schema 1: Synthetisierte tetradentate Liganden, 3 und 4 und deren Koordination an Rhodium. Reagenzien: a) \([\text{RhCl} \text{(COD)})_2]\; b) \text{AgOTf}.

Die Rhodium Komplexe beider Liganden wurden als Katalysatoren für die Transferhydrierung und dehydrierende Kopplungsreaktionen verwendet. \([\text{Rh(tropNHStilbPPh}_2)]\text{OTf}\) 5 zeigte zu Beginn der Reaktionen eine hohe Umsatzgeschwindigkeit, jedoch wurde die Deaktivierung von 5 im Verlauf der katalytischen Reaktion beobachtet. \([\text{Rh(tropNHtropPPh}_2)]\text{OTf}\) 6 ist ein stabiler Katalysator, welcher Umsatzzahlen (englisch: turn over numbers; TON) bis \(9 \cdot 10^5\) in der Transferhydrierung von Acetophenon erreichte.

Leistungsdiichten bis 24 mW cm$^{-2}$ wurden bei 60 °C mit einer Lösung aus Ethanol (10%) und KOH (2 M) als Brennstoff erreicht. Die Leistung der Brennstoffzelle nahm jedoch schnell ab. Der Grund für den Aktivitätsverlust ist die Bildung von kristallinem [Rh(OAc)(trop$_2$N)(PPh$_3$)]$^7$. 7 selbst ist ein aktiver Katalysator aber die Bildung von Kristallen von bis zu 1 μm Durchmesser reduziert die katalytisch aktive Oberfläche. Die Bildung von kristallinen Komplexen auf der Oberfläche des Kohlenstoff Supports wurde durch den Austausch des Phosphan Liganden PPh$_3$ mit P($p$-BuPh)$_3$ (P($p$-BuPh)$_3$ = tris(4-Butylphenyl)phosphan) und den Einsatz eines Kohlenstoff Supports mit fünfmal grösserer Oberfläche vermieden.

Die verbesserte Brennstoffzelle zeigte eine viel bessere Rezyklierbarkeit (nur 14% Aktivitätsverlust bei 3 Zyklen) und die Katalysatormenge konnte auf 0.1 mg cm$^{-2}$ reduziert werden. Spezifische Aktivitäten bis 10$^7$ A g$^{-1}$ (Rh) wurden gemessen, dies sind die höchsten Werte die je für die Ethanol Elektrooxidation berichtet wurden.

Neben der erfolgreichen Anwendung von molekularem Sauerstoff in einer Brennstoffzelle wurde O$_2$ aus der Luft als Wasserstoffakzeptor in der homogenen Katalyse mit dem Sauerstofftoleranten Katalysator [Rh(trop$_2$NH)(TMIY)]OTf 8 eingesetzt. Eine Serie von primären Alkoholen wurde mit Wasser in Gegenwart von 8 dehydrierend zu Carbonsäuren gekoppelt. Ein Sauerstoff Atom von O$_2$ wurde zu Wasser konvertiert während das andere Sauerstoff Atom zu DMSO, welches sowohl als Sauerstoffakzeptor als auch als
Lösungsmittel dient, transferiert; es bildete sich Me₂SO₂. Daher wurde die folgende netto Reaktionsgleichung für diese dehydrierende Kopplungsreaktion gefunden (Eq. 1):

\[
R-\text{CH}_2\text{OH} + 2 \text{O}_2 + 2 \text{DMSO} \rightarrow R-\text{COOH} + 2 \text{Me}_2\text{SO}_2 + \text{H}_2\text{O} \quad \text{(Eq. 1)}
\]

Wie oben beschrieben benötigt O₂ einen Sauerstoff Akzeptor um erfolgreich als Wasserstoffakzeptor eingesetzt werden zu können. Als Alternative zu Sauerstoff wurde Lachgas (N₂O) verwendet, welches, als Wasserstoffakzeptor eingesetzt, sauber zu molekularem Stickstoff und Wasser reagierte. Das gebildete Wasser konnte mit Molekularsiub aus der Reaktionsmischung entfernt werden. Unter diesen Bedingungen wurden zwei primäre Alkohole zum Ester gekoppelt (Eq. 2). Wenn die Reaktion ohne Molekularsiub aber in Gegenwart von einem Äquivalent Base durchgeführt wurde, reagierten primäre Alkohole zu den Carboxylaten (Eq. 3).

\[
2 \text{R-CH}_2\text{OH} + 2 \text{N}_2\text{O} \rightarrow \text{R-C(O)O-CH}_2-\text{R} + 2 \text{H}_2\text{O} + 2 \text{N}_2 \quad \text{(Eq. 2)}
\]

\[
\text{R-CH}_2\text{OH} + 2 \text{N}_2\text{O} + t-\text{BuOK} \rightarrow \text{R-C(O)OK} + \text{H}_2\text{O} + 2 \text{N}_2 + t-\text{BuOH} \quad \text{(Eq. 3)}
\]

Verschiedene primäre Alkohole wurden als Substrate mit beiden katalytischen Protokollen umgesetzt. Die entsprechenden Ester und Carboxylate wurden generell in hohen Ausbeuten bis 98% isoliert.

Bisher waren Carbonsäuren, Carbonsäureester und Amide die einzigen Produkte die durch die Dehydrierung mit [Rh(trop₂N)(LA)] Komplexen erhalten wurden. Wenn jedoch 2 Äquivalente Nitrosobenzol als Wasserstoffakzeptor verwendet wurden, konnten die Aldehyde in bis 96% Ausbeuten mit einem Substrat zu Katalysator Verhältnis von bis zu 1000 isoliert werden. Nitrosobenzol wurde unter den Reaktionsbedingungen reduktiv zu Azoxybenzol gekoppelt (Eq. 4).

\[
\text{R-CH}_2\text{OH} + 2 \text{PhNO} \rightarrow \text{R-CHO} + \text{PhN=NO(Ph)} + \text{H}_2\text{O} \quad \text{(Eq. 4)}
\]

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1 Introduction
1.1 Transfer hydrogenation

Transfer hydrogenation of various unsaturated substrates has proven to be a very useful tool in organic synthesis, therefore a wide range of catalysts were studied.\cite{1} The complexes used as catalysts incorporate various transition metal such as zirconium,\cite{2} hafnium,\cite{2} iron,\cite{1a} ruthenium,\cite{3} molybdenum,\cite{4} rhenium,\cite{5} rhodium\cite{3f, 6} and iridium.\cite{7} High enantioselectivity is often reported with asymmetric catalysts,\cite{3f, 8} whereas non-enantioselective catalysts impresses frequently with very high activity. In fact, turn over number (TON) and turn over frequencies at 50% conversion (TOF\textsubscript{50}) up to $1.8 \cdot 10^7$\cite{3c} and $2.5 \cdot 10^6$ h$^{-1}$\cite{3a, 3b} were reported.

Transfer hydrogenation offers a valuable alternative to classical hydrogenation with highly flammable hydrogen gas using either heterogeneous\cite{9} or homogeneous\cite{10} catalysts. Furthermore, transfer hydrogenation also has the potential to substitute LiAlH\textsubscript{4}\cite{11} or NaBH\textsubscript{4},\cite{12} which produces large amounts of waste, as stoichiometric reducing agents in organic synthesis.

Early transfer hydrogenation catalysts often required refluxing isopropanol (85 °C), which serves as hydrogen donor, as a reaction solvent in order to achieve high TON and TOF\textsubscript{50}.\cite{13} Nowadays the focus has shifted to transfer hydrogenation catalysts which exhibit a high performance at room temperature (25 °C).\cite{6a-c, 14}

As an alternative to isopropanol as hydrogen donor, often a mixture of NEt\textsubscript{3}/HCOOH\cite{14-15} or another readily available alcohol, such as ethanol, can be employed.\cite{6a-c, 16} Ethanol is particularly useful as a solvent and hydrogen donor using [Rh(trop\textsubscript{2}N)(PPh\textsubscript{3})] \textit{I} as transfer hydrogenation catalyst, because acetaldehyde, formed by the dehydrogenation of ethanol, is irreversibly coupled with another molecule of ethanol in the presence of \textit{I} to ethyl acetate.\cite{6a-c}

The advantage of this system is that it overcomes the intrinsic reversibility of the transfer hydrogenation reaction. Consequently unmatched high substrate concentrations, up to 2 M, could be applied, reaching TON and TOF\textsubscript{50} values of up to $9 \cdot 10^5$ and $5 \cdot 10^5$ h$^{-1}$.\cite{6a-c}

Calculation indicated that the dehydrogenation of an alcohol and the reverse reaction, the hydrogenation of a carbonyl function, proceeds via the established Noyori-Morris-mechanism (see Scheme 2).\cite{17}
Scheme 2: Simplified Noyori-Morris-mechanism of the hydrogenation of a carbonyl compound with an amino hydride complex (left to right) and the dehydrogenation of an alcohol with an amido complex (right to left). A concerted transfer of the proton and the hydride takes place. Note that the ketone does not coordinate to the metal centre; the reaction occurs in the outer coordination sphere.

Although 1 has proven to be a very efficient transfer hydrogenation catalyst, it was also demonstrated that the intermediately formed amino hydride complex [RhH(trop$_2$NH)(PPh$_3$)]$^2$ is prone to deactivation by an isomerisation reaction.$^{[6a]}$ This problem is addressed in this work by the synthesis of tetradeionate ligands and their coordination to rhodium. The formed complexes resemble the coordination sphere of 1; however, an isomerisation as described for 2 is avoided due to the ligand design.

### 1.2 Dehydrogenation

As described above, the transfer hydrogenation reaction using alcohols as a hydrogen donor is intrinsically reversible. This reversibility can cause incomplete conversion because an equilibrium between reactants and products is established. To overcome this problem, often a large excess of hydrogen donor is applied,$^{[3c-e, 7a, 7b, 13b, 18]}$ or alternatively the dehydrogenated hydrogen donor is reacted further in order to remove it from the equilibrium.$^{[6a-c]}$ The intrinsic reversibility, often considered a flaw of the transfer hydrogenation, became however, a feature of the reaction type because it allows dehydrogenating various alcohol substrates to carbonyl compounds using established transfer hydrogenation catalyst.$^{[6a-c, 19]}$

The advantage of the catalytic dehydrogenation of an organic substrate would be that it can be performed under mild conditions and it provides an alternative to standard oxidation procedures, which often requires stoichiometric amounts of oxidants$^{[20]}$ which might be toxic and produce large amounts of waste.

Ideally, hydrogen gas is released directly from the catalyst, however for most organic substrates this reaction is thermodynamically unfavored and would require an energy source such as heat$^{[19b]}$ or light$^{[21]}$ and a catalyst which is stable to these conditions. A successful example is the Ru PNP complex from Milstein et al., which dehydrogenates secondary alcohols to ketones releasing molecular hydrogen.$^{[22]}$ A similar complex was found to
dehydrogenatively couple primary alcohols with amines to amides liberating molecular hydrogen.[23]
If hydrogen gas cannot be released from the catalyst, a sacrificial hydrogen acceptor must be used. With the above mentioned catalyst [Rh(trop$_2$N)(PPh$_3$)] $\textbf{1}$ primary alcohols were successfully dehydrogenated and subsequently coupled with water, methanol or amine to the carboxylic acids, methyl ester and amide respectively.$^{[6a, 24]}$ These reactions gave generally excellent yields and were run under relatively mild conditions. However, an excess of hydrogen acceptor, such as cyclohexanone or methyl methacrylate (MMA) had to be employed. Therefore the atom efficiency of these dehydrogenative coupling reactions is quite low.
Although it is possible to regenerate cyclohexanone from cyclohexanol by oxidation with diluted hydrogen peroxide in the presence of 0.1 mol% [Na$_9$(SbW$_9$O$_{33}$)],$^{[6a, 24-25]}$ it is desirable to find an alternative hydrogen acceptor. The requirements of such hydrogen acceptors would be that they are inexpensive and readily available, non-toxic and are not required in an excess. Also the by-products, which are formed by the hydrogenation of the hydrogen acceptor should be non-toxic and require no special waste treatment. Furthermore, the dehydrogenated products should be easily purified from any residual hydrogen acceptor and their hydrogenated by-products.
Most probably the simplest hydrogen acceptor which meets most of the above mentioned requirements is molecular oxygen. Oxygen is readily available from air, non-toxic, and the expected hydrogenated product, water, is unproblematic. Another alternative might be nitrous oxide (N$_2$O), which is a waste product in the industrial synthesis of nitric acid$^{[26]}$ and 6,6-Nylon.$^{[27]}$ Therefore it is relatively inexpensive. Furthermore N$_2$O is non-toxic and the by-products, which are expected to form water and molecular nitrogen, are also unproblematic.
2  Mimicking the coordination sphere of the trop$_2$NH and PPh$_3$ with tetradeinate ligands
2.1 Introduction

It was shown that late transition metals with low oxidation state are efficiently stabilized by the amine diolefin ligand trop$_2$NH (trop = bis(5$H$-dibenzo[a,d]cyclohepten-5-yl) amine).\cite{6a, 28}

The formed late transition metal complexes all adapt a trigonal bipyramidal or a butterfly structure whereas an axial and, depending on the ligands nature, an equatorial ligand completes the structure.\cite{6a, 28a, 28d, 28g}

Rhodium$^I$ complexes of the above described type have proven to be the most promising candidates for catalysis.\cite{6, 24, 28a, 29} Out of a series of [Rh(trop$_2$NH)(L$_A$)]OTf (L$_A$ = axial ligand; OTf = CF$_3$SO$_3^-$) the one complex with PPh$_3$ as axial ligand has proven to be the most active catalyst for transfer hydrogenation. Turn over numbers (TON) up to $9 \cdot 10^5$ and turn over frequency at 50\% conversion (TOF$_{50}$) up to $5 \cdot 10^5$ h$^{-1}$\cite{6a-c} were measured using acetophenone as substrate.

Mechanistic investigations of the catalytic reaction led to the following mechanism: The cationic triflate complex [Rh(trop$_2$NH)(PPh$_3$)]OTf 9 is deprotonated\cite{28d} to the amido complex [Rh(trop$_2$N)(PPh$_3$)] 1. The amido complex 1 then dehydrogenates a primary or secondary alcohol in a Noyori-type mechanism\cite{6a-c, 29-30} to the aldehyde or ketone and forms the amine hydride complex [RhH(trop$_2$NH)(PPh$_3$)] 2. The amine hydride complex 2 then transfers hydrogen to the substrate reforming the amido complex 1.\cite{6a-c, 29} The simplified mechanism is shown in Figure 1.

An advantage of the described catalyst is that it not only dehydrogenates primary alcohols to aldehydes but also couples them in a Tishchenko type reaction to esters.\cite{6a-c, 24, 31} The formed aldehydes are therefore removed from the equilibrium which allows a much lower excess of hydrogen donor than generally reported for other transfer hydrogenation systems.\cite{3c-e, 7a, 7b, 13b,
Indeed, reaction mixtures with substance concentration of up to 2 M in ethanol, which serves as hydrogen donor, were fully converted.\textsuperscript{[6a-c]}

However this catalyst is deactivated over time by isomerisation of 2 as shown in Scheme 3. This isomerisation is caused by base or heat. The formed axial hydride complex 10 was determined to be 40 kcal mol\textsuperscript{-1} more stable than 2 by quantum chemical calculation.\textsuperscript{[6a-c]}

**Scheme 3**: Isomerisation of amine hydride complex 2 triggered by base or heat.

A solution to the problem of catalyst isomerisation could be to bind the triphenylphosphane ligand to the rest of the amine bisolefin ligand system, creating a tetradentate ligand. One idea to do this is to substitute one trop-unit by a stilbene-unit which connects the phosphane-part with the tropNH-part of the ligand (ligand 3). Another way could be to directly connect the phosphane to the trop\textsubscript{2}NH system (ligand 4) or to substitute both trop-units by a stilbene-unit which however would demand to produce a macrocyclic ligand (ligand 11). Figure 2 shows the three proposed ligands.

**Figure 2**: Proposed ligands for mimicking the coordination sphere of trop\textsubscript{2}NH and PPh\textsubscript{3} as ligands.
2.2 Retrosynthetic analysis

2.2.1 Retrosynthetic analysis for ligand 3

The most promising way to successfully synthesise ligand 3 is to first synthesise smaller parts of the ligand which are then connected in the second part of the synthetic route. One good point to connect two smaller parts is the C-N bond of the tropNH-part and the rest of 3. The connection can be achieved by the condensation of the amine to an aldehyde followed by the reduction of the formed imine to the targeted amine,[6a] a reaction sequence known to work well with tropNH₂ and aldehydes.[6a]

The other point to connect two smaller parts is the double bond of the stilbene part of 3, which can be formed by a Wittig reaction.[32] However Wittig reactions are known to form mainly the Z-product in case of aliphatic substituents[32a,33] and a mixture of Z-and E-product in case of aromatic substituents.[32a,33] Since the target product is the E-product, as shown in Figure 2, the standard Wittig reaction was expected to lead to a low yield and would require a difficult separation of the Z-and E-isomers. After a detailed literature search on the selectivity of the Wittig type reactions, the Wittig-Horner reaction was found to suit best for the synthesis of the desired E-isomer.[34]

Principally it should be possible to perform the proposed connecting reactions in any order but the Wittig-Horner reaction requires strong bases, such as BuLi or t-BuOK. If tropNH₂ is reacted with the aldehyde prior to the Wittig-Horner reaction, the considerably acidic NH might be deprotonated first thus requiring a second equivalent of strong base. Furthermore an unpublished experience of former co-workers is that a C-NHtrop-unit is easily decomposed under strong basic conditions. Therefore it was determined to first perform the Wittig Horner reaction followed by condensation of tropNH₂ to a benzylic aldehyde in ortho-position of the formed double bond. Figure 3 summarizes the above made conclusions showing the bonds, which will be formed to put the ligand together and which fragments result from this analysis.

Figure 3: Retrosynthetic analysis with the proposed disconnections made on 3 and the three fragments with which the connections will be made.
Two of the fragments, namely 2-(diphenylphosphino)benzaldehyde $12^{[35]}$ and tropNH$_2^{[36]}$ are already known in the literature. The third compound diethyl 2-formylbenzylphosphonate $13$ cannot be applied as drawn to the Wittig-Horner reaction, because $13$ contains an aldehyde and would react with itself. Therefore the aldehyde must be protected. The most often used protection group for aldehydes are acetals,$^{[37]}$ which are formed by the condensation of an aldehyde and a diol such as ethylene glycol.$^{[35c, 37-38]}$ The phosphonate group can be introduced by the Arbuzov reaction$^{[34b, 39]}$ of triethyl phosphite and the bromide $14$ which can be obtained from the literature known (2-(1,3-dioxolan-2-yl)phenyl)methanol $15^{[38]}$. In Figure 4 the retrosynthetic analysis for diethyl 2-(1,3-dioxolan-2-yl)benzylphosphonate $16$ is summarized.

![Figure 4](image)

**Figure 4**: The retrosynthetic analysis of diethyl 2-(1,3-dioxolan-2-yl)benzylphosphonate $16$.

The bromination of $15$ might pose a problem since most brominating reactions create an acidic milieu in which the acetal protection group could be hydrolysed.$^{[38]}$ Therefore the mild brominating agent dibromotriphenyl-phosphorane$^{[40]}$ was proposed. Dibromotriphenyl-phosphorane can be made *in-situ* from triphenylphosphane and elemental bromine. In Scheme 4 the full synthetic plan for ligand $3$ from commercially available substances is given including the proposed reagents.
Scheme 4: Synthetic plan for ligand 3. Reagents: (a) MeI; (b) ethylene glycol, \( p \)-TsOH; (c) LiAlH₄; (d) PPh₃, pyridine, Br₂; (e) P(OEt)₃; (f) ethylene glycol, \( p \)-TsOH; (g) BuLi, PCIPh₂; (h) acetone, H₂O, \( p \)-TsOH; (i) BuLi; (j) acetone, H₂O, \( p \)-TsOH; (k) NH₂OH, pyridine; (l) Zn, NH₄OAc, aq. NH₃; (m) Na₂SO₄; (n) NaBH₄.

2.2.2 Retrosynthetic analysis for ligand 4

Also the retrosynthetic analysis of the ligand 4 was focused on connecting smaller parts yielding the target molecule. Three suitable bonds for such connections were identified in 4. One is reaction of tropNH₂ with a tropCl-derivative under basic conditions.\(^{[6a, 41]}\) The connection between the central trop-unit and the central phenyl-ring can be made by the palladium catalysed coupling reaction between an aryl boronic acid and a trop-unit which was before brominated at one carbon atom of the C-C double bond.\(^{[42]}\) The last connection can be made between the central phenyl-ring and the PPh₂-part of the ligand. This connection can be achieved by a variety of reaction procedures,\(^{[35b, 35c, 43]}\) therefore it was decided to set this connection to the end of the synthetic route since the last connecting reaction often must tolerate the most functional groups. With many possible synthetic procedures at hand, it was estimated that suitable conditions can be found easier. In Figure 5 the retrosynthetic analysis
of ligand 4 with the three bonds suitable for connecting reactions is shown. Furthermore it also displays the proposed smaller parts which need to be connected.

Figure 5: The three bonds of ligand 4, which are suitable for connecting reactions and the proposed fragments. X is a suitable leaving group and Y is either hydrogen or chlorine, both depending on the chosen conditions to connect the central phenyl-ring to the PPh₂-unit.

As described above, tropNH₂ is known in the literature. Fragment 18 can be made by reacting commercially available dibenzosuberone with bromine followed by an elimination reaction. Starting to build up the new ligand from the centre, first the central trop-unit with the central phenyl ring has to be connected. To do so, X should not be a bromide in order to avoid the oxidative addition reaction between the Pd⁰ catalyst and the aryl halide. Without having a bromide substituent at position X, the synthetic intermediate cannot be reacted easily to a Grignard reagent or an organo-lithium compound which could be reacted with CIPPh₂. Therefore the Pd-catalysed coupling reaction of HPPh₂ and the aryl triflate was proposed. Consequently X was chosen to be a phenolic OH-group, however the phenolic alcohol group needed to be protected prior to the introduction of the boronic acid group, therefore intermediate 19 should be (2-(methoxymethoxy)phenyl)boronic acid, which is known in the literature.

After the first coupling reaction is achieved, the phenolic alcohol group could be deprotected and then turned into an OTf-substituent. After this reaction sequence the ketone of the central trop-unit is reduced and the formed alcohol is turned to a chlorine substituent, which serves as leaving group for the connection of tropNH₂. As final step the HPPh₂ is coupled with the OTf-substituent to yield the desired ligand 4. The full synthetic procedure is summarized in Scheme 5.
Scheme 5: Synthetic plan for ligand 4. Reagents: (a) Br₂; (b) KOH; (c) dimethoxymethane, p-TsOH; (d) BuLi, B(OCH₃)₃, then aq. NH₄Cl; (e) 0.64 mol% [Pd(PPh₃)₄], K₂CO₃; (f) 10% HCl; (g) TF₂O, pyridine; (h) 0.2 mol% [Rh(trop₂NH)(P(OPh)₃)]OTf, 0.2 mol% LiHMDS, EtOH; (i) SOCl₂; (j) tropNH₂, DIPEA; (k) 6 mol% Pd(OAc)₂, 6 mol% dppe, HPPh₂, DIPEA.

2.2.3 Retrosynthetic analysis for ligand 11

Ligand 11 could be synthesised analogous to ligand 3 with the difference that two stilbene units need to be set up instead of one. Furthermore, the ring closure could be obtained by the reductive amination[48] of ammonium with two aldehydes.[48a] The bonds suitable for the connection reaction and the molecules which should be connected are shown in Figure 6.

Figure 6: Retrosynthetic analysis with the proposed disconnections made on 11 and the fragments with which the connections will be made.

16 is the same fragment which will already be made for ligand 3 (see chapter 2.2.1); 23 is known to literature.[49] However the most challenging reaction will be the ring closing by reductive amination. In order to favour the ring closing reaction over dimerization reactions it
was proposed to keep a low concentration of both the bisaldehyde 24 and the ammonium source. This can be accomplished by choosing ammonium acetate as ammonium source which has a low solubility in the chosen solvent. Furthermore a diluted solution of 24 would be added slowly to the reaction mixture. The synthetic procedure for ligand 11 is shown in Scheme 6.

\[ \text{16} + \text{23} \xrightarrow{a} \text{25} \]

\[ \xrightarrow{b} \]

\[ \text{c} \]

\[ \text{11} \]

\[ \xrightarrow{c} \text{24} \]

**Scheme 6**: Synthetic plan for ligand 11. Reagents: a) BuLi, then 23; b) 10% HCl; c) NH₄OAc, NaBH(OAc)$_3$. 
2.3 Synthesis of the ligands and coordination to rhodium(I)

2.3.1 Synthesis of ligand 3

While synthesising intermediate 12 it was found that the isolation of the protected intermediate (2-(1,3-dioxolan-2-yl)phenyl)diphenylphosphane\[35c\] was tedious and led to loss of product. Therefore a one pot synthesis of 12 with direct deprotection of the intermediate was performed. This new procedure was found to be more convenient and gave also a higher yield of the desired product.

The success of the bromination reaction to 14 was strongly dependent on the chosen brominating reagent. Acidic reagents such as PBr\(_3\) did indeed deprotect the aldehyde. Even with the addition of an excess of pyridine the deprotection was observed. The successful preparation of 14 could however be achieved in high yields using the mild brominating agent dibromotriphenyl-phosphorane.\[40\] After the reaction the residue was suspended in hexane whereupon 14 was dissolved and the by-product triphenylphosphane oxide was mostly precipitated and could be filtered of. This procedure simplified the following purification by column chromatography.

The Arbuzov reaction run smoothly with high yield but after the aqueous work-up of the Wittig-Horner reaction a mixture of the protected and unprotected aldehyde was obtained as product. Consequently the obtained mixture of protected and unprotected aldehyde was directly used in the deprotection reaction, but the overall yield was rather low.

Another unexpected problem with the chosen protection group was the synthesis of 15. If it comes in contact with traces of acid it reacts irreversibly to the hemiacetal 1,3-dihydroisobenzofuran-1-ol as shown in Scheme 7.

Scheme 7: Undesired reaction of 15 to the hemiacetal 1,3-dihydroisobenzofuran-1-ol.

Therefore it was decided to use the more acid resistant 5,5-dimethyl-1,3-dioxane as protection group.\[37, 50\] The equivalent to 15 with the newly chosen protection group, (2-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)methanol 26 is already known in the literature\[50\] and could be prepared without difficulty. The following bromination and Arbuzov-reaction were executed without any problems giving diethyl 2-(5,5-dimethyl-1,3-dioxan-2-yl) benzylphosphonate 27
in excellent yield. The subsequent Wittig-Horner reaction formed the stilbene double bond with the correct geometry giving \((E)-(2-(2-(5,5\text{-dimethyl}-1,3\text{-dioxan}-2\text{-yl})\text{styryl})\text{phenyl})\) diphenylphosphane 28 in good yield.

The deprotection of 28 to the aldehyde 17 needed strongly acidic conditions[37] and high dilution of the substrate in order to completely depolymerize the aldehyde function. The imine produced by the condensation of the aldehyde 17 and tropNH₂ proved to be quite sensitive to hydrolysis, therefore the imine was not isolated; instead it was directly reduced to the amine after filtration of the Na₂SO₄.

The overall yield starting from commercially available 2-(2-formylphenyl)acetic acid was 39% over 9 steps.

2.3.2 Coordination of ligand 3 to rhodium(I)

The reaction of 3 with either \([\text{Rh}_2(\mu_2\text{-Cl})_2(C_2H_4)_2]\) or \([\text{Rh}_2(\mu_2\text{-Cl})_2(COD)_2]\) as Rh¹ precursor was fast and yielded a mixture of two isomers of \([\text{RhCl}(\text{tropNHCH}_2\text{stilbPPh}_2)]\) 29 in excellent yield. Abstraction of the chloride ligand of 29 was achieved using AgOTf in a similar procedure as for the preparation of \([\text{Rh(PPh}_3)(\text{trop}_2\text{NH})]\)OTf 9.[6a-c, 28d] Also the OTf-complex 5 was obtained as two isomers. Fortunately one of the two isomers could be characterised by X-ray diffraction revealing the structure of one isomer (Figure 7).

In Table 1 bond lengths and -angles of the crystallised isomer of 5 are compared to complexes of the type of \([\text{M}(\text{trop}_2\text{NH})(\text{LA})]\)OTf, whereas M is a d⁸-transition metal and LA a phosphane ligand.

Comparing the bond lengths and angles around the metal centre with known complexes, the largest difference found is the N-Rh-P angle, which is by about 4° smaller for 5 than for the listed phosphane and phosphole complexes; however the same angle is even smaller for the phosphite complex. Furthermore, it can be seen that the structure of the crystallised isomer of 5 resembles the structure of the other complexes quite well except for the phosphite complex, which however is also quite different to the phosphane complexes. Especially encouraging is that the differences between 5 and \([\text{Rh}(\text{trop}_2\text{NH})(\text{PPh}_3)]\)OTf 9 are almost negligible, which was the original aim of synthesising tetradequate ligands which resemble the coordination sphere of 9 as good as possible.
Figure 7: Ortep plot (at 50% probability) of the structure of one isomer of [Rh(tropNHCH₂stilbPPh₂)]OTf 5. The OTf-anion and most of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C19=C20): Rh1-N1 2.153(3), Rh1-P1 2.258(1), Rh1-ct1 2.038(4), Rh1-ct2 2.023(4), Rh1-C4 2.152(4), Rh1-C5 2.166(4), Rh1-C19 2.136(4), Rh1-C20 2.153(4), C4=C5 1.425(6), C19=C20 1.427(7), N1-Rh1-P1 175.9(1), ct1-Rh1-ct2 138.0(2).

Table 1: Comparison of selected bond lengths and angles of the crystallised isomer of 5 with other complexes of the type [M(trop₂NH)(L)]OTf. [a] TPP = 1,2,5-triphenylphosphole.

<table>
<thead>
<tr>
<th>Complex</th>
<th>5</th>
<th>M = Rh; L_A = PPh₃ (9)</th>
<th>M = Ir; L_A = PPh₃ [6a]</th>
<th>M = Rh; L_A = P(OPh)₃ [6a, 6c]</th>
<th>M = Rh; L_A = TPP [a][51]</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-N1 [Å]</td>
<td>2.153(3)</td>
<td>2.150(2)</td>
<td>2.163(5)</td>
<td>2.147(1)</td>
<td>2.135(2)</td>
</tr>
<tr>
<td>M-P1 [Å]</td>
<td>2.258(1)</td>
<td>2.278(7)</td>
<td>2.284(2)</td>
<td>2.203(6)</td>
<td>2.300(4)</td>
</tr>
<tr>
<td>M-ct1 [Å]</td>
<td>2.038(4)</td>
<td>2.040(2)</td>
<td>2.038(6)</td>
<td>2.074(2)</td>
<td>2.077(2)</td>
</tr>
<tr>
<td>M-ct2 [Å]</td>
<td>2.023(4)</td>
<td>2.075(2)</td>
<td>2.041(6)</td>
<td>2.133(2)</td>
<td>2.067(2)</td>
</tr>
<tr>
<td>C4=C5 [Å]</td>
<td>1.425(6)</td>
<td>1.404(3)</td>
<td>1.46(1)</td>
<td>1.412(2)</td>
<td>1.406(4)</td>
</tr>
<tr>
<td>C19=C20 [Å]</td>
<td>1.427(7)</td>
<td>1.422(4)</td>
<td>1.44(1)</td>
<td>1.396(2)</td>
<td>1.403(4)</td>
</tr>
<tr>
<td>N1-M-P1 [°]</td>
<td>175.9(1)</td>
<td>179.17(6)</td>
<td>178.7(2)</td>
<td>170.88(4)</td>
<td>179.1(6)</td>
</tr>
<tr>
<td>ct1-M-ct2 [°]</td>
<td>138.0(2)</td>
<td>139.9(1)</td>
<td>138.5(3)</td>
<td>145.47(6)</td>
<td>138.2(1)</td>
</tr>
</tbody>
</table>
The crystallised isomer of 5 is actually the isomer which was expected when the ligand synthesis was planned. Unfortunately the exact conformation of the second isomer could not be proven. However by studying a model of the ligand, it is assumed that the ligand is inverted at the nitrogen atom. As shown in Figure 7, the N-H bond of the known isomer points to the front and the N-CH₂ bond points to the back. In the other isomer it is assumed to be just vice versa as shown in Figure 8.

![Figure 8](image-url)

Figure 8: The two isomers of 5. On the left side the crystallised isomer is shown and on the right side the proposed conformation of the other isomer.

Unfortunately the deprotonation of either the chloro-complex 29 or the OTf-complex 5 gave inseparable mixtures of products. Also attempts to form the hydride complex by deprotonation of 29 in the presence of ethanol as hydrogen donor failed. No hydride signal was found in the ¹H-NMR. An explanation for this observation could be that the benzylic CH₂ group is quite acidic and could therefore be deprotonated with a strong base or after deprotonation of the NH-function the complex undergoes an internal C-H activation.

### 2.3.3 Synthesis of ligand 4

The synthesis of intermediates 18 and 19 was accomplished according to the reported procedures.[42, 44, 46] The intermediate 19 was not further purified but directly used after its synthesis. This procedure was chosen because it is known stated that the MOM-protection group of 19 is slowly hydrolysed by the boronic acid function when left at room temperature.[42a] The following four steps, namely the palladium catalysed coupling, the deprotection of the MOM-ether, the conversion to the OTf-compound 21 and the subsequent reduction of the ketone, were performed without problems giving the desired products in high to excellent yields.

For the chlorination of intermediate 30 prior to the coupling of tropNH₂ it was found that highly purified SOCl₂ was needed to produce the chlorinated intermediate in high purity. This allowed skipping the purification procedure of this intermediate, which is potentially sensitive to hydrolysis. tropNH₂ was then reacted with the chlorinated intermediate under basic
conditions yielding intermediate \( \text{22} \) in high yield. Later it was found that \( \text{22} \) could be made by a more convenient procedure using trifluoroacetate as leaving group. Starting from \( \text{30} \) the intermediate \( \text{22} \) could be made in a one-pot reaction first reacting \( \text{30} \) with trifluoroacetic anhydride in the presence of DIPEA then simply adding tropNH₂. The advantages of the new procedure are, beside of the simpler protocol, that the tedious purification of the reagent could be avoided and the yield of the two step reaction was even improved.

The last step, the coupling of HPPh₂ to intermediate \( \text{22} \), proved to be the most difficult. Although the final ligand \( \text{4} \) was obtained once in a good yield of 72%, it was realised that already small changes, such as slightly higher reaction temperature, might decrease the yield drastically. As alternative route to ligand \( \text{4} \), the coupling reaction of HPPh₂ was performed directly after introduction of the OTf-group.

With \( \text{21} \) as substrate, the coupling reaction proved to be much more reliable, giving the new intermediate \( \text{31} \) in high yields. Furthermore the amount of catalyst needed was much lower compared to the similar reaction described above. The next step, reduction of \( \text{31} \) with NaBH₄ to the alcohol intermediate \( \text{32} \), was performed without problems. However, turning the alcohol function in a suitable leaving group prior to the coupling with tropNH₂ posed some problems. Many reagents, such as tosyl chloride or triflic anhydride, oxidise the phosphane function. Finally trifluoroacetate was found to be a suitable leaving group, because tropNH₂ easily substitutes this leaving group and trifluoroacetic anhydride did not attack the phosphane. The one pot reaction could be performed analogous to the above described formation of intermediate \( \text{22} \) in high yield. Scheme 8 summarises the alternative synthetic route coupling first HPPh₂ then tropNH₂ to intermediate \( \text{21} \).

**Scheme 8:** Alternative synthetic route from intermediate \( \text{21} \) to the final ligand \( \text{4} \). Reagents: (a) 2.5 mol% Pd(OAc)$_2$, 2.5 mol% dppe, HPPh₂, DIPEA; (b) NaBH₄; (c) (CF₃CO)$_2$O, DIPEA, then tropNH₂.
The advantages of the new synthetic route are more convenient and better reproducible reaction protocols and a higher yield starting form \(21\); 77\% compared to 65\% by the initially chosen route.

The overall yield starting from the literature known \([42b, 44]\) was 62\%.

Surprisingly 8 conformers of \(4\) were observed by NMR characterisation. Only 4 conformers were actually expected due to the two different trop-units, which both can adopt an endo- and exo-conformation.\([52]\) NMR studies of \(4\) revealed that all conformers belong to the same molecule. Furthermore, reacting the same sample that was analysed by NMR with [RhCl(COD)]\(_2\) yielded clearly the mixture of two isomers of [RhCl(tropNHtropPhPPh\(_2\))] \(33\) (see discussion in the following section). Therefore any possibility of having a sample in which ligand \(4\) is partially degraded was excluded. It is speculated that the 8 conformers observed are originated not only from the inversion of the two different trop units, but also by the inhibited rotation around the bond between the central trop unit and the central phenyl ring.

### 2.3.4 Coordination of ligand 4 to rhodium(I)

The coordination reaction of ligand \(4\) with [RhCl(COD)]\(_2\) needed to be run overnight at room temperature in order to get full conversion. Compared to \(3\), which fully reacts with the same Rh\(_I\) precursor within a few minutes, the coordination reaction is rather slow. However it takes about the same time as the reaction trop\(_2\)NH with [RhCl(COD)]\(_2\).\([6a, 6d, 6e, 28a]\)

Analogous to \(29\) [RhCl(tropNHtropPhPPh\(_2\))] \(33\) was obtained as a mixture of two isomers. Also after removing the chloro-ligand from \(33\) with AgOTf two isomers of [Rh(tropNHtropPhPPh\(_2\))]OTf \(34\) were obtained.

In contrast to \(29\), the chloro-complex \(33\) could be cleanly deprotonated to the amide complex \(35\) using the same reaction conditions as described for [Rh(trop\(_2\)N)(PPh\(_3\))] \(1.\)[6] In contrast to the chloro- \(33\) and OTf-complex \(34\) the amido complex \(35\) was obtained as single isomer. By having a closer look at the coordination of ligand \(4\) to rhodium, it became obvious that the olefinic carbon, to which the PhPPh\(_2\) part is connected to, can be found in two different positions (see Figure 9a).

In former investigations it was found that amido complexes of the type [Rh(trop\(_2\)N)(PR\(_3\))] undergo an inversion at the nitrogen atom.\([6a, 28a]\) It is assumed that a similar inversion at the nitrogen atom takes place in the amido complex [Rh(tropNtropPhPPh\(_2\))] \(35\). In Figure 9b it is shown that the two isomers are converted in one another by such an isomerisation. Therefore
the fast equilibrium (Figure 9b) could be the reason why only one set of signals is found by NMR; however it is not ruled out that one isomer is thermodynamically much more favoured and therefore only one isomer was found.

Figure 9: a) Two possible isomers of [RhCl(tropNHtropPhPPh$_2$)] $33$, the olefinic carbon, to which the phosphane part is connected to, is highlighted. b) The two isomers of the deprotonated complex $35$, which are assumed to be interconverted by inversion of the nitrogen atom.

Adding a hydrogen source, such as hydrogen gas or a primary alcohol, to the amido complex $35$ the hydride complex [RhH(tropNHtropPhPPh$_2$)] $36$ was obtained also as single isomer. The reason for this could be that one of the possible isomers of $35$ reacts preferably with the hydrogen source.

Addition of diluted hydrochloric acid to $in$-$situ$ generated $36$ gave back the chloro-complex, however as single isomer ($37$, see Scheme 9). The OTf-complex could then also be obtained as single isomer $6$ by treating $37$ with AgOTf.

Scheme 9: Synthesis of one isomer of the chloro-complex $37$ from the two isomeric forms $33$ and subsequent treatment of $37$ to get the OTf-complex as single isomer $6$. 

- 20 -
2.3.5 Attempted synthesis of ligand 11

Although described in literature,[49] the synthesis of 23 proved to be inconvenient because under the acidic aqueous conditions needed for the deprotection of the two aldehydes, the target molecule undergoes a series of reactions leading to useless phosphane oxides.[49a] In order to avoid this problem, it was decided to perform the Wittig-Horner reaction with commercially available 2-bromobenzaldehyde. Due to the experience with the synthesis of ligand 3 phosphonate 27 was used instead of 16.

The Wittig-Horner reaction was followed by treating the produced aryl bromide 38, first with BuLi then with half an equivalent of Cl$_2$PPh. However, after deprotection of the aldehydes the reductive amination failed to form 11.

In order to simplify the procedures, the air sensitive phosphanes 39 and 24 were protected with sulphur, however, despite all effort, the ring closing could not be achieved. In Scheme 10 the attempted synthesis of ligand 11 is summarised.

The experience made with the catalyst deactivation of rhodium complexes with ligand 3, which is suspected to be caused by the benzylic CH$_2$-group (see chapters 2.3.2 and 2.4) and the fact that ligand 11 features even two benzylic CH$_2$-groups led to the expectation of even faster catalyst deactivation of metal complexes with ligand 11. Because of this expectation and the synthetic problem the synthesis of ligand 11 was discarded.
Scheme 10: Attempted synthesis of ligand 11. Reagents: a) BuLi, then 2-bromobenzaldehyde; b) BuLi, then 0.5 eq. Cl₂PPh; c) 10% HCl; d) NH₄OAc, NaBH(OAc)₃; e) S₈; f) 10% HCl; g) NH₄OAc, NaBH(OAc)₃.
2.4 Comparison of the catalytic behaviour of the new complexes compared to [Rh(trop$_2$NH)(PPh$_3$)]OTf 9

The original goal of the synthesis of the tetradentate ligand was to mimic the coordination sphere of the catalyst [Rh(trop$_2$N)(PPh$_3$)] 1 in order to maintain its high TON and TOF$_{50}$ and additionally inhibit the isomerisation of the hydride complex 2 as described above. Therefore the new complexes were tested in transfer hydrogenation and dehydrogenative coupling reactions.

2.4.1 Transfer hydrogenation

The highest TON and TOF$_{50}$ with the catalyst 9 were achieved in the transfer hydrogenation reaction of acetophenone in ethanol under basic conditions. Therefore this reaction type was the first tested with the new catalysts. In Table 2 the obtained results are summarised.

With catalyst precursor 5 a deactivation over time can be observed. The catalyst has a very high turnover frequency at the beginning, which then decreases fast (see Table 2, entries 1-3). As described in chapter 2.3.2 the deprotonated form of catalyst precursor 5 could not be isolated, however a mixture of products was observed. Therefore it is likely that the catalyst was decomposed under the catalytic conditions. Consequently the conversions with higher substrate to catalyst ratios were low.

On contrary, the turnover frequency for catalyst precursor 34, which consists of 2 isomers, seems to increase over time (entries 6-8). A reason for this could be that one isomer is inactive and first needs to be deprotonated and then isomerise to the catalytically active species. Unfortunately with high substrate to catalyst ratio the conversion is still low.

The single isomer catalyst precursor 6 was found to be widely superior to the other two tested catalysts. Both the TON and the rate of conversion are higher, it even matches the high TON reported for [Rh(trop$_2$NH)(PPh$_3$)]OTf 9. Although it would be expected that the mixture of the two isomers would be converted to the active isomer under catalytic conditions, the results show clearly that it is worth to prepare the single isomeric form before using it as catalyst.
Table 2: The results of the transfer hydrogenation of acetophenone in ethanol with the newly synthesised catalysts. Reaction conditions: 2 M acetophenone in ethanol, 1 mol% K$_2$CO$_3$, catalyst specified below. [a] The conversion was determined by the ratio of the integrals of the $^1$H-NMR signals of the CH$_3$-group.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>S/C</th>
<th>Time (h)</th>
<th>Conversion$^{[a]}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>$10^4$</td>
<td>0.5</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>$10^4$</td>
<td>1</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>$10^4$</td>
<td>2</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>$10^5$</td>
<td>24</td>
<td>34</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>$10^6$</td>
<td>48</td>
<td>17</td>
</tr>
<tr>
<td>6</td>
<td>34</td>
<td>$10^4$</td>
<td>0.5</td>
<td>26</td>
</tr>
<tr>
<td>7</td>
<td>34</td>
<td>$10^4$</td>
<td>1</td>
<td>77</td>
</tr>
<tr>
<td>8</td>
<td>34</td>
<td>$10^4$</td>
<td>2</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>9</td>
<td>34</td>
<td>$10^6$</td>
<td>48</td>
<td>18</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
<td>$10^4$</td>
<td>0.5</td>
<td>99</td>
</tr>
<tr>
<td>11</td>
<td>6</td>
<td>$10^4$</td>
<td>1</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>$10^6$</td>
<td>48</td>
<td>91</td>
</tr>
</tbody>
</table>

Beside of acetophenone also benzophenone, ethyl cinnamate and benzalacetone were tested as substrates under transfer hydrogenation conditions; the results are shown in Table 3.

The results of the transfer hydrogenation of benzophenone are similar to the one of acetophenone. Using catalyst precursor 5 the rate of conversion is very high at the beginning, but then slows down fast, indicating catalyst decomposition. Also 6 proved to be the more efficient catalyst precursor than 34, which is made of two isomers.

The reduction of the C=C double bond adjacent to an ester function was already known to proceed slower than the reduction of a ketone.$^{[51]}$ Therefore it is not surprising that catalyst precursor 5 only reached a low conversion, as shown in entry 6 of Table 3, because of its deactivation. However applying 34 or 6 very high conversion were obtained which even exceeded largely the reported conversion of 52% using the standard [Rh(trop$_2$NH)(PPh$_3$)]OTf 9.$^{[51]}$
Table 3: The results of the transfer hydrogenation of benzophenone, ethyl cinnamate and methyl geranate. Reaction conditions: 2 M substrate concentration in ethanol, 0.1 mol% catalyst, 1 mol% K₂CO₃. [a] The conversion was determined by GC.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Substrate</th>
<th>Time</th>
<th>Conversion [a] [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>benzophenone</td>
<td>10 min</td>
<td>31</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>benzophenone</td>
<td>20 min</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>benzophenone</td>
<td>30 min</td>
<td>93</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>benzophenone</td>
<td>50 min</td>
<td>97</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>benzophenone</td>
<td>90 min</td>
<td>98</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>ethyl cinnamate</td>
<td>18 h</td>
<td>32</td>
</tr>
<tr>
<td>7</td>
<td>34</td>
<td>benzophenone</td>
<td>10 min</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>34</td>
<td>benzophenone</td>
<td>20 min</td>
<td>53</td>
</tr>
<tr>
<td>9</td>
<td>34</td>
<td>benzophenone</td>
<td>30 min</td>
<td>69</td>
</tr>
<tr>
<td>10</td>
<td>34</td>
<td>benzophenone</td>
<td>50 min</td>
<td>92</td>
</tr>
<tr>
<td>11</td>
<td>34</td>
<td>benzophenone</td>
<td>90 min</td>
<td>99.5</td>
</tr>
<tr>
<td>12</td>
<td>34</td>
<td>ethyl cinnamate</td>
<td>18 h</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>13</td>
<td>6</td>
<td>benzophenone</td>
<td>10 min</td>
<td>32</td>
</tr>
<tr>
<td>14</td>
<td>6</td>
<td>benzophenone</td>
<td>20 min</td>
<td>64</td>
</tr>
<tr>
<td>15</td>
<td>6</td>
<td>benzophenone</td>
<td>30 min</td>
<td>84</td>
</tr>
<tr>
<td>16</td>
<td>6</td>
<td>benzophenone</td>
<td>50 min</td>
<td>98</td>
</tr>
<tr>
<td>17</td>
<td>6</td>
<td>benzophenone</td>
<td>90 min</td>
<td>99.5</td>
</tr>
<tr>
<td>18</td>
<td>6</td>
<td>ethyl cinnamate</td>
<td>18 h</td>
<td>&gt;99.9</td>
</tr>
</tbody>
</table>
The substrate benzalacetone contains two different functions which could both be reduced; a ketone and, adjacent to the carbonyl function, an olefin. Consequently the question of selectivity aroused. However, as shown in Figure 10, none of the newly synthesised catalysts selectively reduced benzalacetone to either the allyl alcohol or the saturated ketone. This finding is consistent to the result reported for [Rh(trop$_2$NH)(PPh$_3$)]OTf $^9$ which also showed no selectivity but contrasts strongly with the quite similar [Rh(trop$_2$NH)(TPP)]OTf (TPP = 1,2,5-triphenylphosphole) which strongly favoured the formation of the allyl alcohol.$^5$1
2.4.2 Dehydrogenative coupling reaction

Related to the transfer hydrogenation is the dehydrogenative coupling reaction, in which hydrogen is abstracted from a primary alcohol substrate. The produced aldehyde is then coupled in a Cannizzaro-type reaction with water to the corresponding acid or with an alcohol to the corresponding ester.[6a, 24]

\[ \text{[Rh(trop}_2\text{N)}(\text{PPh}_3)] \text{ I generated \textit{in-situ} by the deprotonation of [Rh(trop}_2\text{NH)}(\text{PPh}_3)]OTf 9 is known to efficiently catalyse both, the dehydrogenation of primary alcohol and the subsequent Cannizzaro reaction.}\]

Therefore it is worth testing the newly synthesised complexes as catalyst for the dehydrogenative coupling reaction of primary alcohols to acids and methyl ester under the same conditions described for [Rh(trop}_2\text{NH)}(\text{PPh}_3)]OTf 9.[6a, 24] The results obtained using the newly synthesised complexes as catalysts for the dehydrogenative coupling of primary alcohols with water to acids are summarised in Table 4.

Table 4: Results obtained for the dehydrogenative coupling reaction of primary alcohols with water to the acids. Reaction conditions: 5 eq. cyclohexane, 66 eq. H₂O, 1.2 eq. NaOH, catalyst and substrate specified below reaction time: 20 hours. [a] all yields refer to isolated products; the identity of the products was determined by ¹H and ¹³C NMR spectroscopy.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Substrate</th>
<th>S/C</th>
<th>Yield[^a] [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>benzyl alcohol</td>
<td>10³</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>benzyl alcohol</td>
<td>5·10³</td>
<td>54</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>1-octanol</td>
<td>10³</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>34</td>
<td>benzyl alcohol</td>
<td>10³</td>
<td>81</td>
</tr>
<tr>
<td>5</td>
<td>34</td>
<td>benzyl alcohol</td>
<td>5·10³</td>
<td>80</td>
</tr>
<tr>
<td>6</td>
<td>34</td>
<td>1-octanol</td>
<td>10³</td>
<td>92</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>benzyl alcohol</td>
<td>10³</td>
<td>77</td>
</tr>
<tr>
<td>8</td>
<td>6</td>
<td>benzyl alcohol</td>
<td>5·10³</td>
<td>81</td>
</tr>
<tr>
<td>9</td>
<td>6</td>
<td>1-octanol</td>
<td>10³</td>
<td>93</td>
</tr>
</tbody>
</table>

With catalyst precursor 5 high yields are only achieved with high catalyst loadings. Using 0.02 mol% the yield dropped remarkably (entry 2). Applying the other two complexes, 34 and 6, high yields of the products were isolated even with a low catalyst loading (entries 5 and 8). This finding is once again a confirmation of the observed decomposition of 5 under basic conditions as described in the previous sections.
The differences between the results obtained with the catalyst precursors 34 and 6 are quite small and probably insignificant. A possible reason for this could be that under the strongly basic conditions the two isomers of 34 are fast converted to the active isomer. Consequently no difference in the obtained yields would be expected.

For 0.1 mol% [Rh(trop2NH)(PPh3)]OTf 9 benzoic acid and octanoic acid were obtained in 92% and 89% yield respectively.\textsuperscript{[6a, 24]} The yields obtained with the newly synthesised catalysts are comparable or slightly below the results obtained with 9. However, applying catalyst precursor 34 or 6 showed that high yields could also be obtained with lower catalyst loading.

Besides the coupling with water, also the performance of the coupling reaction with methanol was compared to the standard [Rh(trop2NH)(PPh3)]OTf 9. The conversions obtained are listed in Table 5.

\textbf{Table 5}: Results obtained for the dehydrogenative coupling reaction of primary alcohols with methanol to the methyl esters. Reaction conditions: 5 eq. cyclohexanone, 10 eq. methanol, 5 mol\% K$_2$CO$_3$, 0.1 mol\% catalyst (specified below). [a] conversion determined by GC; [b] S/C = 10$^4$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Substrate</th>
<th>Time [h]</th>
<th>Conversion to methyl esters$^{[a]}$ [%]</th>
<th>Conversion to aldehyde$^{[a]}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>benzyl alcohol</td>
<td>2</td>
<td>93</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>benzyl alcohol</td>
<td>3</td>
<td>96</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>5$^{[b]}$</td>
<td>benzyl alcohol</td>
<td>24</td>
<td>98</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>1-octanol</td>
<td>4</td>
<td>84</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>34</td>
<td>benzyl alcohol</td>
<td>4</td>
<td>66</td>
<td>26</td>
</tr>
<tr>
<td>6</td>
<td>34</td>
<td>benzyl alcohol</td>
<td>8</td>
<td>68</td>
<td>24</td>
</tr>
<tr>
<td>7</td>
<td>34$^{[b]}$</td>
<td>benzyl alcohol</td>
<td>24</td>
<td>31</td>
<td>51</td>
</tr>
<tr>
<td>8</td>
<td>34</td>
<td>1-octanol</td>
<td>4</td>
<td>94</td>
<td>2</td>
</tr>
<tr>
<td>9</td>
<td>6</td>
<td>benzyl alcohol</td>
<td>5</td>
<td>29</td>
<td>68</td>
</tr>
</tbody>
</table>

In contrast to the results reported above, the performance of 5 is the best of the tested complexes and even matches the high conversion reported for 9.\textsuperscript{[6a, 24]} Furthermore it was also possible to obtain high conversions with a low catalyst loading applying catalyst precursor 5. This result and the normally observed high initial conversion rate were encouraging to further develop ligand 3 in a way that catalyst decomposition would be suppressed.
Applying catalyst precursor 34 large amounts of benzaldehyde as by-product were found. With lower catalyst loading (entry 7) or with the single isomer catalyst 6 (entry 9) benzaldehyde was even the main product observed. A possible explanation is that 34 and 6 are much less active catalysts for the Tishchenko reaction than expected. However this effect is only observed for benzyl alcohol but not for the aliphatic alcohol 1-octanol.
2.5 Attempted synthesis of a tetradeionate ligand similar to 3 with protected benzylic position

As described in the previous chapters the amide of the catalyst precursor 5 could not be isolated because it rapidly decomposed and consequently the catalytic system was not able to maintain the initial high rate of conversion. The benzylic CH₂-group was suspected to be involved in the degradation process. Therefore the idea to substitute the two benzylic protons by alkyl groups arose. This alkyl groups would be required to be as small as possible in order to not interfere with the adjacent catalytic active centre of the catalyst. Therefore it was chosen to either use two methyl-groups or a cyclopropyl-group.

A thorough literature search on how to synthesise a quaternary benzylic carbon, which is furthermore bound to an amine function, yielded the reduction of a nitrile-group with Grignard or organ lithium reagents in the presence of either Ti(OiPr)₄[53] or anhydrous CeCl₃.[54]

In Scheme 11 this key transformation for the modified ligand is shown.

Scheme 11: Possible synthetic procedures to obtain a quaternary carbon next to an amine function.

A suitable starting material would be commercially available 2-(bromomethyl)benzonitrile. The bromide was reacted directly to the phosphonate 43 by the Arbuzov reaction as described in literature.[55] 43 was then coupled with 2-(diphenylphosphino) benzaldehyde 12 by the Wittig Horner reaction to obtain stilbene 44. In order to avoid side reactions of BuLi with the nitrile group, in-situ generated lithium diisopropyl amide (LDA) was used as base.

Unfortunately the subsequent reduction of the nitrile group failed with any of the above mentioned conditions. Therefore the transformation of the nitrile group was performed at the very beginning of the synthetic pathway even though this decision required more synthetic
steps including the use of an amine protection group and a radical bromination reaction. Then the standard synthetic pathway with Arbuzov- and Wittig-Horner-reaction would be followed. Subsequently the amine group would be deprotected and reacted with tropCl. In Scheme 12 the proposed synthetic pathway is described.

Scheme 12: Proposed synthetic pathway yielding ligand 48. Reagents: a) Ti(OiPr)4, EtMgBr, then BF3; b) Boc2O, I2; c) NBS, 10 mol% AIBN; d) P(OEt)3; e) LDA, then 12; f) 10% HCl; g) tropCl, DIPEA.

The free amine produced with the introduction of the cyclopropyl group slowly decomposed, therefore after distillation the Boc protection group was immediately introduced. The bromination and subsequent Arbuzov reaction could be performed without problem. Unfortunately the Wittig-Horner reaction with the phosphonate 46 failed repeatedly under various conditions.

Another approach was to simply build a ligand with the amine function directly connected to one phenyl ring of the stilbene-part. The synthesis was started with the literature known tert-butyl (2-(bromomethyl)phenyl)carbamate 49 which was turned by the Arbuzov-reaction in high yields into the phosphate 50. However, the Wittig-Horner reaction failed also with 50 and it was concluded that the Wittig-Horner reaction does not tolerate Boc-protection group. In Scheme 13 the tested synthetic pathway is displayed.
Scheme 13: Tested synthetic pathway to produce a tetradentate ligand similar to 3, but without the benzylic CH₂-group. Reagents: a) P(OEt)₃; b) LDA, then 12; c) 10% HCl; d) tropCl, DIPEA.

Since the Wittig-Horner reaction of a phosphonate substrate having a Boc-protection group proved to be a dead end, the synthetic pathway needed to be altered again. The new approach started with the synthesis of a phosphane stilbene with a methyl ester function in the position of the NH-Boc or the nitrile group in the previous approaches. The methyl ester would then be treated with two equivalents of Grignard reagents to furnish a tertiary alcohol 51. The alcohol would then be turned into a leaving group and finally would be reacted with tropNH₂. Scheme 14 shows the outline of the new approach starting from literature known methyl 2-((diethoxyphosphoryl)methyl)benzoate.²⁵⁷

Scheme 14: New approach to synthesise a ligand similar to 3 with the two benzylic protons exchanged for methyl groups. Reagents: a) LDA, then 12; b) MeMgBr; c) TsCl, DIPEA, then tropNH₂.

Although LDA and low temperature were applied in the Wittig-Horner reaction, some side reactions took place and aldehyde 12 was not fully converted. However, the desired product could be isolated in low yield. The subsequent Grignard reaction could be performed without problems. However, transforming the alcohol function into a leaving group yielded a terminal olefin. The olefin was formed under the reaction conditions by a subsequent elimination reaction after introducing the leaving group.

As all approaches failed, the synthetic path for 3, which worked with only minor adjustments, was reconsidered: tropNH₂ was condensed with the aldehyde 17 and the intermediate imine was reduced to the finished ligand (see chapter 2.3.1). In order to introduce two methyl-groups at the benzylic carbon, it would be necessary to condensate tropNH₂ to the methyl ketone followed by treating the formed imine with MeMgBr or MeLi.²⁵⁸
The ketone 53 can be produced from commercially available 2'-methylacetophenone, following the standard synthetic pathway: Protection, radical bromination, Arbuzov then Wittig-Horner reaction and finally deprotection as shown in Scheme 15.

Scheme 15: Proposed synthesis for ligand 52 by condensation of tropNH₂ to a ketone. Reagents: a) 2,2-dimethyl-1,3-propanediol, TsOH; b) NBS, AIBN; c) P(OEt)₃; d) BuLi, then 12; e) 10% HCl; f) tropNH₂, TsOH, 4 Å molecular sieves, then MeMgBr.

All synthetic steps till intermediate 53 were executed in high yields without problems. However, the last step, the condensation of the ketone 53 with tropNH₂, failed; no formation of the imine intermediate was observed and addition of the methyl Grignard reagent to the reaction mixture formed the previously prepared tertiary alcohol 51.

Unfortunately the synthesis of a ligand without benzylic hydrogen atoms needed to be discarded because all attempts to synthesise it led to a dead end.
2.6 The phosphane-olefin-alcohol intermediates as ligands for rhodium(I)

Although all synthetic attempts described in the previous section failed to produce the targeted ligands, they yielded a lot of new substances. One of them, the alcohol 51, is of particular interest, because it can also be used as ligand for rhodium(I). No tridentate ligand having a phosphane, olefin and alcohol coordination side could be found in literature. Also examples of complexes with a phosphane, olefin and oxygen coordination side, not even delivered from the same ligand, are rare. However, 51 nicely reacted with [RhCl(COD)]$_2$ yielding [RhCl(OHMe$_2$StilbPPh$_2$)] 57.

Similar to 51, the intermediate 32 in the total synthesis of 4 has a phosphane, olefin and alcohol coordination side. Therefore also 32 was reacted with [RhCl(COD)]$_2$ giving the complex [RhCl(OHtropPhPPh$_2$)] 58. From both complexes the chloro ligand could be abstracted with AgOTf giving the corresponding OTf-complexes 59 and 60 (Scheme 16).

**Scheme 16**: Synthesis of rhodium complexes with a phosphane, olefin and alcohol coordination side. Reagents: a) [RhCl(COD)]$_2$; b) AgOTf.

The new synthesised complexes were tested in transfer hydrogenation reactions but even with low substrate to catalyst ratios no conversion was observed. Also the attempted deprotonation of 59 or 60 failed and led to decomposition of the complex. Although initial catalysis tests failed, 51 and 32 still represents a new ligand class and the potential catalytic properties of their complexes still needs to be investigated.
2.7 Outlook

As mentioned above further work needs to be done to evaluate the catalytic properties of the complexes with ligands having a phosphane, olefin and alcohol coordination side. In the literature, many ligands featuring phosphorus and oxygen coordination side are known.\cite{59-60} Beside their ability to coordinate to a large number of transition metal ions, their key advantage is their hemilability, which results from a hard and a soft donor.\cite{60a}

Consequently these complexes are interesting with respect to all kind of oxidative addition reactions,\cite{60a} metal catalysed coupling reactions,\cite{59, 61} carboxylation,\cite{60a, 62} hydrogenation,\cite{59-60, 60c, 60d, 63} hydroformylation,\cite{60a, 63b, 64} hydrosilylation\cite{60c, 65} and even transfer hydrogenation.\cite{63d, 66} Even though transfer hydrogenation with the newly synthesised complexes failed, there are many catalytic reactions which should be tested.

The ligands described in literature bear rarely an alcohol as oxygen donor but rather an ether function.\cite{60a, 60e, 61, 62e, 64a, 64b, 64f} Also ligands with phosphane and other chalcogen donors, such as sulphur and selenium, are known.\cite{60a, 62a, 62b, 62d, 62f, 63c, 64e, 66a} It would therefore be interesting to slightly alter the ligands 51 and 32 in order to introduce as chalcogen donor methyl ether, thioether or selane. However, direct synthesis from 51 or 32 is not advised because typical reagents for the transformations required, such as methyl iodide or Lawesson’s reagent, also reacts with phosphane producing phosphonium salts or phosphane sulphides. Therefore it is suggested to start from commercially available 2-bromotoluene and produce 2-(o-tolyl)propan-2-ol by Grignard reaction, as known in literature.\cite{67} The alcohol group can then be turned into the desired ether, thioether or selane group. Afterwards the usual chain of bromination, Arbuzov and Wittig-Horner reaction should yield the desired ligands as shown in Scheme 17.
Scheme 17: Proposed synthetic pathway to produce tridentate phosphane-olefin-chalcogen ligands similar to 51. R = Me or Ph. Reagents: a) NaH or KH, then MeI; b) Lawesson’s reagent; c) MeI, aq. NaOH; d) PhSeSePh, La, TMSCl, I₂, CuI; e) NBS, AIBN; f) P(OEt)₃; g) BuLi or LDA, then 12.

Scheme 18: Proposed synthetic pathway to produce tridentate phosphane-olefin-chalcogen ligands similar to 32. R = Me or Ph. Reagents: a) NaH or KH, then MeI; b) Lawesson’s reagent; c) MeI, aq. NaOH; d) PhSeSePh, La, TMSCl, I₂, CuI; e) 5 mol% Pd(OAc)₂, 5 mol% dppe, HPPh₂, DIPEA.
In order to produce ligands similar to 32 it is suggested to introduce the ether, thioether or selane groups to intermediate 30, followed by the palladium catalysed coupling of HPPh₂ as outlined in Scheme 18.

Beside the above described phosphane-olefin-chalcogen ligands it would also be interesting to vary the famous trop₂NH ligand.⁶, ²⁴ One way to do so would be to substitute to trop-olefins by phosphane donors. However by simply substituting the trop-units in the proposed way a typical PNP pincer ligand would be produced.⁶¹, ⁷² Such a ligand would strongly favour a square planar coordination sphere for d⁸-metal ions.⁶¹, ⁷² In order to force a PNP ligand into a trigonal bipyramidal coordination geometry it is proposed to bind the two phosphorus atoms together via an alkyl chain. Studying models of the proposed ligands, it was concluded that a propyl group would fit best as connecting chain. As shown in Scheme 19, the ligand could either be synthesised from bis(2-fluorophenyl)amine⁶¹, ⁷³ and 1,3-bis(phenylphosphino)propane⁷⁴ or from bis(2-bromophenyl)amine⁶¹, ⁷⁵ and 1,3-bis(chloro(phenyl)phosphino)propane.⁷⁶

Scheme 19: Proposed synthesis of a PNP non-pincer ligand. Reagents: a) KH; b) BuLi.

Beside of being an interesting substitute for trop₂NH it would also, to our knowledge, be the first PNP-non pincer ligand.

An interesting modification of the above described ligand would be to exchange the amine by a borane group to produce a PBP ligand analogous to the literature known one.⁷⁷ However connecting both phosphorus atoms by a propyl chain should prevent the formation of square planar complexes. The synthesis of the proposed PBP non-pincer ligand as shown in Scheme 20 could be achieved by slight alteration of the literature procedure.⁷⁷
Scheme 20: Proposed synthesis of a PBP-non pincer ligand. Reagents: a) paraformaldehyde, then \( o \)-phenylenediamine; b) BH\(_3\)-SMe\(_2\), then \( n \)-Pr\(_2\)NH.

The proposed synthetic procedures for the proposed non-pincer ligands are well established in literature with analogous substrates.\(^{[61, 77]}\) Therefore the main synthetic challenge will be to cleanly form the ring, which is necessary in order to prevent the subsequent formation of square planar complexes.
3 A biologically inspired organometallic fuel cell (OMFC) that converts renewable alcohols into energy and chemicals
3.1 Introduction

To simultaneously convert alcohols and sugars in chemicals and harvest electrical energy from this reaction is a target of primary importance for the sustainable chemistry. The realisation of such a process would provide renewable energy with no CO₂ emission and, at the same time, lead to the production of industrially relevant feed stocks, such as aldehydes, ketones and carboxylic acids, from biomass. Two established fuel cells operating in alkaline media can convert the free energy of alcohols (RCH₂OH) into electrical energy and the corresponding carboxylate product: the alkaline direct alcohol fuel cell (ADAFC, see Figure 11a) and the enzymatic bio fuel cell (EBFC, see Figure 11b). In the former, the anode electrocatalyst is generally constituted by a nanostructured noble metal, supported on a conductive carbon black and, as electrolyte, an anion exchange membrane is used. In an EBFC, the oxidation of ethanol to acetate involves oxidation enzymes such as alcohol and aldehyde dehydrogenase, in conjunction with the nicotinamide adenine dinucleotide redox mediator NAD⁺/NADH which transfers the released protons and electrons to the anode.

\[
\text{Anode: } C_2H_5OH + 5 OH^- \rightarrow CH_3COO^- + 4 H_2O + 4 e^- \quad E^0 = -0.72 \text{ V} \quad \text{(Eq. 5)}
\]

\[
\text{Cathode: } O_2 + 2 H_2O + 4 e^- \rightarrow 4 OH^- \quad E^0 = 0.40 \text{ V} \quad \text{(Eq. 6)}
\]

**Figure 11:** a) Working scheme of an ADAFC in alkaline environment. b) Working scheme of an ethanol/O₂ EBFC. Alcohol dehydrogenase and aldehyde dehydrogenase catalyse a stepwise oxidation of ethanol to acetaldehyde and then to acetate, passing electrons to the anode via the mediator NAD⁺/NADH.
Overall:  \[ \text{C}_2\text{H}_5\text{OH} + \text{O}_2 + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + 2 \text{H}_2\text{O} \quad E^0 = 1.12 \text{ V} \]  (Eq. 7)

In either case, alcohol substrates, such as ethanol, are oxidised to the corresponding carboxylates. The four electrons released by the alcohol oxidation (Eq. 5) are utilised to reduce one oxygen molecule to four hydroxide ions on the cathode (Eq. 6).

Efficient ADAFC have been recently developed for a variety of renewable alcohols and polyalcohols, such as ethylene glycol, glycerol, 1,2-propanediol, and C6 and C5 sugars. [78a, 78b, 78d, 78e] Nowadays the performance of a traditional ADAFC (>50 mW cm\(^{-2}\)) [78a-c] surpasses that of an EBFC (<0.5 mW cm\(^{-2}\)) [79a] by more than two orders of magnitude.

[Rh(trop2N)(PPh3)]\(^{1}\) is an efficient catalyst for the dehydrogenative coupling reaction of primary alcohols with water, methanol or amines to produce acids, methyl ester or amides respectively. [6a, 24, 80] In order to regenerate 1 from the amino hydride 2, which was produced by the reaction of 1 with the alcohol substrate, an excess of hydrogen acceptor is needed in the reaction mixture. A simplified catalytic cycle is shown in Figure 12. As hydrogen acceptors cyclohexanone, [6a, 24] methyl methacrylate [6a, 24] and palladium nanoparticle were used. The latter transfers hydrogen further to a terminal acceptor such as olefins. [80]

![Figure 12: Simplified catalytic cycle of the dehydrogenative coupling reaction of primary alcohols. A = hydrogen acceptor.](image)

The application of hydrogen acceptors in the dehydrogenative coupling reaction is however a waste of chemicals and leads to the formation of unwanted by-products from which the target product must be separated. Although it is sometimes possible to recycle the hydrogen
acceptor, it would be advantageous to regenerate the amido complex 1 from the amino hydride 2 by another method.

Therefore the idea arouse to produce an organometallic fuel cell (OMFC), which has the same working scheme as the ADAFC (Figure 11a) but as anode electrocatalyst 1 or its precursor [Rh(trop₂NH)(PPh₃)]OTf 9 is used. The hydride 2 will then be oxidised to 1 and the released electrons will be transferred to the cathode where molecular oxygen is reduced to water. The advantages of this system would be that oxygen from air, which is readily available, would then serve as hydrogen acceptor and water is the only by-product formed. Furthermore also electrical energy could be harvested.
3.2 Results and discussion of the OMFC using 9 as anode electrocatalyst

[Rh(trop₂NH)(PPh₃)]OTf 9 was deposited intact onto Vulcan XC-72 (Cv), a conductive carbon support that is often utilised for the preparation of electrocatalysts for DAFCs.⁷⁸ᵃ, ⁷⁸ᶜ, ⁷⁸ᶠ

Inks for the fabrication of electrodes, suitable for either cyclic voltammetry (CV) studies or membrane electrode assembly (MEA) manufacturing, were prepared by standard procedures.⁸ᵃ The CV response of 9@Cv in a 2 M KOH solution did not show any electrochemical activity up to the oxygen discharge potential (Figure 13a, □). In contrast, a relatively high current density was observed at +0.65 V (vs. the reversible hydrogen electrode (RHE)) by adding a mixture of ethanol/2 M KOH (Figure 13a, ■). Such a low onset oxidation potential is typical for the most efficient nano-sized palladium electrocatalysts for ethanol oxidation in alkaline media.⁷⁸ᵃ, ⁷⁸ᶜ, ⁷⁸ᶠ, ⁸₁

A MEA was fabricated for a fuel cell comprising a nickel foam anode coated with 9@Cv (ca. 1 mg cm⁻² rhodium), a carbon-paper cathode coated with either commercial or proprietary Fe-Co/C electrocatalyst and a Tokuyama A006 anion-exchange membrane.⁷⁸ᵃ, ⁷⁸ᵇ, ⁷⁸ᵈ Therefore the OMFC differs from the ADAFC only for the electrocatalyst, all other components are identical.

The anode compartment was loaded with 10.5 mL of a water solution of ethanol (10 wt%) and 2 M KOH. Figure 13b shows the polarisation and power density curves of this passive cell recorded at 22 °C (■). A maximum power density of 7 mW cm⁻² was supplied at 22 °C, which is far higher than that of any EBFC, yet slightly lower than the one observed with a traditional ADAFC equipped with a palladium-based anode.⁷⁸ᵇ, ⁸₁ The power density supplied by the OMFC increases remarkably by increasing the working temperature of the MEA in an active cell under control of the oxygen and fuel fluxes. Indeed, 24 mW cm⁻² were obtained at 60 °C with a fuel flow of 4 mL min⁻¹ and an oxygen flow 0.2 L min⁻¹ (Figure 13b, □). Such a value is still lower than that obtainable with the best anode palladium based electrocatalysts reported to date (Pd-(Ni-Zn)/C),⁷⁸ᵇ yet it falls in the upper range of power densities produced by the vast majority of ADAFCs containing nano-sized noble metal electrocatalysts.⁷⁸ᵃ, ⁷⁸ᶜ, ⁷⁸ᶠ

⁸ᵃ Impregnation of the carbon support and the assembling of the fuel cell were done by our collaborators, Bianchini et al.; interested readers are referred to the published paper (S. P. Annen, V. Bambagioni, M. Bevilacqua, J. Filippi, A. Marchionni, W. Oberhauser, H. Schönberg, F. Vizza, C. Bianchini, H. Grützmacher, Angew. Chem. 2010, 122, 7387-7391; Angew. Chem. Int. Ed. 2010, 49, 7229-7233.) and the supporting information therein.
Figure 13: a) CV responses of a glassy carbon electrode coated with 9@Cv in 2 M KOH (∙) and in 2 M KOH and ethanol (10 wt%) (■). b) Polarization and power density curves of OMFCs fuelled with 10 wt% ethanol in 2 M KOH (anode: 9@Cv on Ni mesh; cathode: Fe-Co/C on carbon paper; membrane: Tokuyama A006). Air-breathing OMFC at 22 °C (■); active OMFC at 60 °C (□; fuel flow: 4 mL min⁻¹; oxygen flow 0.2 L min⁻¹).

The passive OMFC was subjected to galvanostatic experiments at constant currents of 25 and 50 mA. At lower current intensities, the cell kept on working for 44.3 h, producing selectively 14.4 mmol of potassium acetate, which corresponds to 48% conversion of the starting ethanol. A comparable conversion and selectivity was obtained from the galvanostatic experiment at 50 mA. Importantly, ICP-AES analysis of the anode exhausts after the galvanostatic experiments ruled out any rhodium leaching from the electrode into the solution.

Extraction of the used anode by THF gave quantitatively the η¹-O-acetato complex [Rh(eq-OAc)(trop₂NH)(PPh₃)] 7 (Scheme 21). XRPD spectra taken on the electrode after the galvanostatic experiments and on a pure sample of 7 proved that the complex embedded into Vulcan XC-72 is 7@Cv.
Scheme 21: Conversion of complex $9@C_v$ into the acetato complex $7@C$ on the electrode surface during the galvanostatic experiment at 50 mA.

7 could be prepared independently by treating the amido complex 1 with acetic acid (Scheme 22a) or by dechlorination of the chloro-complex 61 with AgOAc. As shown in Scheme 22b two different acetato-complexes could be formed by treating 61 with AgOAc depending on the solvent. From DCM the equatorial acetato-complex 7 was isolated, whereas from acetone the axial isomer 62 was obtained. Selected chemical shifts and the rhodium phosphorus coupling constants of 7 and 62 were compared to the OTf-complex 9 (Table 6).

Scheme 22: Two alternative preparation of the acetato-complex 7 by either treating 1 with acetic acid (a) or dehalogenating 61 with AgOAc in DCM (b). When the latter procedure was executed in acetone the axial OAc-complex 62 was obtained.
Table 6: Selected chemical shifts and the rhodium phosphorus coupling constant of the equatorial (7) and axial (62) acetato-complexes compared to the OTf complex 9.

<table>
<thead>
<tr>
<th>Complex</th>
<th>7</th>
<th>62</th>
<th>9[6a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH δ [ppm]</td>
<td>10.90</td>
<td>5.35</td>
<td>5.66</td>
</tr>
<tr>
<td>C\text{H}^{\text{benzyl}} δ [ppm]</td>
<td>4.92</td>
<td>3.74</td>
<td>4.91</td>
</tr>
<tr>
<td>C\text{H}^{\text{olef}} δ [ppm]</td>
<td>4.82</td>
<td>5.52</td>
<td>4.94</td>
</tr>
<tr>
<td>C\text{H}^{\text{olef}} δ [ppm]</td>
<td>4.89</td>
<td>6.68</td>
<td>5.43</td>
</tr>
<tr>
<td>C\text{H}^{\text{benzyl}} δ [ppm]</td>
<td>71.8</td>
<td>73.0</td>
<td>72.7</td>
</tr>
<tr>
<td>C\text{H}^{\text{olef}} δ [ppm]</td>
<td>67.4</td>
<td>67.7</td>
<td>74.0</td>
</tr>
<tr>
<td>C\text{H}^{\text{olef}} δ [ppm]</td>
<td>69.0</td>
<td>68.5</td>
<td>74.2</td>
</tr>
<tr>
<td>P δ [ppm]</td>
<td>38.9</td>
<td>10.3</td>
<td>40.6</td>
</tr>
<tr>
<td>$^{1}J_{\text{RhP}}$ [Hz]</td>
<td>131.2</td>
<td>109.9</td>
<td>137.7</td>
</tr>
</tbody>
</table>

The largest difference between 7 and 9 is the resonance of the NH-proton, which is over 5 ppm shifted to higher frequency. The reason for this was found to be a strong hydrogen bonding interaction between the amino function of the trop$_2$NH ligand and the acetate. The resonances of the olefinic protons and carbons are slightly shifted to lower frequency which might result from a slightly stronger $\pi$-bonding of the olefins and the rhodium. Furthermore the rhodium phosphorus coupling constant is over 5 Hz smaller for 7 compared to 9. The reason for this could be a slightly weaker bond between rhodium and phosphorus.

Not surprisingly the differences between 62 and 9 are larger, because the phosphane ligand of 62 is in the equatorial position; therefore the coordination sphere has changed largely. The largest difference found are the shifts of the benzylic proton and the phosphorus atom and the rhodium phosphorus coupling constant. However these three values are similar to the ones reported for the chloro-complex 61 ($\delta$ (C\text{H}^{\text{benzyl}}) = 3.85 ppm; $\delta$ (PPh$_3$) = 7.7 ppm; $^{1}J_{\text{RhP}} = 111$ Hz) in which the PPh$_3$-ligand also occupies in equatorial position.[6a, 28a]
**Figure 14**: Ortep plot (at 50% probability) of the structure of [Rh(eq-OAc)(trop₂NH)(PPh₃)] 7. Most of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C19=C20): Rh1-N1 2.134(2), Rh1-P1 2.3132(9), Rh1-ct1 2.062(3), Rh1-ct2 2.040(3), Rh1-O1: 2.263(2), Rh1-C4 2.177(3), Rh1-C5 2.183(3), Rh1-C19 2.177(3), Rh1-C20 2.143(3), C4=C5 1.414(4), C19=C20 1.416(4), N1-O2 (distance): 2.263(2), N1-Rh1-P1 177.22(6), ct1-Rh1-ct2 132.6(1).

**Table 7**: Selected bond lengths and angles of 7 compared to 9. a) shortest distance between an oxygen atom of the OAc- or the OTf-anion and the nitrogen atom.

<table>
<thead>
<tr>
<th>Complex</th>
<th>7 [Å]</th>
<th>9 [28a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh1-N1 [Å]</td>
<td>2.134(2)</td>
<td>2.150(2)</td>
</tr>
<tr>
<td>Rh1-P1 [Å]</td>
<td>2.3132(9)</td>
<td>2.2789(7)</td>
</tr>
<tr>
<td>Rh1-ct1 [Å]</td>
<td>2.062(3)</td>
<td>2.040(2)</td>
</tr>
<tr>
<td>Rh1-ct2 [Å]</td>
<td>2.040(3)</td>
<td>2.075(2)</td>
</tr>
<tr>
<td>N1-O1 [Å]</td>
<td>2.263(2)</td>
<td>2.381(2)</td>
</tr>
<tr>
<td>C4=C5 [Å]</td>
<td>1.414(4)</td>
<td>1.404(3)</td>
</tr>
<tr>
<td>C19=C20 [Å]</td>
<td>1.416(4)</td>
<td>1.422(4)</td>
</tr>
<tr>
<td>N1-Rh1-P1 [°]</td>
<td>177.22(6)</td>
<td>179.17(6)</td>
</tr>
<tr>
<td>ct1-Rh1-ct2 [°]</td>
<td>132.6(1)</td>
<td>139.9(1)</td>
</tr>
</tbody>
</table>
Figure 15: Ortep plot (at 50% probability) of the structure of \([\text{Rh(ax-OAc)(trop}_2\text{NH)(PPh}_3\text{)}]\) _62_. Most of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C19=C20): Rh1-N1 2.134(2), Rh1-P1 2.3132(9), Rh1-ct1 2.041(3), Rh1-ct2 2.033(3), Rh1-O1: 2.263(2), Rh1-C4 2.177(3), Rh1-C5 2.183(3), Rh1-C19 2.177(3), Rh1-C20 2.143(3), C4=C5 1.414(4), C19=C20 1.416(4), N1-O2 (distance): 2.263(2), N1-Rh1-P1 94.05(3), N1-Rh1-O1 177.22(6), ct1-Rh1-ct2 132.6(1).

Beside of the NMR data also selected bond lengths and angles of the crystal structure of _7_ (Figure 14) compared to _9_ (Table 7). It is remarkable that the shortest distance between N1 and an oxygen atom (in case of _7_: O2) of the counterion is over 0.1 Å smaller for _7_ than for _9_. Furthermore in _7_ the distance between the NH hydrogen atom and O2 is slightly below 2 Å thus also indicating the hydrogen bond between the NH and the oxygen atom. Another striking observation is the bond angle between the two olefins and the rhodium atom which is over 7° shorter in _7_ compared to _9_. The reason for this significant difference could be that for _7_ the OAc-anion is considerably closer to the metal centre than the OTf-anion of _9_.

The bond lengths of the olefins and the rhodium atom of _7_ are comparable to the ones of _9_. This is however in contrast to the NMR resonances of the olefinic carbons, which were considerably shifted to lower frequency for _7_ compared to _9_. The reason for this disagreement could be that the bond angle between the two olefins and the rhodium atom is different for both complexes and therefore also the chemical environment for the olefinic carbons are slightly different, which reflects in a discrepancy in the chemical shifts. Another reason might be a slight difference of the structure in solid and solution state.
Furthermore the rhodium nitrogen bond is shortened and the rhodium phosphorus bond is elongated in complex 7 compared to 9. This finding is in good agreement with the NMR data, which revealed a significantly smaller rhodium phosphorus coupling constant for 7, which was interpreted as a weaker bond between the rhodium and the phosphorus atom.

The assumption that the reaction of the chloro complex 61 with AgOAc in acetone yielded the axial acetato complex 62 was proven by X-ray analysis (Figure 15).

Scheme 23: Slow conversion of 7@Cv into the catalytically active hydroxo complex 63@Cv.

The stability of the acetato complex 7 embedded into Vulcan XC-72 (7@Cv) was investigated (Scheme 23). When 7@Cv was treated with a 2 M aqueous solution of KOH for 12 hours and the products subsequently extracted with [D8]THF, 50% of the acetato complex 7 was still recovered. The other half consisted of the equatorial hydroxo complex 63 along with minor quantities of its axial isomer 64. 63 was found to have a key function in the catalysis, see discussion below. It is assumed that the slow conversion of 7@Cv into 63@Cv is responsible for the drop of the activity of the cell after about 50% conversion of ethanol into acetate.

Under open-circuit conditions, 9@C reacts with the fuel solution at room temperature with no need of external exchange of electrons and after 44 hours gives the acetato complex 7 (48.5%) and the hydride 2 (48.5%) as major products beside small amounts of the equatorial and axial hydroxo rhodium complexes 63 (1%) and 64 (2%).

It was found that the hydroxo complex 63 reacts with CO₂ to the hydrogen carbonate complex 65. The chemical shift of the NH proton of 65 at 10.80 ppm indicates hydrogen bonding similar as in the acetato complex 7. It is therefore assumed that 65 is also similarly stable as 63 and its formation in the OMFC would decrease the activity of the fuel cell. CO₂ should therefore be avoided in the OMFC.
Model reactions in homogeneous solution were performed to rationalise the single reaction steps at the anode surface (Scheme 26). The formation of the equatorial hydroxo complex 63 was observed by treating a solution of the precursor [Rh(trop2NH)($\text{PPh}_3$)]OTf 9 with aqueous 2 M KOH (Scheme 26a). However, isolation of pure 63 in high yields was found to be much easier by the reaction of the amido complex 1 with water followed by rapid work-up of the reaction mixture. Longer reaction times led to isomerisation of 63 into the axial isomer 64. The equatorial hydroxo complex 63 is in rapid equilibrium with the amido complex 1 (Scheme 26b), which is a rare case where a water molecule is added reversibly across a late transition amido bond.[82] The equilibrium constant of this reaction (Eq. 8) was estimated form $^{31}$P-NMR (results in Table 8).

$$[\text{Rh(trop}_2\text{N})(\text{PPh}_3)] + \text{H}_2\text{O} \rightleftharpoons [\text{Rh(eq-OH)(trop}_2\text{NH})(\text{PPh}_3)] \quad (\text{Eq. 8})$$

**Table 8:** Results of the $^{31}$P NMR analysis of samples with different concentrations of 1 and 63 at 213 K.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample content</th>
<th>Chem. Shift (ppm)</th>
<th>$^1J_{\text{RhP}}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>40.7</td>
<td>123.6</td>
</tr>
<tr>
<td>2</td>
<td>63 with approximately 100 eq. H$_2$O</td>
<td>41.1</td>
<td>134.3</td>
</tr>
<tr>
<td>3</td>
<td>63</td>
<td>40.9</td>
<td>130.5</td>
</tr>
<tr>
<td>4</td>
<td>30% 1 and 70% 63</td>
<td>40.9</td>
<td>128.9</td>
</tr>
</tbody>
</table>

It is assumed that in entry 2 the excess of water shifts the equilibrium of equation Eq. 8 fully to the right side and only complex 63 is observed. The equilibrium constant $K$ is determined by the law of mass action (Eq. 9; the following abbreviations are used: $[OH] = \text{relative concentration of } [\text{Rh(eq-OH)(trop}_2\text{NH})(\text{PPh}_3)] \; 63$; $[Amid] = \text{relative concentration of } [\text{Rh(trop}_2\text{N})(\text{PPh}_3)] \; 1$; $[H_2O] = \text{relative concentration of water})$.

$$K = \frac{[OH]}{[Amid][H_2O]} \quad (\text{Eq. 9})$$

The relative concentration of the 63 ([OH]) and 1 ([Amid]) were calculated from chemical shift or the rhodium phosphorus coupling constant (Eq. 10 and Eq 11; the following abbreviations are used: $cs = \text{chemical shift measured in an equilibrium mixture of 63 and 1}$; $cs_{Amid} = \text{chemical shift of pure 1 taken from entry 1 in Table 8}$; $cs_{OH} = \text{chemical shift of pure 63 taken from entry 2 in Table 8}$; $J = \text{rhodium phosphorus coupling constant measured in an}$
equilibrium mixture of 63 and 1; $J_{Amid} =$ rhodium phosphorus coupling constant of pure 1 taken from entry 1 in Table 8; $J_{OH} =$ rhodium phosphorus coupling constant of pure 63 taken from entry 2 in Table 8).

$$[OH] = \frac{c_{S} - c_{S_{Amid}}}{c_{S_{OH}} - c_{S_{Amid}}}; \text{respectively } [OH] = \frac{J - J_{Amid}}{J_{OH} - J_{Amid}} \quad \text{(Eq. 10)}$$

$$[Amid] = 1 - [OH] \quad \text{(Eq. 11)}$$

The relative concentration of water can be set in relation to the relative concentration of 1 (see Eq. 8) depending on the content of the analysed sample (Eq. 12).

$$[H_{2}O] = [Amid] \text{ in case of entry 3; } [H_{2}O] = [Amid] - 0.3 \text{ in case of entry 4} \quad \text{(Eq. 12)}$$

The calculated equilibrium constants calculated by the measured values of entry 3 or 4 in Table 8 by either using the chemical shift ($K_{CS}$) or the rhodium phosphorus coupling constant ($K_{J}$) are summarised in Table 9.

| Table 9: Results of the calculation of the equilibrium constant $K$. [a] calculated with the values of entry 3 in Table 8; [b] calculated with the values of entry 4 in Table 8. |
|---|---|---|
| Entry | $K_{CS}$ [L mol$^{-1}$] | $K_{J}$ [L mol$^{-1}$] |
| 1$^{[a]}$ | 4.2 | 5.0 |
| 2$^{[b]}$ | 5.6 | 5.0 |

The differences of the chemical shifts of the hydroxo complex [Rh(eq-OH)(trop$_2$NH)(PPh$_3$)] 63 and amido complex [Rh(trop$_2$N)(PPh$_3$)] 1 is not sufficiently large (see Table 8) to obtain very accurate data (see the rather large variation of $K_{CS}$ in Table 9). Consistent data are obtained using the rather different rhodium phosphorus coupling constants of the hydroxo complex 63 versus the amido complex 1. Taking all data an equilibrium constant of $K = 5$ L mol$^{-1}$ is estimated at $T = 213$ K.

In order to verify the assumption that the sample of entry 2 in Table 8 contains only the hydroxo complex 63, the equilibrium concentration $[OH]$ was calculated with Eq 9 and Eq. 11 and $[H_{2}O] = 100$ as estimated from $^1$H NMR (see Eq. 13).

$$[OH] = \frac{100K}{1 + 100K} \quad \text{(Eq. 13)}$$
Inserting the obtained value for $K$ the relative concentration of the hydroxo complex 63 is 0.998 or in other words, only 0.2% of the rhodium complexes are present in the form of the amido complex 1, whereas 99.8% is the hydroxo complex 63. Therefore it is concluded that the error made by assumption, that only the hydroxo complex 63 is present in this sample, is negligible compared to the experimental error.

Beside the equilibrium (Eq. 8) also the reaction of 63 with aldehydes and alcohols was examined. Reacting 63 with an excess of acetaldehyde led to the immediate formation of the acetato complex 7 as confirmed by $^{31}$P NMR. Furthermore, analysis by $^1$H NMR revealed the formation of ethanol. GC analysis of the reaction of 63 with an excess of octanal, not only revealed the formation of 1-octanol, but also a small amount of octanoic acid was found. It is assumed that the acid was obtained by partial hydrolysis of the formed octanoate complex.

Scheme 24: Reaction of acetaldehyde with the hydroxo complex 63. a) oxidation of acetaldehyde and formation of the amino hydride complex 2; b) transfer hydrogenation of acetaldehyde; c) addition of acetic acid to the amido complex 1.

The observed reaction was rationalised as follow: First the hydroxo complex 63 reacts with acetaldehyde giving the acetic acid and the amino hydride complex 2 (Scheme 24a). 2 reacts subsequently with another acetaldehyde molecule, present in excess, to ethanol and the amido complex 1 (Scheme 24b). 1 finally reacts with the formed acetic acid to the acetato complex 7 (Scheme 24c).

The hydroxo complex 63 reacts with ethanol to a 2:1 mixture of the amino hydride complex 2 and the acetato complex 7. Likewise, reacting 1-octanol with 63 yielded a similar 2:1 mixture.
of the amino hydride complex 2 and the octanoate complex. Analysis by GC revealed the presence of a small amount of octanal. It is proposed that the amido complex 1, which is always present in a solution of the hydroxo complex 63 (see Eq. 8), dehydrogenate ethanol to acetaldehyde, forming the amino hydride complex 2 (Scheme 25a). Acetaldehyde reacts with the hydroxo complex 63 to acetic acid and another molecule of 2 (Scheme 25b). Acetic acid is added to the amido complex 1 forming the acetato complex 7 (Scheme 25c). In conclusion, one molecule of ethanol reacts with three molecules of hydroxo complex 63 to 2 molecules of the amino hydride complex 2 and one molecule of the acetato complex 7, thus giving the observed 2:1 ratio of these two complexes.

Scheme 25: Reaction of ethanol with the hydroxo complex 63. a) dehydrogenation of ethanol by the amido complex 1 present in solution because of the equilibrium shown in Eq. 8; b) oxidation of acetaldehyde and formation of the amino hydride complex 2; c) addition of acetic acid to the amido complex 1.
Scheme 26: Model reaction in homogeneous solution of the precursor complex 9, the amido complex 1 and the hydroxo complex 63 with KOH, water, ethanol and acetaldehyde in THF.
When 63 was reacted with ethanol the amino hydride complex 2 and the acetato complex 7 were obtained immediately in a 2:1 ratio (Scheme 26b). This result is in accord with the reaction mechanism indicated in the dashed box of Scheme 26b.[6a-c, 24b] The amido complex 1 is constantly present through the fast equilibrium $\text{63} \rightleftharpoons \text{1} + \text{H}_2\text{O}$, and dehydrogenates ethanol in a fast reaction according to the established Noyori-Morris-mechanism.[17] Acetaldehyde was never detected at any stage of the reaction because it reacts rapidly and selectively with the hydroxo complex 63 to give the acetato complex 7 and ethanol (Scheme 26c). In the dashed box of Scheme 26c, the relevant reactions which rationalise this catalysed Cannizaro-type disproportion reaction (Eq. 14) are shown.

$$2 \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{OH}. \quad \text{(Eq. 14)}$$

The oxidation of acetaldehyde to acetic acid is performed exclusively by the equatorial hydroxo complex 7; the axial isomer 64 is not reactive. The hydride 2 reacts with acetic acid to give the acetato complex 7 and H$_2$, which in turn is rapidly cleaved across the Rh-N bond of the amido complex 1 to give the hydride 2.[6d, 6e] Alternatively, the amido complex 1, which is present in the reaction mixture by the equilibria $\text{63} \rightleftharpoons \text{1} + \text{H}_2\text{O}$ and $\text{2} + \text{CH}_3\text{CHO} \rightleftharpoons \text{1} + \text{CH}_3\text{CH}_2\text{OH}$, adds acetic acid across the Rh-N bond to give 7. Finally, the equatorial hydroxo complex 63 reacts with CH$_3$COOH to give the acetato complex 7 and H$_2$O (not shown in Scheme 26).

In an experiment where equimolar quantities of propionaldehyde and ethanol were reacted with the equatorial hydroxo complex 7, the propionato complex [Rh(O$_2$CC$_2$H$_5$)(trop$_2$NH)(PPh$_3$)] was obtained exclusively together with 1-propanol. This clearly shows that a) the hydroxo complex 7 reacts selectively with aldehydes; b) this reaction is faster than the dehydration of 7 to the amido complex 1; and c) the conversion of aldehyde into carboxylic acid is faster than the dehydrogenation of an alcohol to the corresponding aldehyde.

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[b] This experiment was performed by our collaborators Bianchini et al. It is however stated here as verification of statements made above.
Among the several rhodium complexes that are involved in the oxidation of ethanol to acetate, only the amino hydride complex 2 acts as H-transfer mediator and is ultimately responsible for the current produced by the OMFC. In this process, 2 is converted into the amido 1, and two electrons are released over the anode with concomitant release of two protons. Figure 16 shows the CV response of a glassy carbon electrode coated with 2@C in 2 M KOH (■) and, by comparison, the response of a similar electrode coated with 9@C (□). No current was generated by the latter electrode until the oxygen discharge potential was attained, whereas a relatively high current density was generated upon oxidation of 2@Cv at the same onset potential observed for 9@Cv in a 2 M KOH solution containing 10 wt% ethanol (Figure 13b). The experimental data are in agreement with the mechanism shown in Figure 17. On the electrode surface, the precursor 9@Cv is rapidly converted into the hydroxo complex 63@Cv, which is in a rapid equilibrium with the amido complex 1@Cv and water. The amido complex 1@Cv dehydrogenates ethanol to acetaldehyde; the aldehyde reacts further with 63@Cv to form the acetate ion and the hydride 2@Cv. The latter complex is oxidised at the electrode, releasing two protons (neutralised to give water under the basic conditions) and two electrons with regeneration of the amido complex 1@Cv. The stability of the acetato complex 63@Cv is responsible for the drop of the current density. At about 50% conversion, the displacement of the acetate by OH⁻ to regenerate 63@Cv becomes too slow and current flow stops.

**Figure 16:** CV responses of a glassy carbon electrode coated with 2@C (■) and 9@C (□) in 2 M KOH.
Figure 17: Proposed mechanism for the reactions occurring on the surface of the OMFC anode coated with 9@Cv. The function of an enzymatic biofuel cell (EBFC; top) is included for comparison. Similar colours relate to similar functions (orange: aldehyde dehydrogenation, pink: alcohol dehydrogenation, green: hydrogen/electron transfer).

The resemblance with the EBFC is that in both fuel cells three specific catalysts for the three key functions, alcohol dehydrogenation (the amido complex 1; alcohol dehydrogenase), aldehyde dehydrogenation (the hydroxo complex 63; aldehyde dehydrogenase) and for the H⁺/electron transfer (the hydride 2; NADH/NAD⁺). However, the assembly of the OMFC is analogous to the ADAFC. The main characteristic of the OMFC is that one molecular rhodium complex is capable of evolving through fast chemical equilibria in the course of the catalytic cycle to form all three specific catalysts.
It is assumed that nano sized metal electrocatalysts, which are generally platinum-group metals, oxidise alcohols to carboxylic acids via aldehyde intermediates that undergo C-H bond cleavage to form an adsorbed acyl.[78a, 78c, 78f, 83] The coupling of the latter group with adsorbed OH gives the carboxylic acid. Herein an alternative mechanism is proposed in which no acyl$_{ads}$ is formed and the alcohol dehydrogenation to aldehyde and the aldehyde oxidation to carboxylic acid are carried out by metal-amido and metal-hydroxo species with no need of preliminary C-H bond cleavage (see dashed boxes in Scheme 26b, c).

The use of a molecular complex as anode electrocatalyst in an ADAFC may be a breakthrough in fuel cell technology, and the possibilities and range of applications of OMFC technology is very large. From a practical point of view, molecular metal complexes that are soluble in different solvents and allow dispersion on very small surfaces, but are capable of delivering high power densities upon oxidation of alcohols and sugars, could indicate a way to the further miniaturisation of fuel cells for biological applications and biosensors.[79, 83b, 84] Molecular metal complexes can be easily embedded in a wide range of nanosized conductive supports, such as functionalised fullerenes, carbon nanotubes, nanofibers, and other nanosized matrices (such as titania nanotubes). The combination of a well-defined molecular architecture with a matching support might allow the selective oxidation of polyalcohols into valuable chemicals under waste-free conditions, which is very difficult to achieve by traditional methods.
3.3 Synthesis of new Rh\textsuperscript{I} trop\textsubscript{2}NH complexes with substituted axial PAr\textsubscript{3} ligands and their performance in homogeneous catalysis

3.3.1 Phosphane and complex synthesis

The results obtained with the OMFC were strongly encouraging, however the formation of the acetato complex 7 proved to be a severe disadvantage of the proposed system. The reaction of 7@Cv to the catalytically active 63@Cv was very slow; consequently the performance of the fuel cell was strongly decreased. Therefore complexes similar to 9 with slightly different phosphane ligands were synthesised.

The phosphane ligands, if not commercially available, were synthesised generally by lithiation of the corresponding aryl bromide with BuLi followed by treating the \textit{in-situ} generated organo lithium compounds with Cl\textsubscript{2}PPh or PCl\textsubscript{3} in order to produce phosphanes with two or three substituted phenyl rings.\textsuperscript{[85]} In Figure 18 all synthesised phosphane derivatives and the used abbreviations are shown.

\begin{align*}
\text{P(3,5-diMePh\textsubscript{3})} & \quad \text{P(3,5-diCF\textsubscript{3}Ph\textsubscript{3})} & \quad \text{P(3,5-di'BuPh\textsubscript{3})} & \quad \text{P(3,5-di'PrPh\textsubscript{3})} \\
\text{P(2-OMePh\textsubscript{3})} & \quad \text{PPh(3,5-diMePh\textsubscript{2})} & \quad \text{PPh(3,5-diCF\textsubscript{3}Ph\textsubscript{2})} & \quad \text{PPh(3,5-di'BuPh\textsubscript{2})} \\
\text{DBP} & \quad \text{P(py\textsubscript{3})} & \quad \text{P(p-BuPh\textsubscript{3})} \\
\end{align*}

\textbf{Figure 18:} Synthesised phosphane derivatives and the corresponding abbreviations.
Figure 19: Ortep plot (at 50% probability) of the structure of [RhCl(trop2NH)(PPh3)] 61. Most of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C19=C20): Rh1-N1 2.101(2), Rh1-P1 2.4405(5), Rh1-ct1 2.076(2), Rh1-ct2 2.028(2), Rh1-Cl1: 2.3626(5), Rh1-C4 2.204(2), Rh1-C5 2.184(2), Rh1-C19 2.146(2), Rh1-C20 2.159(2), C4=C5 1.417(3), C19=C20 1.444(3), N1-Rh1-P1 93.65(4), N1-Rh1-Cl1 175.73(4), ct1-Rh1-ct2 132.0(1).

The chloro- and OTf-complexes of the [RhCl(trop2NH)(L)] and [Rh(trop2NH)(L)]OTf types were synthesised in generally high yields by first splitting the chloro bridged dimer [RhCl(trop2NH)]2 by addition of the ligand followed by treating the produced chloro-complexes with AgOTf.
Figure 20: Ortep plot (at 50% probability) of the structure of [RhCl(trop2NH)(P(3,5-diMePh)3)] 69; crystallised with two independent molecules in the asymmetric unit cell. One is not shown, but the distances are given in brackets []. Most of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C19=C20): Rh1-N1 2.103(5) [2.111(5)], Rh1-P1 2.445(2) [2.459(2)], Rh1-ct1 2.057(6) [2.044(6)], Rh1-ct2 2.049(7) [2.044(6)], Rh1-Cl1: 2.372(2) [2.386(2)], Rh1-C4 2.182(6) [2.163(6)], Rh1-C5 2.186(6) [2.163(6)], Rh1-C19 2.179(7) [2.151(6)], Rh1-C20 2.173(7) [2.174(6)], C4=C5 1.42(1) [1.427(8)], C19=C20 1.42(1) [1.423(8)], N1-Rh1-P1 93.8(2) [91.9(2)], N1-Rh1-Cl1 176.3(2) [175.1(2)], ct1-Rh1-ct2 132.0(3) [133.7(3)].

However, the reactions didn’t work smoothly with three phosphane derivatives, namely tris(3,5-di-tert-butylphenyl)phosphane (P(3,5-di’Bu3Ph)3), tris(2-methoxyphenyl)phosphane (P(2-OMePh)3) and tri(pyridin-2-yl)phosphane (P(py)3). Although the 31P-NMR of the reaction mixture of [RhCl(trop2NH)]2 and P(3,5-di’Bu3Ph)3 showed the clean formation of the desired chloro complex [RhCl(trop2NH)(P(3,5-di’Bu3Ph)3)], its isolation failed and only the starting complex [RhCl(trop2NH)]2 was obtained. It was rationalised that this triaryl phosphane with six t-butyl groups is too bulky, therefore the rhodium phosphorus bond is not strong enough and consequently a considerable amount of starting material is always present. Unfortunately, the dimer [RhCl(trop2NH)]2 is quite insoluble in most solvents and hence it is the only substance that precipitates after layering the reaction mixture with hexane.
Figure 21: Ortep plot (at 50% probability) of the structure of [RhCl(trop2NH)(P(3,5-di’iPrPh)3)] 70. Most of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C19=C20): Rh1-N1 2.093(2), Rh1-P1 2.4621(5), Rh1-ct1 2.042(2), Rh1-ct2 2.037(2), Rh1-Cl1 2.3716(5), Rh1-C4 2.168(2), Rh1-C5 2.156(2), Rh1-C19 2.157(2), Rh1-C20 2.161(2), C4=C5 1.422(3), C19=C20 1.432(3), N1-Rh1-P1 90.05(5), N1-Rh1-Cl1 176.14(5), ct1-Rh1-ct2 129.86(7).

In order to avoid this problem the in-situ produced RhCl(trop2NH)(P(3,5-di’Bu3Ph)3) was directly dehalogenated with AgOTf. However, by layering the filtrate with hexane, the obtained precipitate did not contain any phosphane. Therefore the solvent of the filtrate was simply evaporated and the residue analysed by NMR. It turned out that the tested solution contained the desired complex [Rh(trop2NH)(P(3,5-di’Bu3Ph)3)]OTf 66 and the excess phosphane, which was employed in the synthesis. Therefore the residue was applied to the catalytic tests described below without further purification.

The phosphane P(2-OMePh)3 was unable to split the starting dimer [RhCl(trop2NH)]2, however, by addition of AgOTf to the reaction mixture the desired OTf-complex [Rh(trop2NH)(P(2-OMePh)3)]OTf 67 was obtained in high yields.

On the other hand P(py)3 could easily split the dimer yielding the chloro-complex [RhCl(trop2NH)(P(py)3)] 68, however the dechlorination with AgOTf could only be achieved after prolonged reaction times and in exceptionally low yield.
Selected examples of the newly synthesised chloro- and OTf-complexes were analysed by single crystal X-ray analysis. In order to compare the chloro-complexes, the already known complex [RhCl(trop₂NH)(PPh₃)]₆₁ [6a, 6d, 6e, 28a] was analysed by single crystal X-ray diffraction. The axial acetato-complex 62 was also compared to the chloro-complex, because of the structural similarities of 62 and the chloro-complexes (compare Figure 15 to Figure 19-Figure 21). Selected bond lengths and angles of the chloro-complexes are compared in Table 10.

Table 10: Comparison of selected bond lengths and angles of [RhCl(trop₂NH)(PPh₃)] 61, [Rh(ax-OAc)(trop₂NH)(PPh₃)] 62, [RhCl(trop₂NH)(P(3,5-diMePh)₃)] 69 and [RhCl(trop₂NH)(P(3,5-diPrPh)₃)] 70. a) Rh1-O1 bond length; b) N1-Rh1-O1 bond angle.

<table>
<thead>
<tr>
<th>Complex</th>
<th>61</th>
<th>62</th>
<th>69</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh1-N1 [Å]</td>
<td>2.101(2)</td>
<td>2.134(2)</td>
<td>2.103(5)</td>
<td>2.093(2)</td>
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<tr>
<td>Rh1-P1 [Å]</td>
<td>2.4405(5)</td>
<td>2.134(9)</td>
<td>2.445(2)</td>
<td>2.4621(5)</td>
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<tr>
<td>Rh1-ct1 [Å]</td>
<td>2.076(2)</td>
<td>2.041(3)</td>
<td>2.057(6)</td>
<td>2.042(2)</td>
</tr>
<tr>
<td>Rh1-ct2 [Å]</td>
<td>2.028(2)</td>
<td>2.033(3)</td>
<td>2.049(7)</td>
<td>2.037(2)</td>
</tr>
<tr>
<td>Rh1-Cl1 [Å]</td>
<td>2.3626(5)</td>
<td>2.263(2)⁹</td>
<td>2.372(2)</td>
<td>2.3716(5)</td>
</tr>
<tr>
<td>C4=C5 [Å]</td>
<td>1.417(3)</td>
<td>1.414(4)</td>
<td>1.42(1)</td>
<td>1.422(3)</td>
</tr>
<tr>
<td>C19=C20 [Å]</td>
<td>1.444(3)</td>
<td>1.416(4)</td>
<td>1.42(1)</td>
<td>1.432(3)</td>
</tr>
<tr>
<td>N1-Rh1-P1 [°]</td>
<td>93.65(4)</td>
<td>94.05(3)</td>
<td>93.8(2)</td>
<td>90.05(5)</td>
</tr>
<tr>
<td>N1-Rh1-Cl1 [°]</td>
<td>175.73(4)</td>
<td>177.22(6)⁹</td>
<td>176.3(2)</td>
<td>176.14(5)</td>
</tr>
<tr>
<td>ct1-Rh1-ct2 [°]</td>
<td>132.0(1)</td>
<td>132.6(1)</td>
<td>132.0(3)</td>
<td>129.86(7)</td>
</tr>
</tbody>
</table>

The largest difference between the axial acetato-complex 62 and the chloro complex is the approximately 0.13 Å shorter rhodium phosphorus bond in complex 62. It is assumed that the substitution of the chloro-ligand with a harder oxygen-ligand strengthened the bond between the soft metal centre and the also soft phosphorus atom, which results in a shorter bond. Compared to the OTf-complexes (Table 13), which also do not have another soft donor ligand such as a chloride, the rhodium phosphorus bond of the axial acetato-complex 62 is only slightly longer.
Figure 22: Ortep plot (at 50% probability) of the structure of [Rh(trop2NH)(P(3,5-diMePh)3)]OTf 77. The OTf-anion and most of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C19=C20): Rh1-N1 2.147(2), Rh1-P1 2.3085(7), Rh1-ct1 2.072(3), Rh1-ct2 2.033(3), Rh1-C4 2.202(3), Rh1-C5 2.174(3), Rh1-C19 2.161(3), Rh1-C20 2.149(3), C4=C5 1.399(4), C19=C20 1.436(4), N1-Rh1-P1 177.45(7), ct1-Rh1-ct2 136.4(1).

Substituting PPh3 with the slightly bulkier P(3,5-diMePh)3 yielded almost the same bond lengths and angles, however with the more bulkier P(3,5-di′PrPh)3 the bond angle between the two olefins and the metal centre is, not unexpected, significantly decreased. Surprisingly also the N-Rh-P bond angle is also decreased by approximately 3.5°. The reason for this could be that the aryl in the cavity of the two trop-units is sterically more demanding in complex 70 and therefore pushed up out of the small cavity of the two trop-units. Consequently the N-Rh-P bond angle is decreased.

It is therefore not surprising that with the even bulkier phosphane P(3,5-di′BuPh)3 the rhodium phosphorus bond is even weaker and consequently this complex could not be isolated.
Table 11: Comparison of selected \(^1\)H NMR shifts of $[\text{RhCl(trop}_2\text{NH})(\text{PPh}_3)]$ 61, $[\text{RhCl(trop}_2\text{NH})(\text{P(3,5-diMePh})_3)]$ 69, $[\text{RhCl(trop}_2\text{NH})(\text{P(3,5-diCF}_3\text{Ph})_3)]$ 71, $[\text{RhCl(trop}_2\text{NH})(\text{P(3,5-diPrPh})_3)]$ 70, $[\text{RhCl(trop}_2\text{NH})(\text{PPh(3,5-diBuPh})_2)]$ 72, $[\text{RhCl(trop}_2\text{NH})(\text{PPPh(3,5-MePh})_2)]$ 73, $[\text{RhCl(trop}_2\text{NH})(\text{PPh(di-3,5-CF}_3\text{Ph})_2)]$ 74, $[\text{RhCl(trop}_2\text{NH})(\text{DBP})]$ 75, $[\text{RhCl(trop}_2\text{NH})(\text{P(p-BuPh})_3)]$ 76 and $[\text{RhCl(trop}_2\text{NH})(\text{P(py})_3)]$ 68. [a] Two isomers (61%; 39%) of 73 were found; [b] The chemical shifts of the benzylic and olefinic protons of the two isomers of 73 could not be distinguished; [c] The chemical shifts of the NH proton of the two isomers of 75 could not be distinguished; [d] Two isomers (50%; 50%) of 75 were found at 223 K.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\text{NH} \delta$ [ppm]</th>
<th>$\text{CH}^\text{olef} \delta$ [ppm]</th>
<th>$\text{CH}^\text{benzyl} \delta$ [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>61 [^{[6a, 6c, 28a]}]</td>
<td>1.59</td>
<td>5.27; 5.42</td>
<td>3.85</td>
</tr>
<tr>
<td>69</td>
<td>2.29</td>
<td>5.11; 5.34</td>
<td>3.96</td>
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<tr>
<td>71</td>
<td>2.02</td>
<td>5.17; 5.86</td>
<td>4.17</td>
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<tr>
<td>70</td>
<td>2.50</td>
<td>5.39; 5.61</td>
<td>3.96</td>
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<tr>
<td>72</td>
<td>1.49</td>
<td>5.35; 5.64</td>
<td>3.80</td>
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<tr>
<td>73</td>
<td>2.27; 1.56[^{[a]}]</td>
<td>5.37; 5.63[^{[b]}]</td>
<td>3.98; 3.83[^{[a]}]</td>
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<tr>
<td>74</td>
<td>1.50</td>
<td>5.17; 5.78</td>
<td>3.93</td>
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<tr>
<td>75</td>
<td>2.63[^{[c]}]</td>
<td>4.36; 5.26; 4.95[^{[d]}]; 5.57[^{[d]}]</td>
<td>4.09; 4.49[^{[d]}]</td>
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<td>76</td>
<td>1.64</td>
<td>5.18; 5.40</td>
<td>3.78</td>
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<tr>
<td>68</td>
<td>8.39</td>
<td>5.21; 5.58</td>
<td>4.31</td>
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</table>

Beside the crystal structure, also selected chemical shifts and the rhodium-phosphorus coupling constant of the newly synthesised complexes were compared (Table 11 and Table 12).

The NMR data of the complexes with alkyl substituents on the phenyl rings of the phosphane ligand are only slightly different from the PPh\(_3\)-complex 61. The CF\(_3\)-substituents led to chemical shifts at slightly higher frequency. The largest differences were found with the P(py)\(_3\) ligand (complex 68) and the phosphole ligand DBP (complex 75). The resonance of the NH proton of complex 68 is 5-6 ppm shifted to higher frequency which indicates a considerable hydrogen bonding between the nitrogen atom of one pyridyl ring and the NH-function.

It is also worth mentioning that the rotation around the rhodium phosphorus bond is considerably hindered. It was already known that the signals of the PPh\(_3\) protons are broadened for complex 61. The phosphole ligand DBP is similarly bulky as PPh\(_3\) and
consequently the complex 75 needed to be measured at lower temperature in order to observe both rotamers. With the bulkier phosphane P(3,5-diMePh)_3 the two rotamers were visible even at room temperature, however only in the ^31P NMR. With even bulkier phosphanes only one isomer was found, indicating that the rotation is inhibited on the NMR-time scale. Also with the phosphane P(py)_3 only one isomer was observed although this phosphane is similarly bulky as PPh_3 or DBP. The reason for this observation could be that the proposed hydrogen bonding between a pyridyl ring and the amino group of trop_2NH inhibits the rotation of the phosphane on the NMR-time scale.

**Table 12**: Selected carbon chemical shifts, as well as the ^31P chemical shift and the rhodium phosphorus coupling constant of the newly synthesised chloro-complexes. [a] Two isomers (84%; 16%) 69 were observed, however only in the ^31P NMR; [b] The chemical shifts of the olefinic carbons of the two isomers of 73 could not be distinguished; [c] Two isomers (61%; 39%) of 73 were found; [d] Two isomers (50%; 50%) of 75 were found at 223 K; [e] The two isomers of 75 could not be distinguished in the ^31P NMR.

<table>
<thead>
<tr>
<th>Complex</th>
<th>CH^{olef} δ [ppm]</th>
<th>CH^{benzyl} δ [ppm]</th>
<th>P δ [ppm]</th>
<th>J_{RhP} [Hz]</th>
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<tr>
<td>69</td>
<td>66.8; 70.7</td>
<td>73.1</td>
<td>8.8; 9.3[a]</td>
<td>109.8; 113.6[a]</td>
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<tr>
<td>71</td>
<td>68.4; 74.7</td>
<td>73.1</td>
<td>13.2</td>
<td>113.2</td>
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<td>70</td>
<td>66.3; 70.6</td>
<td>73.1</td>
<td>11.7</td>
<td>110.7</td>
</tr>
<tr>
<td>72</td>
<td>66.0; 70.8</td>
<td>72.9</td>
<td>11.9</td>
<td>110.5</td>
</tr>
<tr>
<td>73</td>
<td>66.6; 70.8[b]</td>
<td>73.1; 72.9[c]</td>
<td>8.2; 6.8[c]</td>
<td>110.6; 109.1[c]</td>
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<tr>
<td>74</td>
<td>67.5; 73.3</td>
<td>72.8</td>
<td>11.5</td>
<td>114.4</td>
</tr>
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<td>75</td>
<td>67.9; 68.7; 67.3[d]; 71.0[d]</td>
<td>72.3; 72.9[d]</td>
<td>3.8[e]</td>
<td>111.3[e]</td>
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<td>76</td>
<td>66.2; 70.7</td>
<td>73.2</td>
<td>6.9</td>
<td>111.3</td>
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<tr>
<td>68</td>
<td>68.3; 71.2</td>
<td>73.1</td>
<td>15.6</td>
<td>112.9</td>
</tr>
</tbody>
</table>

Complex 73 which has a phosphane ligand with two phenyl groups with methyl substituents in meta position and one unsubstituted phenyl ring also shows two rotamers. In one of the isomers the two substituted phenyl rings of the PPhAr_2 were chemically equivalent, therefore it was concluded that the unsubstituted phenyl ring points into the cavity of the trop_2NH ligand giving an isomer with C_8 symmetry. For the other isomer, distinct signals were obtained for the two substituted phenyl groups, thus indicating that one of these two aryl groups point into the cavity of the trop_2NH ligand resulting in a C_1 symmetry. Assuming there is no preference for one of the two isomers, they would be observed in a 2:1 ratio. However,
the measured ratio was approximately 3:2 thus indicating that the unsubstituted and thus less bulky phenyl group is slightly favoured in the position pointing between the two trop units.

Figure 23: Ortep plot (at 50% probability) of the structure of [Rh(trop$_2$NH)(P(2-OMePh)$_3$)]OTf $67$; crystallised with two independent molecules in the asymmetric unit cell. One is not shown, but the distances are given in brackets []. The OTf-anion and most of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C19=C20): Rh1-N1 2.160(2) [2.140(2)], Rh1-P1 2.266(1) [2.270(1)], Rh1-ct1 2.092(3) [2.022(3)], Rh1-ct2 2.021(3) [2.018(3)], Rh1-O1 (distance) 2.419(2) [2.401(2)], Rh1-C4 2.218(3) [2.151(3)], Rh1-C5 2.198(3) [2.138(3)], Rh1-C19 2.145(3) [2.201(3)], Rh1-C20 2.144(3) [2.198(3)], C4=C5 1.410(4) [1.427(4)], C19=C20 1.430(4) [1.424(4)], N1-Rh1-P1 172.43(6) [170.87(6)], ct1-Rh1-ct2 137.4(1) [136.0(1)].NMR-analysis of the two other complexes with a PPh$_2$Ar ligand, namely $72$ and $74$, with the bulkier tert-butyl and CF$_3$ substituents in meta position, yielded only one isomer. In both complexes the two substituted aryl groups are chemically equivalent, therefore it was concluded that only the isomer with the unsubstituted phenyl group pointing into the cavity of the trop$_2$NH ligand was observed. It is therefore concluded that the bulkier a substituent of the phosphane is, the less favoured its positioning is between the two trop-units.
Table 13: Comparison of selected bond lengths and angles of \(\text{[Rh(trop}_2\text{NH})(\text{PPh}_3)]\text{OTf} \), \(\text{[Rh(trop}_2\text{NH})(\text{P}(3,5\text{-diMePh})_3)]\text{OTf} \) \(77\), \(\text{[Rh(trop}_2\text{NH})(\text{P}(2\text{-OMePh})_3)]\text{OTf} \) \(67\) and \(\text{[Rh(trop}_2\text{NH})(\text{DBP})]\text{OTf} \) \(78\) (DBP = 5-phenyl-5H-dibenzophosphole).

<table>
<thead>
<tr>
<th>Complex</th>
<th>9(^{[28a]})</th>
<th>77</th>
<th>67</th>
<th>78</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh1-N1 [Å]</td>
<td>2.150(2)</td>
<td>2.147(2)</td>
<td>2.160(2)</td>
<td>2.139(2)</td>
</tr>
<tr>
<td>Rh1-P1 [Å]</td>
<td>2.2789(7)</td>
<td>2.3085(7)</td>
<td>2.266(1)</td>
<td>2.2543(7)</td>
</tr>
<tr>
<td>Rh1-ct1 [Å]</td>
<td>2.040(2)</td>
<td>2.072(3)</td>
<td>2.092(3)</td>
<td>2.035(2)</td>
</tr>
<tr>
<td>Rh1-ct2 [Å]</td>
<td>2.075(2)</td>
<td>2.033(3)</td>
<td>2.021(3)</td>
<td>2.065(2)</td>
</tr>
<tr>
<td>C4=C5 [Å]</td>
<td>1.404(3)</td>
<td>1.399(4)</td>
<td>1.410(4)</td>
<td>1.420(4)</td>
</tr>
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<td>C19=C20 [Å]</td>
<td>1.422(4)</td>
<td>1.436(4)</td>
<td>1.430(4)</td>
<td>1.410(3)</td>
</tr>
<tr>
<td>N1-Rh1-P1 [°]</td>
<td>179.17(6)</td>
<td>177.45(7)</td>
<td>172.43(6)</td>
<td>177.47(6)</td>
</tr>
<tr>
<td>ct1-Rh1-ct2 [°]</td>
<td>139.9(1)</td>
<td>136.4(1)</td>
<td>137.4(1)</td>
<td>137.5(1)</td>
</tr>
</tbody>
</table>

In Table 13 selected bond lengths and angles of crystallised OTf-complexes were compared to \(\text{[Rh(trop}_2\text{NH})(\text{PPh}_3)]\text{OTf} \) \(9\).

The phosphole complex \(78\) showed the smallest differences to the \(\text{PPh}_3\) complex \(9\); the rhodium phosphorus bond of complex \(77\) is significantly larger compared to \(9\). Consequently, a weaker rhodium phosphorus bond is expected not only in \(77\), but also in the other complexes with even bulkier substituents, such as \(\text{CF}_3\), \(\text{iso}\)-propyl or \(\text{tert}\)-butyl groups.

The N-Rh-P bond angle of \(67\) is almost 7° smaller compared to \(9\) and about 5° smaller compared to the other analysed OTf-complexes. This result is rationalised to be the consequence of a strong interaction between the metal centre and an oxygen atom of one methyl ether group (see Figure 23). This interaction was actually desired because it should weaken the bond between the rhodium atom and acetate ligands produced in OMFC, because the acetoato-complexes were thought to be responsible for the immense drop of performance of the OMFC using \(\text{[Rh(trop}_2\text{NH})(\text{PPh}_3)]}\) \(9\) as electrocatalyst (see discussion in chapter 3.2).

Beside the crystal structure also selected chemical shifts and the rhodium-phosphorus coupling constant of the newly synthesised complexes were compared (Table 14 and Table 15).

The chemical shift of the NH proton of complexes with \(\text{CF}_3\) substituents on the triaryl phosphane ligand are shifted significantly to higher frequency. This result is not surprisingly, as the shift of the NH proton is considered an indicator of the acidity of this proton; with the electron-poor phosphane ligands a higher acidity is expected. On the other hand the chemical shift of the NH of complex \(67\) is shifted to lower frequency by about 2 ppm. It is assumed that
the interaction of one of the oxygen of the methyl ether substituents on the phosphane ligand (see Figure 23 and the discussion of the crystal structure above) causes this difference. As shown in Table 11 the [RhCl(trop$_2$NH)(L)] complexes have NH chemical shifts between 1.5 and 2.6 ppm. It would therefore be expected that the chemical shift of the NH proton of complex 67 is found between the four-coordinated OTf-complexes and the five-coordinated Chloro-complexes.

Figure 24: Ortep plot (at 50% probability) of the structure of [Rh(trop$_2$NH)(DBP)]OTf 78. The OTf-anion and most of the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct2 = centroid C19=C20): Rh1-N1 2.139(2), Rh1-P1 2.2543(7), Rh1-ct1 2.035(2), Rh1-ct2 2.065(2), Rh1-C4 2.161(2), Rh1-C5 2.150(2), Rh1-C19 2.197(2), Rh1-C20 2.167(2), C4=C5 1.420(4), C19=C20 1.410(3), N1-Rh1-P1 177.47(6), ct1-Rh1-ct2 137.5(1).

Surprisingly, the chemical shifts of the olefinic carbons of complex 67 are shifted by about 20 ppm to lower frequency. The origin of this difference is not yet understood, however it is assumed that it is also associated with the oxygen rhodium interaction.
Furthermore it is found that the electron withdrawing CF₃ substituents, generally lead to phosphorus shifts at slightly higher frequency as well as slightly larger rhodium phosphorus coupling constants.

**Table 14**: Comparison of selected $^1$H NMR shifts of $[\text{Rh(trop}_2\text{NH})(\text{PPh}_3)]$ 9, $[\text{Rh(trop}_2\text{NH})(\text{P}(3,5\text{-diMePh})_3)]\text{OTf}$ 77, $[\text{Rh(trop}_2\text{NH})(\text{P}(3,5\text{-diCF}3\text{Ph})_3)]\text{OTf}$ 79, $[\text{Rh(trop}_2\text{NH})(\text{P}(3,5\text{-di}’\text{BuPh})_3)]\text{OTf}$ 66, $[\text{Rh(trop}_2\text{NH})(\text{P}(\text{C}_{12}\text{H}_{17}))_3]\text{OTf}$ 80, $[\text{Rh(trop}_2\text{NH})(\text{P}(2\text{-OMePh})_3)]\text{OTf}$ 67, $[\text{Rh(trop}_2\text{NH})(\text{PPh}(3,5\text{-diBuPh})_2)]\text{OTf}$ 81, $[\text{Rh(trop}_2\text{NH})(\text{PPh}(\text{di-3,5-MePh})_2)]\text{OTf}$ 82, $[\text{Rh(trop}_2\text{NH})(\text{PPh}(\text{di-3,5-CF}3\text{Ph})_2)]\text{OTf}$ 83, $[\text{Rh(trop}_2\text{NH})(\text{DBP})]\text{OTf}$ 78, $[\text{Rh(trop}_2\text{NH})(\text{P}(\text{p-BuPh})_3)]\text{OTf}$ 84 and $[\text{Rh(trop}_2\text{NH})(\text{P}(\text{py})_3)]\text{OTf}$ 85. [a] The two signals of the olefinic protons could not be distinguished.

<table>
<thead>
<tr>
<th>Complex</th>
<th>NH $\delta$ [ppm]</th>
<th>$\text{CH}^{\text{olef}}$ $\delta$ [ppm]</th>
<th>$\text{CH}^{\text{benzyl}}$ $\delta$ [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>9[a, 6c, 28a]</td>
<td>5.66</td>
<td>4.94; 5.43</td>
<td>4.91</td>
</tr>
<tr>
<td>77</td>
<td>5.56</td>
<td>5.02; 5.46</td>
<td>5.02</td>
</tr>
<tr>
<td>79</td>
<td>6.33</td>
<td>4.80; 5.41</td>
<td>4.95</td>
</tr>
<tr>
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<td>3.93</td>
<td>4.71; 6.27</td>
<td>5.94</td>
</tr>
<tr>
<td>80</td>
<td>5.57</td>
<td>4.93; 5.67</td>
<td>5.18</td>
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<tr>
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<td>3.60</td>
<td>4.72; 5.34</td>
<td>5.37</td>
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<tr>
<td>81</td>
<td>5.46</td>
<td>4.81; 5.63</td>
<td>5.20</td>
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<tr>
<td>82</td>
<td>5.64</td>
<td>5.00; 5.46</td>
<td>4.95</td>
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<tr>
<td>83</td>
<td>6.17</td>
<td>4.88; 5.37</td>
<td>4.94</td>
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<td>78</td>
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<td>4.58; 5.66</td>
<td>4.89</td>
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<tr>
<td>84</td>
<td>5.52</td>
<td>4.89; 5.52</td>
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<tr>
<td>85</td>
<td>5.25</td>
<td>5.86[a]</td>
<td>5.15</td>
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Table 15: Selected carbon chemical shifts, as well as the $^{31}$P chemical shift and the rhodium phosphorus coupling constant of the newly synthesised OTf-complexes compared to [Rh(trop$_2$NH)(PPh$_3$)]OTf 9. [a] The two signals of the olefinic carbons could not be distinguished.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$CH^{olef}$ δ [ppm]</th>
<th>$CH^{benzyl}$ δ [ppm]</th>
<th>P δ [ppm]</th>
<th>$^{1}J_{RhP}$ [Hz]</th>
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</thead>
<tbody>
<tr>
<td>9$^{[6a, 6c, 28a]}$</td>
<td>74.0; 74.2</td>
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<td>40.6</td>
<td>137.7</td>
</tr>
<tr>
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<td>72.6</td>
<td>38.5</td>
<td>136.2</td>
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<tr>
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<td>74.1; 75.0</td>
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<td>48.1</td>
<td>144.8</td>
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<tr>
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<td>79.8; 87.9</td>
<td>70.8</td>
<td>39.9</td>
<td>137.3</td>
</tr>
<tr>
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<td>75.9; 77.2</td>
<td>72.3</td>
<td>41.9</td>
<td>135.8</td>
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<td>53.9; 56.8</td>
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<td>33.4</td>
<td>143.4</td>
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<td>75.0; 77.5</td>
<td>71.9</td>
<td>44.5</td>
<td>135.2</td>
</tr>
<tr>
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<td>74.7$^{[9]}$</td>
<td>73.1</td>
<td>39.3</td>
<td>136.7</td>
</tr>
<tr>
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<td>74.0; 74.3</td>
<td>73.3</td>
<td>45.9</td>
<td>141.9</td>
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<td>71.7; 74.4</td>
<td>73.2</td>
<td>40.0</td>
<td>135.8</td>
</tr>
<tr>
<td>84</td>
<td>74.8$^{[a]}$</td>
<td>72.9</td>
<td>38.7</td>
<td>136.5</td>
</tr>
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<td>85</td>
<td>68.2; 72.2</td>
<td>70.4</td>
<td>26.2</td>
<td>131.9</td>
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</table>

3.3.2 Application of the new synthesised complexes in homogeneous catalysis

In order to compare the catalytic activity of the newly synthesised complexes with [Rh(trop$_2$NH)(PPh$_3$)]OTf 9, they were tested in the transfer hydrogenation of acetophenone (Table 16) and the dehydrogenative coupling reaction of benzyl alcohol with water and methanol to benzoic acid (Table 17) and methyl benzoate (Table 18).

It was found that the catalytic activity of the complexes with three in meta-position substituted phenyl rings on the phosphane is generally lower compared to the complexes with only two substituted phenyl rings. Furthermore, the smaller the substituents in meta-position were the higher the conversions, which were generally reached. However, the high catalytic activity of 9 was unmatched.

The strongly electron withdrawing substituent CF$_3$ (entry 3 and 9 in Table 16; entry 2 and 8 in Table 17 and Table 18) was found to decrease the catalytic activity compared to complexes with alkyl substituents on the phosphane. Also complex 85 with pyridyl- instead of phenyl rings on the phosphane gave only low conversions.
Table 16: The results of the transfer hydrogenation of acetophenone in ethanol with the newly synthesised catalysts. Reaction conditions: 2 M acetophenone in ethanol, 1 mol% K₂CO₃, reaction time: 20 hours, catalyst specified below. [a] The conversion was determined by the ratio of the integrals of the ¹H-NMR signals of the CH₃-group; [b] After 3 hours no further conversion was observed; [c] After 4 hours no further conversion was observed.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>S/C</th>
<th>Conversion[a] [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>77</td>
<td>10³</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
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<td>79</td>
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<td>0</td>
</tr>
<tr>
<td>4</td>
<td>66</td>
<td>10⁴</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>10⁴</td>
<td>50ᵇ</td>
</tr>
<tr>
<td>6</td>
<td>67</td>
<td>10⁴</td>
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<td>7</td>
<td>81</td>
<td>10⁴</td>
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</tr>
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<td>8</td>
<td>82</td>
<td>10⁴</td>
<td>99.9ᶜ</td>
</tr>
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<td>9</td>
<td>83</td>
<td>10⁴</td>
<td>48⁹</td>
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<td>10³</td>
<td>71</td>
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Complex 67 with methoxy substituents in ortho position of the phosphane phenyl rings was originally designed to avoid the formation of the acetato complex, which is responsible for the activity drop of the OMFC. However, with 67 only poor conversions could be achieved. It is assumed that the interaction between the rhodium and the oxygen atom (see discussion in section 3.3.1) is responsible for the low catalytic activity by blocking the active catalytic side too strongly.

With complex 84 benzyl alcohol was completely converted to benzoic acid (Table 17, entry 10). On the other hand, in the transfer hydrogenation and the dehydrogenative coupling reaction with methanol, only moderate conversions were achieved with 84 (see Table 16 entry 13 and Table 18, entry 10). However, in the OMFC the carboxylate are formed, therefore 84 is an interesting candidate as electrocatalyst in the OMFC.
**Table 17**: Results obtained for the dehydrogenative coupling reaction of benzyl alcohol with water to benzoic acid. Reaction conditions: 5 eq. cyclohexane, 66 eq. H₂O, 1.2 eq. NaOH, 0.1 mol% catalyst (specified below). [a] all yields refer to isolated products; the identity of the products was determined by ¹H and ¹³C NMR spectroscopy.

<table>
<thead>
<tr>
<th>Entry</th>
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</thead>
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<tr>
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<td>13</td>
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</table>

**Table 18**: Results obtained for the dehydrogenative coupling reaction of benzyl alcohol with methanol to methyl benzoate. Reaction conditions: 5 eq. cyclohexanone, 10 eq. methanol, 5 mol% K₂CO₃, 0.1 mol% catalyst (specified below). [a] conversion determined by GC; [b] product distribution.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion[α] [%]</th>
<th>Benzaldehyde[β] [%]</th>
<th>Methyl benzoate[β] [%]</th>
<th>Benzyl benzoate[β] [%]</th>
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</tbody>
</table>
As shown in Table 18 none of the catalyst showed high selectivity for the formation of the desired methyl benzoate. Most often, benzaldehyde was found as the major by-product or even as the main product in case of low conversion of benzyl alcohol.

Catalyst \textbf{82, 83 and 85} were found to rather couple two substrates to benzyl benzoate than coupling benzyl alcohol with methanol to methyl benzoate.
3.4 Improved OMFC with [Rh(trop₂NH)(P(p-BuPh)₃)]OTf 84 as electrocatalyst

The newly synthesised complexes described in the previous chapter were tested as electrocatalysts for the OMFC. With [Rh(trop₂NH)(P(p-BuPh)₃)]OTf 84 similarly high activities as with [Rh(trop₂NH)(PPh₃)]OTf 9 were achieved, however, loss of activity during the run was much smaller with 84 compared to 9. The other synthesised complexes described in chapter 3.3 were also tested as electrocatalyst for the OMFC, however, no improvement of the performance was observed.

In order to fully analyse 84, a sample which is totally sliver free was required by our collaborators, Bianchini et al. Therefore an alternative synthetic procedure for 84 without the use of AgOTf or any other silver salt was required. This requirement was met by first synthesising the amido complex [Rh(trop₂N)(P(p-BuPh)₃)] 86. The procedure is similar to the synthesis of [Rh(trop₂N)(PPh₃)] 1.[⁶]

Subsequently 86 was treated with triethylammonium triflate, which yielded the target complex 84 without any silver contamination. Furthermore, 86 was treated with hydrogen gas, water and acetic acid, producing the amino hydride complex 87, the hydroxo complex 88 and the acetato complex respectively 89. The synthesis of these complexes is shown in Scheme 27.

---

[⁶] The electrochemical experiments were performed by our collaborators Binachini et al. Experimental data can be found in Energy Environ. Sci. 2012, 5, 8608-8620.
Scheme 27: Reaction sequence for the synthesis of the OTf, amido, amino hydride, hydroxo and acetato complex (Ar = p-BuPh). Reagents: a) AgOTf; b) t-BuOK; c) (NHEt$_3$)OTf; d) H$_2$; e) H$_2$O; f) CH$_3$COOH.

It was found that the crystallization behaviour of the newly synthesised rhodium complexes is remarkably affected by the flexible $n$-butyl moieties. Analysis by X-ray powder diffraction (XRPD) of the pure compounds indicated that only the chloro complex 76 is crystalline (Figure 25a) whereas the OTf-complex 84 (Figure 25b), amido 86 (Figure 25c) and acetato complex 89 (Figure 25d) are amorphous. For comparison, the XRPD analysis of complex [Rh(trop$_2$NH)(PPh$_3$)]OTf 9 and [Rh(eq-OAc)(trop$_2$NH)(PPh$_3$)] 7 (Figure 26, trace A/B) showed clearly the presence of crystalline material.

XRPD analysis of the OTf complex 84 and the acetato complex 89, deposited on the carbon support, clearly indicate that amorphous material was obtained. It is assumed that amorphous material deposited on the carbon support increases the active surface compared to crystalline support.
Figure 25: XRPD spectra of the chloro complex 76 (a), the OTf complex 84 (b), the amido complex 86 (c) and the acetato complex 89 (d).

The complexes [Rh(trop2NH)(PPh3)]OTf 9, [Rh(OAc)(trop2NH)(PPh3)] 7, [Rh(trop2NH)(P(ρ-BuPh)3)]OTf 84, [Rh(OAc)(trop2NH)(P(ρ-BuPh)3)] 89, were deposited on Ketjenblack EC-600JD (Ck) which exhibits a five times higher surface area as well as a lower hydrophilic character as compared to Cv. As a result, the following new materials were obtained: 9@Ck, 7@Ck, 84@Ck and 89@Ck, each of which containing a 4 wt% and 0.4 wt% rhodium loading. Anode electrodes were prepared by depositing a water dispersion of these products onto Ni foam plates in order to obtain an effective metal loading of 1.0 and 0.1 mg cm\(^{-2}\). MEAs for passive OMFCs were realised assembling these anodes, Tokuyama A-201 membranes and proprietary Fe-Co cathodes. The power densities measured for each cell containing a rhodium loading of 1.0 mg cm\(^{-2}\), and the results of galvanostatic experiments at 50 mA are reported in Table 19. The performance of 7@Cv was not reported in Table 19 because it was extremely low already in the first cycle (max. power density 2.0 mW cm\(^{-2}\) with a turn over number (TON) of 44 (2.3 mmol)).
Table 19: Passive cell performance of OMFCs containing a Rh-loading of 1.0 mg cm$^{-2}$ on the anode. [a] mol of KOAc per mol Rh; [b] mmol of ethanol converted to KOAc; [c] ethanol conversion only at 10 mA.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Supported electrocatalyst</th>
<th>Maximal power density (mW cm$^{-2}$)</th>
<th>Galvanostatic cycles at 50 mA TON$^{[a]}$ (mmol KOAc)$^{[b]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1$^{st}$  2$^{nd}$  3$^{rd}$</td>
</tr>
<tr>
<td>1</td>
<td>9@Cv</td>
<td>6.0</td>
<td>212 (10.3)  ↓$^{[c]}$  -</td>
</tr>
<tr>
<td>2</td>
<td>9@Ck</td>
<td>6.0</td>
<td>204 (9.9)  170 (8.2)  158 (7.7)</td>
</tr>
<tr>
<td>3</td>
<td>7@Ck</td>
<td>6.8</td>
<td>191 (9.2)  156 (7.6)  158 (7.7)</td>
</tr>
<tr>
<td>4</td>
<td>84@Ck</td>
<td>6.0</td>
<td>191 (9.2)  165 (8.0)  157 (7.6)</td>
</tr>
<tr>
<td>5</td>
<td>89@Ck</td>
<td>7.0</td>
<td>212 (10.3)  195 (9.5)  184 (8.9)</td>
</tr>
</tbody>
</table>

As described in chapter 3.2, the OMFC with the 9@Cv anode showed a dramatic activity drop after about a 40–50% conversion of ethanol into acetate under galvanostatic conditions (50 mA) and could not be recycled for a second run (Table 19, entry 1).

A perusal of the data reported in Table 19 allows one to conclude that the support material Ck (entries 2-5) provides a much more stable catalytic system as compared to Cv (entry 1). Indeed, while the Cv anode could not be used even for a second galvanostatic run at the same current intensity, the Ck-based anodes were recycled at least three times with overall activity losses spanning from ca. 22% for the complexes with the PPh$_3$ ligand to 14% for the complexes with the P(p-BuPh)$_3$. In particular, the best performance, both in terms of power density and conversion of ethanol into acetate, was provided by the electrocatalyst 89@Ck. The TONs were rather good, corresponding to ethanol conversions between 50 and 40%.

In an attempt to rationalise the electrocatalytic performances compiled in Table 19, XPRD analysis have been carried out on 9 (A), 7 (B), 84 (C) and 89 (D) as isolated compounds (Figure 26, traces a) but also as Ck-supported complexes, before (traces b) and after galvanostatic experiments at 50 mA (traces c). For comparative purposes, XRPD spectra of 9@Cv, before (a) and after the galvanostatic cycle at 50 mA (c), are shown in Figure 26E.
Figure 26: XPRD analysis of 9 (A), 7 (B), 84 (C) and 89 (D) acquired on isolated complexes (a), Ck-supported complexes before (b) and after (c) galvanostatic cycle at 50 mA in a passive OMFC. (E) 9@Cv before (a) and after (b) galvanostatic cycle at 50 mA in a passive OMFC.
From a comparison of the XRPD traces of the anodes (Figure 26) and the electrochemical results (Table 19), the following conclusions were drawn: (i) in combination with Ck, 89 gives a completely amorphous phase (trace b in Figure 26D), unlike what happens when the support is Cv. (ii) After one or even three galvanostatic cycles 9@Ck is not quantitatively transformed into 7@Ck, thus showing the same XRPD pattern with an attenuation of intensity (Figure 26A, trace b vs. c). This experimental result is in contrast with the quantitative conversion of 9@Cv into 7@Cv (Figure 26E, trace a vs. b) within a single galvanostatic cycle. (iii) 9@Ck and 7@Ck exhibit comparable power density and recyclability (Table 19, entries 2 and 3), thus indicating that the acetato complex 7 is an active electrocatalyst for ethanol oxidation, provided the carbon support is Ck. (iv) The intensity of the XRPD pattern shown in Figure 26A (traces b vs. c) suggest a partial conversion of crystalline 9@Ck into amorphous 7@Ck. The metal complexes on the anode were extracted with [D8]THF after each galvanostatic cycle and the three resulting solutions were analysed by 31p-NMR spectroscopy: in all cases, 9 and 7 were detected in a 3:1 ratio. This experimental evidence and the presence of a crystalline phase of 9 after three galvanostatic cycles indicates that 7, generated during the electrocatalytic process, is amorphous and deposits onto the crystalline phase of 9, thus blocking its further reaction with the ethanol-KOH solution.

In an attempt to provide further experimental evidence supporting the coverage of 9 by 7, XPS measurements have been performed on 9@Ck, prior to and after a galvanostatic cycle. The intensity of the F 1s signal is strongly decreased after the galvanostatic cycle, compared to spectrum measured before. This is in accordance with a surface capping by a species that does not contain fluorine (e.g. 7@Ck).

In an attempt to provide further experimental evidence supporting the coverage of 9 by 7, X-ray photoelectron spectroscopy (XPS) measurements have been performed on 9@Ck, prior to and after a galvanostatic cycle. In Figure 27a and b the XPS wide range (survey) scans collected before and after the galvanostatic cycle are reported, in order to show the sample surface chemical composition. All the photoemission peaks belonging to the Rh complex are present and labelled. The presence of F is witnessed by a clear F 1s signal in the 9@Ck sample which contains the triflate = CF3SO3- anion before the galvanostatic cycle (Figure 27c, upper trace). The same spectrum collected on the 9@Ck after the galvanostatic cycle (Figure 27c, lower trace) shows a remarkable intensity decrease, so that the peak becomes.

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XRPD, NMR and XPS analysis of the anodes was executed by our collaborators Bianchini et al. Interested readers will find further details and experimental data in Energy Environ. Sci. 2012, 5, 8608-8620 and the supporting information therein.
hardly noticeable. This is in accordance with a surface capping by a species that does not contain F (e.g. 7@Ck, see below). Unfortunately, the remarkable roughness of the catalyst surface does not allow carrying out a reliable sputtering analysis.

Figure 27: The result of the XPS analysis on the anode material 9@Ck before and after the galvanostatic cycle at 50 mA lasting 20 hours; (a) and (b) show wide range (survey) scans of the electrocatalyst’s chemical composition before and after a galvanostatic cycle, respectively (peaks labelled with * belong to the sample holder (Ta and Mo) or the copper support); (c) shows the F 1s scan collected before (upper trace) and after (lower trace) the galvanostatic cycle.
Figure 28: (a): BSE-SEM image of crystals of 9 embedded in Vulcan XC-72 carbon black as carbon matrix. (b): EDXS spectrum (relevant section) of the area marked in (a), (c) and (d): SEM images of 89 supported on Ck after 37 hours of usage in a passive cell. (c) SE image showing the morphology of the sample that consists of tiny particles. (d) BSE image of the same area. The inset shows an EDXS analysis (section) of the marked spot (circle) demonstrating the presence of a small amount of rhodium which can be found everywhere. (e) HAADF-STEM (Z contrast) image showing the presence of single rhodium atoms as bright spots.
In order to further characterise the anodes coated with the different molecular catalysts and to bolster the observations from the XRPD measurements, various electron microscopic techniques were applied and the results are displayed in Figure 28a–e. Indeed, 9 forms crystals up to about 1 μm in size upon precipitation on Vulcan XC-72 (Figure 28a). An energy-dispersive X-ray (EDXS) spectrum clearly shows the expected elemental composition, namely Rh, S, P, O, F (the presence of S, O, and F indicates the presence of the triflate anion, CF₃SO₃⁻) (Figure 28b). On the contrary, when amorphous 89 is deposited on Ck as support, no crystalline particles are observed. The image in Figure 28c obtained with secondary electrons (SEs) as well as the image in Figure 28d recorded with back-scattered electrons (BSEs) shows that the electrode material consists of tiny carbon particles on which rhodium is uniformly distributed (see the EDXS analysis in the inset of Figure 28d). Most importantly, the image obtained for a 89@Ck electrode used for 37 hours in a passive cell by scanning transmission electron microscopy using a high-angle annular dark field detector (HAADF-STEM) displayed in Figure 28e gives no indication for rhodium clusters or particles on the nanometer scale. Indeed this highly sensitive Z contrast technique, especially for heavy elements (e.g. Rh) on a light support (e.g. C), shows the presence of single rhodium atoms. These findings strongly support the assumption that indeed molecules containing a single rhodium atom act as catalytically active sites.

Incorporation of the electrochemical, chemical, XRPD, NMR, XPS, and SEM/STEM data leads us to conclude that: (i) Ck, unlike Cv, favours the conversion of crystalline 9 into amorphous 7 upon reaction with ethanol/OH⁻ during the galvanostatic experiment in the passive OMFC; (ii) such a transformation is not complete since only one fourth of the OTf complex 9 is converted into the acetate complex 7; (iii) the amorphous phase of 89, which covers the remaining 84 and hence inhibits the reaction with ethanol/OH⁻, exhibits a good catalytic activity and stability, being recyclable three times with little activity loss (Table 19). This evidence may be interpreted in terms of a higher number of surface complex molecules when the complex is amorphous.
Figure 29: Schematic representation of the morphology evolution of \(9@Cv\) (a), \(9@Ck\) (b), \(84@Ck\) (c) and \(89@Ck\) (d) during the galvanostatic experiment with an anode rhodium loading of 1.0 mg cm\(^{-2}\).

A schematic representation summarising what may happen on the anode surface containing either \(9@Cv\), \(9@Ck\), \(84@Ck\) or \(89@Ck\) during the catalytic oxidation of ethanol to acetate is shown in Figure 29a-d. On \(Cv\), \(9\) converts into crystalline \(7\), which dramatically reduces the rate of ethanol oxidation due to the small number of active molecules at the crystal surfaces (Figure 29a). In contrast, when \(Ck\) is used as the support material, the acetato complex, formed during the galvanostatic experiment (i.e., \(7_{am}\)), is amorphous, hence, maintaining a high number of active surface complex molecules (Figure 29b). On the other hand, \(7_{am}\) covers the residual crystalline \(9\) (i.e., \(9_{cryst}\)) which is then excluded from taking part in further electrooxidation of ethanol.

In light of these considerations, it is not surprising to find that the fully amorphous complexes \(84@Ck\) and \(89@Ck\) generate a fairly stable electrocatalyst that can be re-used three times with less than 14% decay of its original activity (Table 19, entries 4 and 5). Figure 29c and d
illustrate the assumed morphologic evolution of the anode electrocatalysts \(84@\text{Ck}\) and \(89@\text{Ck}\), as ascertained by XRPD analysis, during the galvanostatic experiments. The \(3^1\)P-NMR analysis of the metal complexes extracted from the \(84\) catalysed anode showed that the starting complex is not completely converted into the final acetato compound after a galvanostatic run (i.e. ratio of \(84:89 = 2:1\)). It is therefore assumed that an amorphous phase of \(89@\text{Ck}\) covers the initial amorphous phase of \(84@\text{Ck}\), thereby preventing its conversion into the acetato complex \(89@\text{Ck}\) (Figure 29c). On the other hand, when amorphous \(89\) is used on \(\text{Ck}\), the number of catalytically active sites remains almost constant, explaining the relatively small drop of activity after a couple of galvanostatic runs (Figure 29d).

Table 20: Passive cell performance of OMFCs containing a rhodium load of 0.1 mg cm\(^{-2}\) on the anode. [a] mol of KOAc per mol Rh; [b] mmol of ethanol converted to KOAc; [c] ethanol conversion only at 10 mA.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Supported electrocatalyst</th>
<th>Maximal power density (mW cm(^{-2}))</th>
<th>Galvanostatic cycles at 50 mA TON(^{[a]}) (mmol KOAc)(^{[b]})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(1^{st})</td>
</tr>
<tr>
<td>1</td>
<td>(9@\text{Ck})</td>
<td>1.9</td>
<td>1173 (5.7)</td>
</tr>
<tr>
<td>2</td>
<td>(7@\text{Ck})</td>
<td>3.2</td>
<td>1515 (7.4)</td>
</tr>
<tr>
<td>3</td>
<td>(84@\text{Ck})</td>
<td>2.2</td>
<td>1256 (6.1)</td>
</tr>
<tr>
<td>4</td>
<td>(89@\text{Ck})</td>
<td>4.0</td>
<td>1992 (9.7)</td>
</tr>
<tr>
<td>5</td>
<td>(89@\text{Cv})</td>
<td>3.5</td>
<td>1472 (7.1)</td>
</tr>
</tbody>
</table>

The observation that only a fraction of the starting rhodium complexes reacted with the anolyte (ethanol–KOH–water) the metal loading on the OMFC anode was consequently reduced from 1.0 to 0.1 mg cm\(^{-2}\), while keeping the same membrane and cathode. The results of the cell performance and galvanostatic experiments are given in Table 20. For comparative purposes, \(89\) was supported on \(\text{Cv}\) and tested as an anode electrocatalyst (Table 20, entry 5). In line with the reduced concentration of the Rh-catalyst, the cell voltages were invariably lower than those observed with 1.0 mg cm\(^{-2}\) (see Table 19), but the TONs were higher and the overall ethanol conversions to acetate were comparable. The best performance was obtained with \(89@\text{Ck}\) which was recycled three times with little activity decay (Table 20, entry 4), while the worst recyclability was observed for the \(\text{Cv}\)-supported catalyst (entry 5).
Glassy carbon electrodes coated with $9@C_k$, $84@C_k$ and $89@C_k$ (ca. 1 mg Rh) were analysed by cyclic voltammetry in ethanol (10 wt%) and 2 M KOH solutions at a scan rate of 50 mV s$^{-1}$. The results obtained are shown in Figure 30. The trend of the specific activity (A g$^{-1}$ (Rh)) (mA mg$^{-1}$ see Figure 30) was in line with the passive OMFC performance, with values of $10^3$ A g$^{-1}$ (Rh), $7 \cdot 10^3$ A g$^{-1}$ (Rh) and $10^4$ A g$^{-1}$ (Rh) at 0.9 V for $9@C_k$, $84@C_k$ and $89@C_k$, respectively. It is noteworthy that the current intensity values obtained with $84$ and $89$ are the highest ever reported in the literature for ethanol electrooxidation in alkaline media.

MEAs for active OMFCs were realised using $89@C_k$ as an anode electrocatalyst with a rhodium loading of 0.1 mg cm$^{-2}$. The fuel (10 wt% EtOH and 2 M KOH) was delivered to the anode at a flux of 4 mL min$^{-1}$ while the oxygen flow was regulated at 0.2 L min$^{-1}$. The anode temperature was fixed at 60 °C. Polarization and power density curves for this cell are given in Figure 31(b) that also shows the performance of the $9@C_v$ catalyst with a metal loading of 1 mg cm$^{-2}$ for comparison (■). Indeed, when the metal loading of $9@C_v$ was 0.1 mg cm$^{-2}$, the cell did not show any activity. The cell with the latter catalyst gave a slightly higher maximum power density (24 mW cm$^{-2}$ (see chapter 3.2) vs. 18 mW cm$^{-2}$), but also a much lower electrochemical stability as shown by the galvanostatic traces at 100 mA reported in Figure 31b. In particular, the overall ethanol conversion to acetate starting from 50 mL of anolyte solution was 17% with $89@C_k$ (Rh, 0.1 mg cm$^{-2}$, mmol = 18.7; TON = 3855) and 5% with $9@C_v$ (Rh 1.0 mg cm$^{-2}$ mmol = 5.3; TON = 109).

**Figure 30**: Selected cyclic voltammograms of $9@C_k$ (▼), $84@C_k$ (●) and $89@C_k$ (■) in ethanol (10 wt%) and 2 M KOH solution. Scan rate 50 mV s$^{-1}$. Potential (V) vs. RHE.
Figure 31: a) Polarization and power density of active OMFCs with 89@Ck (0.1 mg cm$^{-2}$, □) or 9@Cv (1.0 mg cm$^{-2}$, ■) as anodes; b) galvanostatic curves at 100 mA.
3.5 Conclusions

The deposition of $89$ on Ck, which exhibits a higher surface area, higher pore volume and lower polarity as compared to Cv, gives a completely amorphous texture of the supported complex. The ameliorating effect of the amorphous phase has been ascribed to its higher number of surface complex molecules as compared to the crystalline phase. A specific activity as high as $10^4 \text{ A g}^{-1}$ (Rh) has been found in the half cell, which is the highest value ever reported for ethanol electrooxidation. The material $89@\text{Ck}$ has been successfully employed as an anode electrocatalyst in a complete alkaline OMFC to convert ethanol into acetate, showing comparable substrate conversions (45%) in three consecutive galvanostatic cycles even at a rhodium loading as low as 0.1 mg cm$^{-2}$. The carbon support Ck seems to significantly contribute to the enhanced electrocatalytic activity of the supported rhodium complex by favouring the formation of an amorphous phase of the rhodium acetato complex in the course of the cell functioning. In contrast, the use of Cv as carbon black leads to the formation of crystalline rhodium-acetato complexes, which reduces remarkably the recyclability of the anode material due to the small number of surface complex molecules. A real turning point in the development of the OMFC technology may be provided by the development of techniques enabling the coating of conductive supports with a single layer of the metal complex, which will involve the design and synthesis of molecular architectures with appropriate chemical–physical properties. Within this context, current studies are aimed at synthesising metal complexes that can be directly sublimed onto conductive materials.
4 Catalytic aerobic dehydrogenative coupling of primary alcohols and water to acids
4.1 Introduction

Petroleum, natural gas and coal are the basis for most of the chemicals we use in our daily lives. These resources form slowly in biological (photosynthesis) and geochemical processes in which carbon dioxide is reduced under formation of oxygen (Eq. 15).

\[
\text{n CO}_2 + \text{n H}_2\text{O} + h\nu \rightarrow (\text{CHOH})_n + \text{n O}_2 \rightarrow (\text{CH}_2)_n + \text{n/2 O}_2 \quad \text{(Eq. 15)}
\]

Consequently, this feedstock is oxygen-poor and carbonyl compounds (aldehydes, ketones, carboxylic acids and their derivatives), as economically highly important organic chemicals, are produced through oxygenation (oxidation) or carbonylation reactions. A wide range of rather efficient catalysts has been developed for both reaction types. The use of plant biomass as a rapidly renewable feedstock, as a replacement for fossil resources, requires new catalysts and catalytic systems. Biomass contains compounds with relatively high oxygen content, such as sugars and other polyalcohols, as main components. Catalysts, converting this oxygen-rich feedstock, not only have to be stable against hydroxy, carbonyl, and carboxyl groups, but also have to operate under mild reaction conditions with low catalyst loadings, show a high functional group tolerance, allow the application of simple protocols including easy workup procedures, and give high chemoselectivity.

Using molecular oxygen from air as terminal hydrogen acceptor for oxidation reactions will lead to a highly atom efficient reaction. Furthermore the reaction can potentially be executed under waste free conditions, if dioxygen is cleanly converted to water. Therefore the interest in the development of catalysts for the oxidation of organic substrates with molecular oxygen as terminal hydrogen acceptor strongly grew over the two last decades.

Transfer hydrogenation (R\textsubscript{1}R\textsubscript{2}CHOH + A \rightarrow R\textsubscript{1}R\textsubscript{2}C=O + AH\textsubscript{2}; A = hydrogen acceptor), promoted by transition metal catalysts as a method for selectively converting alcohols into carbonyl compounds, is a well-studied process. In these reactions, carbonyl compounds such as cyclohexanone and acetophenone are usually used as hydrogen acceptors and impressive conversion rates (>1.2·10\textsuperscript{6} h\textsuperscript{-1}) have been achieved.

Recently, late transition metal amido complexes, [M]–N, where the amido group serves as a “cooperating ligand,” have been discovered for catalytic transfer hydrogenation reactions in which dioxygen serves as hydrogen acceptor (Scheme 28). The most efficient of these catalysts discovered so far are the Cp*Ir\textsuperscript{III}-bis(amido) complex which catalyses the “Knallgas” reaction (2 H\textsubscript{2} + O\textsubscript{2} \rightarrow 2 H\textsubscript{2}O), and Ikariya’s catalyst, which can be used to convert secondary alcohols to carbonyl compounds and primary alcohols to esters according
to $2 \text{RCH}_2\text{OH} + \text{O}_2 \rightarrow \text{RCO(OCH}_2\text{R)} + 2 \text{H}_2\text{O}$. These reactions require rather high catalyst loadings (10 mol%) but otherwise proceed under mild conditions. Peroxo complexes, such as [Ir(OOH)(Cp*)(NH$_2$)$_2$-L)], have been proposed as intermediates. Milstein et al. reported a Ru$^{II}$ complex with a “dearomatised” aminomethylphosphinomethylpyridine as a cooperative pincer ligand (92; Scheme 28), which allowed the dehydrogenative coupling of primary alcohols to symmetrical esters and of alcohols and amines to amides. Remarkably, this complex can also be used to mediate the cleavage of water into H$_2$ and O$_2$ (reverse of the “Knallgas” reaction) in two consecutive steps, one thermal (H$_2$) and one photochemical (O$_2$). Further notable examples of catalysed dehydrogenative coupling reactions have been reported recently, albeit with less well-characterised Ru complexes and under rather harsh conditions (T > 100 °C and/or reaction times > 10 h).

Scheme 28: Amido complexes used in dehydrogenative coupling reactions and aerobic oxidations of alcohols.

The Rh$^1$ amido bisolefin complex 1 (Scheme 28) is a very efficient catalyst for the transfer hydrogenation of C=O and activated C=C double bonds. The reactions can be performed with high substrate concentrations in neat ethanol, which serves as hydrogen donor and is converted irreversibly into ethyl acetate (Eq. 16).
Furthermore, \( \text{I} \) is a very efficient catalyst for the dehydrogenative coupling reaction of primary alcohols with water, methanol or primary amines to give the corresponding acids, methyl esters and amides.\([24]\) Very mild reaction conditions can be applied and molecules derived from biomass (polyalcohols, sugar derivatives) can be used in highly chemoselective transformations in which the primary hydroxy groups are converted into carboxyl or amide groups.\([80, 96]\) Very recently, palladium nanoparticles on SiO\(_2\) as support were found to serve as hydrogen acceptors and cleanly convert an amino hydride \([\text{MH}]–\text{NH}\) (Scheme 28) into the corresponding amide \([\text{M}]–\text{N}\).\([80]\) The hydrogen-loaded metal particles can then be used in the hydrogenation of inactivated olefins. A serious drawback in the catalytic system with \( \text{I} \) is the necessity of employing an excess of a rather expensive hydrogen acceptor. Therefore a catalytic protocol for dehydrogenative coupling reactions, which uses an alternative, readily available and inexpensive hydrogen acceptor, is desired. Oxygen from air fulfills this requirement. Furthermore no waste by-products are expected which simplifies the subsequent isolation and purification protocol of the products.
4.2 Results and discussion

4.2.1 Optimisation of the catalytic conditions

It was anticipated that the phosphane ligand would eventually be oxygenated in reactions with oxygen. Therefore the phosphane was substituted with the stable N-heterocyclic carbene 1,3,4,5-tetramethylimidazole-2-ylidene (TMIY). The reaction between TMIY and the precursor $[\text{RhCl(trop}_2\text{NH)}]_2$ yielded the catalyst precursors $[\text{RhCl(trop}_2\text{NH)(TMIY)}]$ 93 and $[\text{Rh(trop}_2\text{NH)(TMIY)}]\text{OTf}$ 8.[6a, 51]

In first experiments, the carbene complexes 93 and 8 were used as catalyst precursors in a DMSO/H$_2$O (2:1; all solvent ratios refer to volume ratios) mixture in combination with 1.2 equivalents of NaOH as base. These reactions were run with a substrate to catalyst ratio of 100:1 (S/C = 100), at room temperature under air. With the carbene chloride complex 93, a poorly active catalytic system was obtained and only 34% conversion after 12 hours was achieved with 1-octanol as substrate. However, by using the OTf-complex 8, more than 80% conversion was achieved after 12 hours with benzyl alcohol or 1-octanol as substrates.

As products, the carbonic acids (octanoic acid (Aa) and benzoic acid (Ab)) the esters (octyl octanoate (Ea) and benzyl benzoate (Eb)) and dimethylsulfone, Me$_2$SO$_2$, were obtained (Scheme 29). Under these conditions, the acids and esters were formed approximately in a 1.5:1 ratio. No conversion took place in the absence of catalyst. Likewise, no conversion took place when the reaction was performed under exclusion of oxygen under an inert atmosphere of argon gas.

![Scheme 29](image)

**Scheme 29**: Catalytic aerobic dehydrogenative coupling reaction of primary alcohols to acids and esters.

To verify that DMSO serves as both, solvent and oxygen acceptor, the reaction was tested with different solvent mixtures and 1-octanol (Sa) as substrate. In H$_2$O/THF, H$_2$O/t-BuOH, and H$_2$O/DMF mixtures of various ratios, no conversion took place and the starting material
was completely recovered. These results indicate that dehydrogenative coupling reaction under aerobic conditions requires an oxygen acceptor. The replacement of DMSO as oxygen acceptor with thioanisole (Table 21, entries 1, 2) or PPh₃ (Table 21, entries 3-5) was investigated but the conversion did not exceed 25% (with 5 equivalents of PPh₃ as oxygen acceptor, Table 21, entry 5).

**Table 21:** Results of the aerobic dehydrogenative coupling of 1-octanol (Sa) with water with the alternative oxygen acceptor thioanisole and PPh₃. Conditions: 0.26 mmol 1-octanol (Sa), 1 mol% 8, 1.2 eq. NaOH, 0.83 mL H₂O, 1.67 mL THF. [a] conversion determined by GC; [b] product distribution.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxygen acceptor (eq.)</th>
<th>Conversion [a] [%]</th>
<th>Octanoic acid [b] [%]</th>
<th>Octyl octanoate [b] [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Thioanisol (2.2)</td>
<td>15</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Thioanisol (10.0)</td>
<td>18</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>PPh₃ (1.0)</td>
<td>8</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>PPh₃ (2.0)</td>
<td>13</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>PPh₃ (5.0)</td>
<td>24</td>
<td>96</td>
<td>4</td>
</tr>
</tbody>
</table>

Next, the reaction was carried out with DMSO/H₂O ratios of 1:4, 1:2, 1:1, 2:1, and 3:1. The highest conversion (88%) was achieved with the initial 2:1 ratio. Lower DMSO concentrations resulted in low conversions (< 10%). A 3:1 DMSO/H₂O ratio gave lower yield than that of 2:1 (54%) but higher selectivity. The product ratio of Aa to Ea was 26:1 in a 3:1 DMSO/H₂O mixture in contrast to about 1.5:1 in a 2:1 DMSO/H₂O mixture.

**Table 22:** Results of the aerobic dehydrogenative coupling of 1-octanol (Sa) with water and altering DMSO/water ratio. Conditions: 0.26 mmol 1-octanol (Sa), 1 mol% 8, 1.2 eq. NaOH, 2.5 mL DMSO/water (ratio indicated below). [a] conversion determined by GC; [b] product distribution.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent system</th>
<th>Conversion [a] [%]</th>
<th>Octanoic acid [b] [%]</th>
<th>Octyl octanoate [b] [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMSO : H₂O 1:4</td>
<td>9</td>
<td>78</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>DMSO : H₂O 1:2</td>
<td>12</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>DMSO : H₂O 1:1</td>
<td>33</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>DMSO : H₂O 2:1</td>
<td>88</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>DMSO : H₂O 3:1</td>
<td>54</td>
<td>96</td>
<td>4</td>
</tr>
</tbody>
</table>
Table 23: Results of the aerobic dehydrogenative coupling reaction with various amounts of additives. Conditions: 0.26 mmol 1-octanol (Sa), 1 mol% 8, 1.2 eq. NaOH, 2.5 mL DMSO/water (ratio indicated below) and an additive (type and amount indicated below). [a] conversion determined by GC; [b] product distribution.

<table>
<thead>
<tr>
<th>Entry</th>
<th>DMSO: H₂O ratio</th>
<th>Additive (eq.)</th>
<th>Conversion[a] [%]</th>
<th>Octanoic acid[b] [%]</th>
<th>Octyl octanoate[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3:1</td>
<td>THF (4.8)</td>
<td>73</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>3:1</td>
<td>THF (11.9)</td>
<td>71</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>2:1</td>
<td>THF (4.8)</td>
<td>72</td>
<td>79</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>2:1</td>
<td>THF (11.9)</td>
<td>72</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>1:1</td>
<td>THF (4.8)</td>
<td>65</td>
<td>77</td>
<td>23</td>
</tr>
<tr>
<td>6</td>
<td>1:1</td>
<td>THF (11.9)</td>
<td>67</td>
<td>72</td>
<td>28</td>
</tr>
<tr>
<td>7</td>
<td>1:2</td>
<td>THF (4.8)</td>
<td>32</td>
<td>81</td>
<td>19</td>
</tr>
<tr>
<td>8</td>
<td>1:2</td>
<td>THF (11.9)</td>
<td>23</td>
<td>78</td>
<td>22</td>
</tr>
<tr>
<td>9</td>
<td>2:1</td>
<td>Me₂SO₂ (0.1)</td>
<td>86</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>2:1</td>
<td>Me₂SO₂ (0.2)</td>
<td>86</td>
<td>57</td>
<td>43</td>
</tr>
<tr>
<td>11</td>
<td>2:1</td>
<td>Me₂SO₂ (0.5)</td>
<td>83</td>
<td>58</td>
<td>42</td>
</tr>
<tr>
<td>12</td>
<td>2:1</td>
<td>Me₂SO₂ (1.0)</td>
<td>90</td>
<td>58</td>
<td>42</td>
</tr>
<tr>
<td>13</td>
<td>2:1</td>
<td>Me₂SO₂ (2.0)</td>
<td>90</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>14</td>
<td>2:1</td>
<td>Me₂SO₂ (5.0)</td>
<td>81</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>15</td>
<td>2:1</td>
<td>NaOAc (0.1)</td>
<td>90</td>
<td>61</td>
<td>39</td>
</tr>
<tr>
<td>16</td>
<td>2:1</td>
<td>NaOAc (0.2)</td>
<td>82</td>
<td>57</td>
<td>43</td>
</tr>
<tr>
<td>17</td>
<td>2:1</td>
<td>NaOAc (0.5)</td>
<td>84</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>18</td>
<td>2:1</td>
<td>NaOAc (1.0)</td>
<td>80</td>
<td>56</td>
<td>44</td>
</tr>
<tr>
<td>19</td>
<td>2:1</td>
<td>NaOAc (2.0)</td>
<td>75</td>
<td>56</td>
<td>44</td>
</tr>
<tr>
<td>20</td>
<td>2:1</td>
<td>NaOAc (5.0)</td>
<td>90</td>
<td>58</td>
<td>42</td>
</tr>
</tbody>
</table>

In the next step, the effect of various amounts of THF, dimethylsulfone (Me₂SO₂) or sodium acetate (NaOAc) as additives was investigated. These additives had a rather significant effect on the catalytic system with respect to both activity and selectivity. Addition of THF improved the conversion of 1-octanol (Sa) to octanoic acid (Aa) using the 3:1 DMSO/H₂O mixture as solvent system. Furthermore the high selectivity of this solvent system was even further improved (for comparison see Table 22 entry 3 and Table 23 entries 1 and 2). Also THF has a positive effect on the conversion and selectivity of the catalytic system with a different DMSO/H₂O ratio (see Table 23 entries 3-8), however 3:1:0.3 DMSO/H₂O/THF...
mixture (Table 23 entry 1) was found to be the best conditions with respect to conversion and chemoselectivity.

Furthermore it was examined whether the products formed during the catalytic reaction, e. g. Me₂SO₂ and sodium carboxylates, affect the results. NaOAc was used as model for the sodium carboxylate products. However the effects on the conversion and selectivity were negligible; no trend could be found by adding up to 2 equivalents of Me₂SO₂ (Table 23, entries 9-13) or 5 equivalents of NaOAc (Table 23, entries 15-20). Adding 5 equivalents of Me₂SO₂ led to a slightly smaller conversion (Table 23, entry 14); however this amount of Me₂SO₂ will never be formed in the catalytic reaction.

4.2.2 Catalytic aerobic dehydrogenative coupling of various substrates

The experiments to evaluate the optimal reaction conditions revealed that a 3:1 DMSO/H₂O mixture gave the highest selectivity in the formation of the desired carboxylate compared to the ester by-product. Addition of THF improved strongly the total conversion, therefore the solvent system DMSO/H₂O/THF was used in all following experiments with a variety of substrates Sa–k. The reactions were carried out with 1 mol% catalyst loading, 1.2 equivalents of NaOH under air at room temperature for 12 hours (Scheme 30 and Table 24).

\[
\begin{align*}
\text{RCH₂OH} & \quad \xrightarrow{1 \text{ mol\% NaOH, air RT}} \quad \text{RCOOH} + 2 \text{Me₂SO₄} \\
\text{Sa-k} & \quad \xrightarrow{1.2 \text{ eq NaOH, air RT}} \quad \text{Aa-k}
\end{align*}
\]

**Scheme 30**: Catalytic aerobic dehydrogenative coupling of primary alcohols to acids under optimised conditions.

Benzylic alcohols are rather smoothly converted with greater than 70% conversion (Table 24, entries 2 and 3), whereas alkyl benzyl alcohols with electron-donating substituents underwent only moderate conversion (Table 24, entries 1, 4 and 5).

The conversion of 4-(methylthio)phenylmethanol (Se) to 4-(methylthio)benzoic acid (Ae) proceeded with neither poisoning of the catalyst nor oxygenation at the sulphur centre. 1,4-phenylenedimethanol (Sf) was exclusively converted to 4-(hydroxymethyl)benzoic acid (Af), although in only 27% yield (Table 24, entry 6).
Table 24: Catalytic dehydrogenative coupling of the substrates Sa-Sk under aerobic conditions with 8 as catalyst. Reaction conditions: 1 mol% 8, 1.2 eq. NaOH, 1.88 mL DMSO, 0.62 mL H₂O, 0.19 mL THF. [a] all yields refer to isolated products; the identity of the products was determined by ¹H and ¹³C NMR spectroscopy.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield [a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₇H₁₅OH</td>
<td>C₇H₁₅OH</td>
<td>64%</td>
</tr>
<tr>
<td></td>
<td>Sa</td>
<td>Aa</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>OH</td>
<td>OH</td>
<td>79%</td>
</tr>
<tr>
<td></td>
<td>Sb</td>
<td>Ab</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>OH</td>
<td>OH</td>
<td>77%</td>
</tr>
<tr>
<td></td>
<td>Sc</td>
<td>Ac</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>MeO-</td>
<td>MeO-</td>
<td>63%</td>
</tr>
<tr>
<td></td>
<td>Sd</td>
<td>Ad</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>MeS-</td>
<td>MeS-</td>
<td>60%</td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>Ae</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>OH</td>
<td>OH</td>
<td>27%</td>
</tr>
<tr>
<td></td>
<td>Sf</td>
<td>Af</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>MeO-</td>
<td>MeO-</td>
<td>36%</td>
</tr>
<tr>
<td></td>
<td>Sg</td>
<td>Ag</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>OH</td>
<td>OH</td>
<td>64%</td>
</tr>
<tr>
<td></td>
<td>Sh</td>
<td>Ah</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>OH</td>
<td>OH</td>
<td>81%</td>
</tr>
<tr>
<td></td>
<td>Sj</td>
<td>Aj</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>OH</td>
<td>OH</td>
<td>65%</td>
</tr>
<tr>
<td></td>
<td>Sk</td>
<td>Ak</td>
<td></td>
</tr>
</tbody>
</table>
The rather electron-rich arene, 4-(hydroxymethyl)-2-methoxyphenol (Sg), is selectively converted to the aldehyde 4-hydroxy-3-methoxybenzaldehyde (Ag). This result indicates that an aldehyde is formed as the initial dehydrogenation product (Scheme 28). In Ag the aldehyde carbon centre was not sufficiently electrophilic to be further converted and a further dehydrogenative coupling reaction to form the acid did not take place.\textsuperscript{[6b, 6c, 24, 80]} The allylic alcohol geraniol Sj and the aliphatic alcohol citronellol Sh were both converted with acceptable yields to give the corresponding acids, geranic acid Aj and citronellic acid Sh (Table 24, entries 8 and 9). These reactions were chemoselective and neither oxidation of the second remote C=C double bond nor isomerization of this double bond was detected.

Furan-2-yl methanol Sk, which is available from sugars through biomass conversion, underwent the dehydrogenative coupling reaction with NaOH/H₂O in 65% yield.

In order to shed some light on the mechanism, the amino hydride complex [RhH(trop₂NH)(TMIY)] 94 was prepared \textit{in-situ} in [D₆]DMSO from [Rh(trop₂NH)(TMIY)]OTf 8 by deprotonation and reaction with hydrogen gas. Subsequently the flask was opened to air. The colour of the reaction mixture changed immediately from pale yellow to greenish yellow and the \textsuperscript{1}H-NMR spectrum indicated the quantitative formation of the amido complex [Rh(trop₂N)(TMIY)] 95 and amino complex [Rh(trop₂NH)(TMIY)]X (8; X = OH⁻, OTf⁻) in a 1.5:1 ratio. Treating this mixture with 0.2 MPa H₂ converted the amido complex 95 back to the amino hydride complex 94, which upon exposure to air regenerated 95 and 8. Hence, O₂ served as hydrogen acceptor and it is assumed that in the reaction with [RhH(trop₂NH)(TMIY)] one oxygen atom was converted to H₂O while the other was transferred to DMSO, yielding Me₂SO₂. The amino complex 8 was formed from the reversible reaction of the amido complex 95 with water (for further discussion of the addition of water to amido complexes see chapters 3.2, 5.3 and 5.4).

In a further experiment, octanal was used as substrate in the catalytic reaction under aerobic conditions using [D₆]DMSO, D₂O, and [D₈]THF as solvent mixture (1:1:0.1 ratio). After 15 min, GC analysis showed almost complete conversion (>99%). The \textsuperscript{1}H NMR spectrum of the reaction mixture revealed the formation of octanoic acid (53%), 1-octanol (42%) and octyl octanoate (5%) as products. This result indicates that the aldehyde as primary oxidation product undergoes relatively fast Cannizaro- and, to some extent, Tishchenko-type reactions. In view of these results in combination with those from previous work,\textsuperscript{[6b, 6c, 24, 80]} the simplified catalytic cycle shown in Scheme 31 is proposed.
Scheme 31: Proposed catalytic cycle of the aerobic dehydrogenative coupling of primary alcohols.

In step (a), deprotonation of the amino complex 8 leads to the catalytically active amido complex [Rh(trop2N)(TMIY)] 95, which, in step (b), dehydrogenates the alcohol substrate to the corresponding aldehyde, following the established Noyori-Morris mechanism.\cite{8,17,91} The resulting amino hydride complex [RhH(trop2NH)(TMIY)] 94 is subsequently dehydrogenated by O2/DMSO to reproduce the amido complex 95 (step (c)). The 1,1-diol derived from the aldehyde (produced in step (a)) under basic conditions is dehydrogenated to the corresponding carboxylate (step (d)). The amino complex 8 is then regenerated by the dehydrogenation of 94 by a second equivalent of O2/DMSO (step (e)).
The formation of the aldehyde in step (a) is likely the rate-determining step, as indicated by the fast formation of one equivalent of carboxylic acid and one equivalent of alcohol when aldehyde is added as substrate. Indeed, slow formation of aldehyde is observed when the carbonyl group is slightly electrophilic (Table 24, entry 7). Based on previously reported computational studies,[6b,6c,24] it is assumed that both reactions, the Cannizaro-type reaction in step (d) and the formation of the diol in step (h), are catalysed reactions promoted by the rhodium complexes. However the possibility, that 1,1-dihydroxy compounds and hemiacetals were formed in classical nonmetal-catalysed reactions is not excluded, although these reactions were much slower under the experimental conditions without metal catalyst.

Alternatively to the dehydrogenation of the diol to form the carboxylate it is also possible that water is added to the amido complex \( \text{95} \) forming the hydroxo complex \( \text{96} \) (step (f)). Subsequently \( \text{96} \) oxidises an aldehyde to the carboxylate (step (g)) and forms the amino hydride complex \( \text{94} \), which is then dehydrogenated by \( \text{O}_2/\text{DMSO} \) (step (e); the reaction of rhodium hydroxo complexes with aldehyde is described in more detail in chapter 3.2; complex \( \text{96} \) is further studied in chapters 5.3 and 5.4). It cannot be excluded that both catalytic pathways (step (d) vs. step (e) and (f)) take place simultaneously.

4.3 Conclusion

Impressive progress in the oxidation of alcohols with \( \text{O}_2 \) using homogeneous and heterogeneous transition metal[97] or organocatalysts[98] has been achieved the recent years. Mostly the corresponding aldehydes or especially ketones from secondary alcohols, which are generally more reactive, were obtained. The aerobic chemoselective oxidation of primary alcohols to the corresponding carboxylic acids has been much less investigated.[90m, 99] With respect to the substrates \( \text{Sa-Sk} \) investigated herein (Table 24), the oxidation reactions were mostly carried out with pure oxygen and frequently needed special conditions. Whereas benzyl alcohol \( \text{Sb} \) was rather conveniently oxidised (96% conversion, 0.1 MPa \( \text{O}_2 \) with 1.7% of \( \text{Co(acac)}_2 \) as catalyst; \( \text{acac} = \text{acetylacetonate} \)),[100] \( \text{1-octanol} \) needed trifluoromethylbenzene as solvent and a rather high loading of a special catalyst (\( \text{Co/Ce/Ru; 10 mol% Ru} \)) to achieve high conversions.[101] The oxidation of 4-isopropyl benzyl alcohol \( \text{Sc} \) in water with \( \text{Pt nanoparticles} \) required 0.1 MPa \( \text{O}_2 \) at 80 °C and 8 hours reaction time.[102] The oxidation of 4-(methoxy)phenyl methanol \( \text{Sd} \) with 0.6 mol% of a Mn-oxamato complex needed three equivalents of pivalaldehyde as co-oxidant alongside \( \text{O}_2 \).[103] Air was used for the oxidation of 4-(methylthio)phenyl methanol but the reaction required 125 °C, 4.1 MPa of air, and 1 mol%
Pd catalyst to give only 13% yield of the carboxylic acid (87% of 4-methylthiobenzaldehyde). The almost quantitative enzymatic aerobic oxidation of furan-2-ylmethanol \(\text{Sk}\) under mild conditions was recently described but required 21 h and 3.5 (w/w) cells per substrate. The Rh-amide \(\text{95}/\text{DMSO/air}\) system reported herein proved to be significantly more efficient for the conversion of citronellol \(\text{Sh}\) and geraniol \(\text{Sj}\), which previously only gave 6% (Au/Al\(_2\)O\(_3\), 0.1 MPa O\(_2\), 80 °C)[106] and 38% conversions (Pb(OAc)\(_2\), Pd/C, 1 MPa O\(_2\)), respectively.

In summary, the amido complex [Rh(trop\(_2\)N)(TMIY)] \(\text{95}\) and amino hydride complex [RhH(trop\(_2\)NH)(TMIY)] \(\text{94}\) are promising catalysts for the aerobic dehydrogenative coupling of alcohols with water to the corresponding acids. Primary alkyl, benzyl, and allyl alcohols can be employed as substrates and further functional groups including thioethers, which are prone to oxidation or catalyst poisoning, are tolerated. Although higher conversion rates and yields are certainly desirable, the results reported herein compare well or are superior to those previously reported with respect to reactions conditions.

It is assumed that the reactions catalysed by \(\text{95}\) proceed stepwise: Aldehydes are formed first in the dehydrogenation of the primary alcohol function and are then further converted with H\(_2\)O via diols to the corresponding acids. Only when the carbonyl function in the aldehyde is not sufficiently electrophilic the aldehyde is the final product. The reason of the slow formation of the aldehyde may be due to the increased steric hindrance of the catalytically active site, the Rh-N function, caused by the \(N\)-bonded substituents in the TMIY ligand.

These substituents are pointing towards the rhodium amido group, whereas in the phosphane complexes [Rh(trop\(_2\)N)(PR\(_3\))] the phosphorous bonded substituents are orientated away from the rhodium amido unit.

Preliminary experiments showed that \(\text{95}\) is also a less efficient catalyst than the corresponding phosphane complexes in classical transfer hydrogenations, where the latter perform excellently.[6c, 24a] DMSO was necessary as both, solvent and oxygen acceptor, because only one O atom of O\(_2\) is converted to H\(_2\)O while the other oxygenates a DMSO molecule. Whereas the dehydrogenation of the alcohols and diols very likely proceed via the Noyori-Morris mechanism,[8, 17, 91] the mechanism of the transfer of the proton and the hydride from \(\text{94}\) to O\(_2\) in the presence of DMSO remains unknown and requires further investigations.

Given that a ligand can be found which replaces TMIY and restores the catalytic activity, the advantage of the presented protocol is the usage of inexpensive and nontoxic stoichiometric reagents in a highly chemoselective oxidation (dehydrogenation) reaction. Primary hydroxy
functions were converted to carboxylic groups and no toxic by-products were produced. The remaining challenges are to replace rhodium with a cheaper metal and to find reaction conditions that allow the synthesis of aldehydes which are often the desired product of higher value. Additional effort to achieve this goal will be put in the investigation of the dehydrogenation reaction under anhydrous conditions.
Nitrous oxide as an environmentally friendly hydrogen acceptor for the dehydrogenative coupling of alcohols
5.1 Introduction

Nitrous oxide (N\textsubscript{2}O) is an industrial waste product formed mainly as substoichiometric by-product in the synthesis of nitric acid\cite{26} and as stoichiometric by-product in synthesis of adipic acid\cite{27} which is used as an intermediate for the Nylon-6,6 production. The release of waste N\textsubscript{2}O-gas from the chemical industry into the atmosphere should be minimised due to its high potential as greenhouse gas.\cite{108} Furthermore N\textsubscript{2}O released into the atmosphere has severe ozone depleting effects.\cite{27b}

Since N\textsubscript{2}O is a thermodynamically instable molecule with a heat of formation of +82 kJ/mol\cite{109} most N\textsubscript{2}O abating processes focus on decomposing N\textsubscript{2}O to nitrogen and oxygen. To overcome the inertness of N\textsubscript{2}O a huge variety of heterogeneous catalysts have been proposed,\cite{27a} for example pure metals,\cite{110} pure metal oxides,\cite{111} perovski\cite{112} and spinell type metal oxides\cite{113} as well as metals and metal oxides supported on alumina\cite{114} or silica\cite{115} and transition metals incorporated in zeolites.\cite{115-116}

The Fe containing zeolites FeZSM-5 are also able to use the oxidative power of N\textsubscript{2}O to oxidise methane to methanol\cite{27b, 117} and benzene to phenol.\cite{27b, 118} The latter process is very promising to improve the industrial adipic acid synthesis by reusing the formed N\textsubscript{2}O as oxidant in the first step (Scheme 32).\cite{27b,119}

\begin{center}
\begin{tikzpicture}
\node (1) at (0,0) {\includegraphics[width=0.8\textwidth]{scheme32.png}};
\end{tikzpicture}
\end{center}

\textbf{Scheme 32}: The upper route shows the standard industrial procedure from benzene to adipic acid. The alternative procedure using waste N\textsubscript{2}O from the third step to oxidise benzene to phenol is shown below.

Although N\textsubscript{2}O is often considered to be an inert molecule and poor ligand,\cite{120} many examples of N\textsubscript{2}O reacting with transition metal complexes have been described.\cite{121} A very common reaction type is the formation of a metal oxo-species and the release of molecular nitrogen.\cite{120, 122} Molecular oxygen and nitrogen formation derived from N\textsubscript{2}O catalysed by a Ru complex has also been reported (Scheme 33).\cite{121}
Scheme 33: The catalytic decomposition of N₂O by a Ru complex.\textsuperscript{[121]}

Cleavage of the N-N bond has also been demonstrated by Cummis \textit{et al.}\textsuperscript{[123]} A 1:1 product mixture of the nitride and nitrosyl complexes was observed (Scheme 34).

\[
2 \text{ArRN-Mo}_2^{\text{NRAr}} + \text{N}_2\text{O} \rightarrow \text{ArRN-Mo}_2^{\text{NRAr}} + \text{N}_2 + \text{NO}
\]

Scheme 34: Reductive denitrification of N₂O.

Another important class of reaction is the insertion of the oxygen atom from N₂O into a metal carbon\textsuperscript{[124]} or a metal hydride\textsuperscript{[82, 124e, 125]} bond yielding an alkoxy, aryloxy or hydroxyl complex. Representative examples are shown in Scheme 35.

Scheme 35: Representative examples of oxygen insertion from N₂O into metal carbon\textsuperscript{[124d]} and metal hydride bonds.\textsuperscript{[125a]}

Although the possibilities of reacting N₂O with metal complexes are abundant, only a small number of metal complexes are presently found which are capable of catalytically harvesting the oxidative power of N₂O. Some complexes are known to transfer oxygen from N₂O to aromatic and aliphatic phosphanes to yield the corresponding phosphane oxides.\textsuperscript{[126]} The oxygen atom was also transferred to olefins producing ketones\textsuperscript{[127]} or epoxides\textsuperscript{[128]} depending on the catalytic system. The Ru-porhyrin complex from Yamada and co-worker also catalyses
the oxidation of secondary alcohols and benzyl alcohol with N₂O to ketones and benzaldehyde respectively.¹²⁸b, ¹²⁹ A summary of these catalytic reactions is shown in Scheme 36.

Scheme 36: Summary of the catalytic oxidative chemistry with N₂O and homogeneous catalysts.

The insertion of N₂O into a metal hydride bond and subsequent formation of a metal hydroxo complex and molecular nitrogen⁸², ¹²⁴e, ¹²⁵ is promising to use N₂O as hydrogen acceptor for dehydrogenative coupling reactions. The hydroxo complex [Rh(OH)(trop₂NH)(PPh₃)]₆₃ was already investigated (see chapter 3.2) and ₆₃ was found to be in a fast equilibrium with the amido complex [Rh(trop₂N)(PPh₃)] ¹. Furthermore ₆₃ also reacted with aldehydes giving the acids and the hydride complex [Rh(H)(trop₂NH)(PPh₃)] ², which then can react with another molecule of N₂O. Scheme 37 summarises the proposed reactions of ² with N₂O and the subsequent reactions with alcohols or aldehydes to give the hydride complex ² back.
Scheme 37: i) Proposed insertion reaction of N₂O into the metal hydride bond of 2, giving the hydroxo complex 63; ii) Fast equilibrium of 63 and 1; iii) Dehydrogenation of a primary alcohol by 1; iv) Reaction of 63 with aldehydes.

The advantage of this catalytic reaction would be that an inexpensive hydrogen acceptor (N₂O) is used. Compared to O₂ (see chapter 4) no oxygen acceptor is needed since N₂O is a single oxygen donor. Scheme 37 also shows that one water molecule is formed per consumed N₂O. The water reacts with the amido complex 1 to the hydroxo complex 63 (ii), which then could attack and aldehyde forming the carboxylic acid (iv). The acid could then protonate the catalyst leaving a catalytically inactive species. Therefore molecular sieve will be applied to remove the formed water and shift the equilibrium (ii) on the side of the amido complex.
5.2 Results and Discussion

5.2.1 Optimisation of the catalytic conditions

Preliminary experiments were done with the standard [Rh(trop<sub>2</sub>NH)(PPh<sub>3</sub>)OTf] 9 and t-BuOK as catalytic system for the dehydrogenative coupling of benzyl alcohol with N<sub>2</sub>O as hydrogen acceptor. Using 1 mol% of catalyst under anhydrous conditions and applying activated 4 Å molecular sieves 18% of the used benzyl alcohol was converted to a 1:10 mixture of benzaldehyde and benzyl benzoate (Table 25, entry 1). Encouraged by these results, the solvent was varied in order to improve the solubility of N<sub>2</sub>O since it was assumed that the reaction of the hydride complex 2 with N<sub>2</sub>O is the rate determining step and could therefore be accelerated by a higher concentration of N<sub>2</sub>O in solution.

Table 25: Results of the dehydrogenative coupling reaction of benzyl alcohol with N<sub>2</sub>O as hydrogen acceptor using different solvents or solvent mixtures. Conditions: 0.25 mmol benzyl alcohol, 1 mol% 9, 10 mol% t-BuOK, 100 mg 4 Å molecular sieves, 8 eq. N<sub>2</sub>O, 3 mL solvent, RT. [a] Determined by GC.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Conversion&lt;sup&gt;[a]&lt;/sup&gt; [%]</th>
<th>Ratio benzaldehyde to benzyl benzoate&lt;sup&gt;[a]&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>THF</td>
<td>18</td>
<td>1:10</td>
</tr>
<tr>
<td>2</td>
<td>DMF</td>
<td>15</td>
<td>1:3</td>
</tr>
<tr>
<td>3</td>
<td>DMSO</td>
<td>&lt; 1</td>
<td>1:8</td>
</tr>
<tr>
<td>4</td>
<td>toluene</td>
<td>9</td>
<td>1:5</td>
</tr>
<tr>
<td>5</td>
<td>THF:toluene 1:1</td>
<td>20</td>
<td>1:4</td>
</tr>
<tr>
<td>6</td>
<td>THF:toluene 1:2</td>
<td>29</td>
<td>1:8</td>
</tr>
</tbody>
</table>

The polar solvents DMF and DMSO (entries 2 and 3 respectively) gave lower conversions and poor product selectivity. Pure toluene also gave lower conversions (entry 4) because the catalyst could not be completely dissolved. Therefore a solvent mixture of toluene and THF was applied, giving up to 29% conversion with a 1:2 THF:toluene mixture (entry 6). Unfortunately with this catalyst no higher conversions were achieved. Furthermore, the reaction of <i>in-situ</i> generated [Rh(H)(trop<sub>2</sub>NH)(PPh<sub>3</sub>)] 2 with N<sub>2</sub>O showed that the reaction is quite slow and needs to be run overnight to reach complete conversion. Beside the slow reaction, the axial ligand PPh<sub>3</sub> was found to end up in equatorial position forming a new metal complex which was no longer able to take up hydrogen. Furthermore small amounts of
triphenylphosphine oxide were detected with $^{31}$P-NMR showing partial decomposition of the complex. Therefore the catalyst was slightly modified by varying the axial ligand L$_A$. This could easily be done by splitting the chloro-bridged dimer $[\text{RhCl(trop}_2\text{NH})]_2$\cite{6a, 6d, 6e, 28a, 28d} with the desired ligand followed by chloride abstraction with AgOTf as shown in Scheme 38 (see also chapter 3.3.1).

![Scheme 38](image)

**Scheme 38**: General procedure to produce $[\text{Rh(trop}_2\text{NH})(L_A)]\text{OTf}$ complexes.

A series of these complexes were tested as catalysts for the dehydrogenative coupling reactions using benzyl alcohol as substrate and N$_2$O as hydrogen acceptor (Table 26).

**Table 26**: Results of the dehydrogenative coupling reaction of benzyl alcohol with N$_2$O as hydrogen acceptor using different catalyst. Conditions: 0.25 mmol benzyl alcohol, 1 mol% catalyst, 10 mol% t-BuOK, 100 mg 4 Å molecular sieves, 8 eq. N$_2$O, 2 mL toluene, 1 mL THF, 50 °C. [a] Determined by GC; b) TPP: 1, 2, 5-triphenyl phosphole.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion$^\text{[a]}$ [%]</th>
<th>Ratio benzaldehyde to benzyl benzoate$^\text{[a]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$[\text{Rh(trop}_2\text{NH})(\text{PPh}_3)]\text{OTf}$ 9</td>
<td>13</td>
<td>8:5</td>
</tr>
<tr>
<td>2</td>
<td>$[\text{RhCl(trop}_2\text{NH})]_2$</td>
<td>5</td>
<td>1:4</td>
</tr>
<tr>
<td>3</td>
<td>$[\text{Rh(trop}_2\text{NH})(\text{t-BuO})]$</td>
<td>2</td>
<td>1:1</td>
</tr>
<tr>
<td>4</td>
<td>$[\text{Rh(trop}_2\text{NH})(\text{TPP})]\text{OTf}^\text{b)}$</td>
<td>23</td>
<td>5:6</td>
</tr>
<tr>
<td>5</td>
<td>$[\text{Rh(trop}_2\text{NH})(\text{TMIY})]\text{OTf}$ 8</td>
<td>49</td>
<td>1:50</td>
</tr>
</tbody>
</table>

Among the evaluated complexes the one with NHC ligand 1,3,4,5-tetramethylimidazole-2-ylidene (TMIY) as axial ligand proved to be superior over the phosphane containing complexes. This complex converted 49% (Table 26, entry 5) of the benzyl alcohol to benzyl benzoate whereas the others reached conversion of 2-23% (entries 1-4).

It was found that the addition of molecular sieves is crucial to obtain high conversions. When the reaction was run without molecular sieves, the conversion dropped to 3% using the carbene catalyst 8 (Table 27, entry 1). Therefore the role of the molecular sieves was investigated and it was found that its water trapping ability was important rather than its
Lewis acidity. This was shown by substituting the molecular sieves with other Lewis acids such as SiO₂, Al₂O₃, TiO₂, ZnCl₂ or anhydrous CeCl₃. With these additives the conversion did not exceed 4% (entries 2-6). On the other hand dried CaO significantly raised the conversion (entry 7). Adding molecular sieves which were not dried before led to low conversion (entry 8).

Surprisingly, when using 0.5 mol% of [Rh(trop₂NH)(TMIY)]OTf and leaving all other concentrations as before the conversion dropped only to 46% but when the concentration of the substrate was doubled the conversion dropped to 32%. It was realised that the amount of added molecular sieves was too low. The optimal amount was determined to be 1.2 g per mmol substrate (Table 27, entry 11). Furthermore, 1 mol% of catalyst and 4 equivalents of N₂O at 1 bar were needed to obtain full conversion. These conditions are further referred to conditions 1 (see Scheme 39).

Table 27: Results of the dehydrogenative coupling reaction of benzyl alcohol with N₂O as hydrogen acceptor using different additives. Conditions: 0.25 mmol benzyl alcohol, 1 mol% 8, 10 mol% t-BuOK, 100 mg of an additive (if not indicated otherwise), 8 eq. N₂O, 2 mL toluene, 1 mL THF, 50 °C. [a] Determined by GC; [b] 40 mg of additive; [c] 500 mg of CaO dried at 400 °C for 1 hour under high vacuum; [d] not dried molecular sieves; [e] 200 mg of additive; [f] 300 mg of additive.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>Conversion(^{[a]})[%]</th>
<th>Ratio benzaldehyde to benzyl benzoate(^{[a]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>4</td>
<td>1:3</td>
</tr>
<tr>
<td>2</td>
<td>SiO₂</td>
<td>1</td>
<td>1:10</td>
</tr>
<tr>
<td>3</td>
<td>Al₂O₃</td>
<td>2</td>
<td>1:2</td>
</tr>
<tr>
<td>4</td>
<td>TiO₂</td>
<td>4</td>
<td>3:4</td>
</tr>
<tr>
<td>5</td>
<td>ZnCl₂</td>
<td>2.5</td>
<td>1:7</td>
</tr>
<tr>
<td>6</td>
<td>CeCl₃(^{[b]})</td>
<td>3</td>
<td>1:6</td>
</tr>
<tr>
<td>7</td>
<td>CaO(^{[c]})</td>
<td>17</td>
<td>1:11</td>
</tr>
<tr>
<td>8</td>
<td>4 Å molecular sieves(^{[d]})</td>
<td>7.5</td>
<td>1:11</td>
</tr>
<tr>
<td>9</td>
<td>4 Å molecular sieves</td>
<td>49</td>
<td>1:50</td>
</tr>
<tr>
<td>10</td>
<td>4 Å molecular sieves(^{[e]})</td>
<td>78</td>
<td>1:50</td>
</tr>
<tr>
<td>11</td>
<td>4 Å molecular sieves(^{[f]})</td>
<td>&gt; 99</td>
<td>1:100</td>
</tr>
</tbody>
</table>

As an alternative, to remove the formed water from the reaction mixture, larger amounts of t-BuOK were added to deprotonate water and precipitate KOH. Surprisingly though, not KOH
was precipitated but potassium benzoate. The highest conversion was obtained with 1.05 equivalents of \textit{t}-BuOK (Table 28, entry 2). Larger amounts of base proved to be disadvantageous (entries 3 and 4).

**Table 28:** Results of the dehydrogenative coupling reaction of benzyl alcohol with \( \text{N}_2\text{O} \) as hydrogen acceptor using different amounts of \( \textit{t}\)-BuOK. Conditions: 0.25 mmol benzyl alcohol, 1 mol\% \textit{t}-BuOK (amount indicated below), 8 eq. \( \text{N}_2\text{O} \), 2 mL toluene, 1 mL THF, 50 \( ^\circ \)C. [a] Determined by GC.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amount of \textit{t}-BuOK</th>
<th>Conversion\textsuperscript{[a]} [%]</th>
<th>Ratio benzoic acid: benzaldehyde: benzyl benzoate\textsuperscript{[a]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5 eq.</td>
<td>53</td>
<td>43 : 2 : 5</td>
</tr>
<tr>
<td>2</td>
<td>1.05 eq.</td>
<td>&gt; 99.9</td>
<td>96.7 : 0.6 : 2.7</td>
</tr>
<tr>
<td>3</td>
<td>1.5 eq.</td>
<td>95</td>
<td>98.5 : 0.6 : 0.9</td>
</tr>
<tr>
<td>4</td>
<td>2 eq.</td>
<td>75</td>
<td>98.7 : 0.8 : 0.5</td>
</tr>
</tbody>
</table>

Since 2 equivalents of \( \text{N}_2\text{O} \) were needed to convert benzyl alcohol to benzoic acid, the amount of used \( \text{N}_2\text{O} \) was doubled. These conditions are further referred to conditions 2. In Scheme 39 the two optimised procedures to produce esters and acids from primary alcohols are summarised.

**Scheme 39:** The two optimal procedures found to produce esters and acids from primary alcohols by dehydrogenative coupling reactions using \( \text{N}_2\text{O} \) as hydrogen acceptor.
5.2.2 Dehydrogenative coupling reaction of various alcohols as substrate with nitrous oxide as hydrogen acceptor

A series of alcohols were tested using the two optimized procedures (see Scheme 39). The results are summarised in Table 29.

Aliphatic alcohols were converted in high yields to the corresponding acids and ester (Table 29, entries 6 and 7). The benzoic acid derivatives were also obtained in high yields but benzyl alcohols substituted with electron donating groups such as methoxy- or thiomethoxy-groups were not fully converted to the corresponding esters (entries 2-4). Up to 12% of the corresponding aldehydes were found (entry 2). Furthermore, the very electron rich arene 4-(hydroxymethyl)-2-methoxyphenol was converted exclusively to the corresponding aldehyde with both reaction protocols (entry 5). These results indicate that aldehydes are the initial products under both reaction conditions. This conclusion is also supported by in-situ GC analysis of the reaction mixture using benzyl alcohol as a substrate. Aside from the starting material and product, up to 6% benzaldehyde, formed as intermediate, were found.

It is also remarkably that 4-(methylthio)phenyl methanol was converted to 4-(methylthio)benzyl 4-(methylthio)benzoate or 4-(methylthio)benzoic acid without poisoning of the catalyst or oxidation of the sulphur centre.

Using the allyl alcohol geraniol, a large mixture of products was obtained under conditions 1 and 2 (entry 8). In order to gain insight, the chemistry of allyl alcohol itself was studied under both conditions. Under condition 1 the only product observed by GC-MS was propyl propionate. Condition 2 converted allyl alcohol to potassium propionate. It had been shown that C-C double bonds, which are polarised by a neighbouring carbonyl function (for example methyl methacrylate MMA[6a, 24]), can be used as hydrogen acceptors. To confirm this result, cinnamyl alcohol was used as substrate giving product mixtures of the saturated and partially saturated ester under conditions 1 and the saturated and unsaturated acid under conditions 2 (entry 9). Also in the case of geraniol, partial reduction of the allylic C-C double bond was found, although this finding is not sufficient to explain the large amount of products found especially under conditions 2.
Table 29: Results of the dehydrogenative coupling reaction of various alcohols applying both dehydrogenative coupling conditions. [a] Conditions 1: 1.25 mmol substrate, 1 mol% [Rh(trop₂NH)(TMIY)]OTf 8, 10 mol% t-BuOK, 1.5 g 4 Å molecular sieves, 5 ml THF, 10 ml toluene, 4 eq. N₂O, isolated yields; [b] Conditions 2: 0.625 mmol substrate, 1 mol% [Rh(trop₂NH)(TMIY)]OTf 8, 1.05 eq. t-BuOK, 2.5 ml THF, 5 ml toluene, 8 eq. N₂O, isolated yields; [c] Beside the ester as main product also the corresponding aldehydes were found in 12%, 3% and 4% yield for entry 3, 4 and 5 respectively; [d] Both conditions yielded the aldehyde vanillin as product; [e] An inseparable mixture of products were obtained; [f] 50 mg of an inseparable mixture of geranic acid and other products was obtained; [g] Beside of the main product 3-phenylpropyl 3-phenylpropanoate also 3-phenylpropyl cinnamate was found in 7% yield; [h] A 7:3 mixture of 3-phenylpropanoic acid and cinnamic acid was obtained; [i] The corresponding ketone was formed; [j] Reaction conditions: 0.625 mmol substrate, 1 mol% [Rh(trop₂NH)(TMIY)]OTf 8, 10 mol% t-BuOK, 0.75 g 4 Å molecular sieves, 2.5 ml THF, 5 ml toluene, 8 eq. N₂O.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alcohol</th>
<th>Conditions 1:</th>
<th>Conditions 2:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Yield Ester[a][%]</td>
<td>Yield Acid[b][%]</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>98</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>MeO-</td>
<td>86[c]</td>
<td>98</td>
</tr>
<tr>
<td>3</td>
<td>MeS-</td>
<td>85[c]</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>O-</td>
<td>84[c]</td>
<td>91</td>
</tr>
<tr>
<td>5</td>
<td>MeO-</td>
<td>54[d]</td>
<td>83[d]</td>
</tr>
<tr>
<td>6</td>
<td>C₂H₅-</td>
<td>89</td>
<td>92</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>92</td>
<td>92</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>Not determined[e]</td>
<td>Not determined[f]</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>92[g]</td>
<td>37[h]</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>90</td>
<td>43</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>97[i,j]</td>
<td>6[i]</td>
</tr>
</tbody>
</table>
A possible explanation could be that geraniol and/or citral, which were found by GC-MS in the reaction mixture, were cyclised under the reaction conditions to intermediates, still containing a primary alcohol or an aldehyde function.[130] These intermediates were then coupled with another primary alcohol or aldehyde present to a number of different esters. This would explain the GC-MS analysis; most products found have an M^+ + 1 of 307 and 309 which would correspond to the single and double reduced esters, respectively. In conclusion, the method cannot be applied to allyl alcohols but remote C-C double bonds are tolerated (entry 7).

The secondary alcohol 1-phenyl ethanol was used as substrate giving acetophenone in high yields under conditions 1, although under conditions 2 only traces of the desired ketone were formed (entry 11). Furthermore it was found that using secondary alcohols no molecular sieves were needed to reach high yields of the product. A possible explanation of this result is that the formed water is not poisoning the catalyst. But the intermediately formed aldehydes (from the primary alcohols) are coupled with water to the acid which then protonates the catalyst to give back the catalyst precursor. This conclusion is also supported by the fact that under conditions 2, the optimal amount of base was determined to be 1.05 equivalents although 2 equivalents of water are formed.
5.3 Mechanistic investigations based on quantum chemical calculations

The simplest possible hydrogen donor system for the N\textsubscript{2}O hydrogenation is H\textsubscript{2}. The reaction of H\textsubscript{2} and N\textsubscript{2}O on a catalyst has been reported in the literature since the 1930s.\textsuperscript{[131]} In 1965 the reaction without a catalyst has also been demonstrated by Dixon-Lewis and co-workers.\textsuperscript{[132]} The reactions of H\textsubscript{2} and N\textsubscript{2}O with Pd,\textsuperscript{[133]} Ag/Al\textsubscript{2}O\textsubscript{3},\textsuperscript{[134]} Cu-, Co-, Fe-Zn spinels,\textsuperscript{[135]} Fe-Zeolites catalysts\textsuperscript{[136]} and their activation on Cu-biological systems,\textsuperscript{[137]} just to mention a few, are well documented in the literature. Recent quantum chemical calculations on a palladium di-phosphane complex illustrates the mechanism for the N\textsubscript{2}O activation with H\textsubscript{2} to produce N\textsubscript{2} and H\textsubscript{2}O.\textsuperscript{[138]} No report in the literature for the N\textsubscript{2}O activation with H\textsubscript{2} on a rhodium centre was found.

As a benchmark for the hydrogenation of N\textsubscript{2}O from alcohols on our rhodium catalyst, quantum chemical calculations on the Rh-catalyst + H\textsubscript{2} + N\textsubscript{2}O system have been performed. Scheme 40 shows the studied reactions; i.e. the H\textsubscript{2} splitting on the Rh-catalyst (i), activation of N\textsubscript{2}O and release of N\textsubscript{2} (ii), and formation of H\textsubscript{2}O (iii).

![Scheme 40: Reaction schemes for the heterolytic addition of H\textsubscript{2} and the splitting of N\textsubscript{2}O on a [Rh(trop\textsubscript{2}NH)(L\textsubscript{A})] complex. L\textsubscript{A} = axial ligand.](image)

For the reactions mentioned above, \(\Delta E\) (gas phase conditions) have been computed using three different methods and basis sets (for details see Table 31). The computed values for each reaction in Scheme 40 are shown in Table 30.
Table 30: Computed relative energies with Z.P.E correction at various levels of theory for the
heterolytic addition of H₂ and splitting of N₂O on a rhodium complex.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔE (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>-47</td>
</tr>
<tr>
<td>(ii)</td>
<td>-202</td>
</tr>
<tr>
<td>(iii)</td>
<td>+85</td>
</tr>
</tbody>
</table>

These calculations clearly suggest that the splitting of H₂ on the rhodium catalyst is
exothermic, regardless of the method / basis set employed. The outcome of this reaction is the
formation of the amino hydride complex 94.

The addition of N₂O to the amino hydride complex 94 activates the N₂O molecule which later
releases N₂ whereas the oxygen atom is inserted into the rhodium-hydride bond (Scheme 40,
reaction (ii)). This reaction is extremely exothermic (Table 30).

The hydroxo complex releases water to form back the starting amido complex (Scheme 40,
reaction (iii)). At the B2-PLYP/TZVPP level of theory this reaction is slightly endothermic.

Experimental evidence has confirmed the equilibrium between the hydroxo complex 96 and
the release of water and formation of the amido complex 95 (see also chapter 3.2 and the
synthesis of 95 and its analysis by X-ray single crystal diffraction in chapter 5.4).

Based on the previous calculated reactions⁹⁶a-c, 24 and experimental evidence, the following
catalytic cycle is postulated. The catalyst precursor 8 is deprotonated under the basic reaction
conditions to the amido complex 95 (Scheme 41a). The addition of hydrogen from a hydrogen
source, such as hydrogen gas or an alcohol (not shown in Scheme 41), to 95 leads to the
formation of the amino hydride complex 94 (Scheme 41b). N₂O then reacts with 94 to the
hydroxo complex 96 and molecular nitrogen (Scheme 41c). The hydroxo complex is known
to be in equilibrium with the amido complex 95 and water (Scheme 41d, see also discussion
in chapter 5.4).
Scheme 41: Proposed catalytic cycle of the heterolytic addition of H₂ and the splitting of N₂O with [Rh(trop₂N)(TMIIY)] type complexes.

In order to get more insight into the catalytic dehydrogenative coupling reaction with N₂O as hydrogen acceptor the three complexes proposed in the catalytic cycle (Scheme 41) were analysed by quantum chemical calculations at three different levels of theory (Table 31). The geometry of the amido 95, the amine hydride 94 and the hydroxo 96 complex at the PBE0/TZVPP level of theory are shown in Figure 32.
Figure 32: Calculated species at the PBE0/TZVPP level of theory. For clarity, all non-relevant H atoms have been removed. Important bond lengths (pm) and angles (°) are shown. Rh atom grey, N atoms blue, Oxygen atom red, H atoms white, C atoms black. For the transition states relevant distances and angles at the reaction centre are given.

At the same level of theory the transition states of the heterolytic addition of H2 to the amido complex 95 (TS-I; reaction b Scheme 41) and the splitting of N2O at the amino hydride complex 94 (TS-II; reaction c Scheme 41) were calculated (Table 31, for the geometries of the transition states see Figure 32). Based on these calculations the reaction profile for the heterolytic addition of H2 and the splitting of N2O shown in Scheme 42 was drawn.
Table 31: Total energies (Hartree) and zero point energy corrections (Hartree) at various levels of theory for all calculated species. [a] As implemented in the program TURBOMOLE; [b] At this level of theory no Z.P.E correction was performed. The values were taken from the PBE0/TZVPP calculations.

<table>
<thead>
<tr>
<th>Complex (symmetry)</th>
<th>BP(86)/SV(P)[a]</th>
<th>PBE0/TZVPP[a]</th>
<th>B2-PLYP/TZVPP[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Energy (kJ mol⁻¹)</td>
<td>Z.P.E (kJ mol⁻¹)</td>
<td>Total Energy (kJ mol⁻¹)</td>
</tr>
<tr>
<td>Rh(trop₂N)(TMIY)] 95(C₆)</td>
<td>-1704.27122</td>
<td>0.59890</td>
<td>-1703.92887</td>
</tr>
<tr>
<td>[RhH(trop₂NH)(TMIY)] 94(C₆)</td>
<td>-1705.47113</td>
<td>0.62056</td>
<td>-1705.13464</td>
</tr>
<tr>
<td>[Rh(OH)(trop₂NH)(TMIY)] 96(C₆)</td>
<td>-1780.65597</td>
<td>0.62617</td>
<td>-1780.33078</td>
</tr>
</tbody>
</table>

Transition State (symmetry)

| [Rh(trop₂N)(TMIY)] 95 +H₂ TS-I (C₆) | not calculated | --- | -1705.06975 | 0.62655 | not calculated | --- |
| [RhH(trop₂NH)(TMIY)] 94 + N₂O TS-II (C₆) | not calculated | --- | -1889.61031 | 0.64300 | not calculated | --- |

Ligand (symmetry)

| H₂ (Dₐ) | -1.16996 | 0.00971 | -1.16849 | 0.01004 | -1.15976 | 0.01004 |
| N₂ (Dₐ) | -109.44895 | 0.00544 | -109.44630 | 0.00566 | -109.37892 | 0.00566 |
| N₂O (Cᵥ) | -184.55679 | 0.01103 | -184.54552 | 0.01155 | -184.41270 | 0.01155 |
| H₂O (C₃v) | -76.34520 | 0.01998 | -76.38098 | 0.02160 | -76.32980 | 0.02160 |
Scheme 42: Reaction profile for the heterolytic addition of H$_2$ and activation and splitting of N$_2$O on rhodium complexes. Computed (PBE0/TZVPP) energies (bold) are given relative to the zero point. NBO charges (italic) are given for the Rh and N atoms and H$_2$ and N$_2$O molecules in TS-I and TS-II.
At the PBE0/TZVPP level of theory, the energy barrier for the H\textsubscript{2} activation on the amido complex \textit{95} is +66 kJ mol\textsuperscript{-1} (Scheme 42). In this transition state (TS-I) the hydrogen molecule is polarised by the rhodium and nitrogen atoms as the NBO analysis clearly shows.

The formation of amino hydride complex \textit{94} is favoured by 66 kJ mol\textsuperscript{-1} over the reactants (Table 30, Scheme 42). Addition of a N\textsubscript{2}O molecule to the amine hydride complex \textit{94} shows a transition state (TS-II) in which the oxygen atom is in direct contact with the hydride (see Scheme 42).

Attempts to find a transition state for the amine-proton-oxygen interaction or the possible N-proton or N-hydride interactions was either not found or energetically higher than the hydride-oxygen interaction depicted in Scheme 42. A similar situation is reported in the literature for the H\textsubscript{2} and N\textsubscript{2}O activations on a palladium-di-phosphane complex.\textsuperscript{[138]} It is therefore assumed that the interaction of the oxygen atom from N\textsubscript{2}O with the hydride of the complex is the decisive step in the activation of N\textsubscript{2}O and the subsequent splitting to give N\textsubscript{2} and the corresponding hydroxide complex.

Once the N\textsubscript{2}O molecule has been activated by the hydride, the release of N\textsubscript{2} is imminent and the hydroxide complex is formed. The reaction is extremely exothermic with respect to the reactants (–253 kJ mol\textsuperscript{-1}, see Table 30).

A possible transition state for the oxygen insertion into the Rh–H bond could not be found. The proposed insertion is based on the different geometries observed during the minimum energy optimisation for the TS-II (see Figure 33).

Once the oxygen atom of the N\textsubscript{2}O molecule gets close to the Rh-hydride there is a strong interaction between these two atoms. The transition state (TS-II, see Figure 32) shows the N\textsubscript{2}O molecule interacting with the hydride via the oxygen atom. The N\textsubscript{2}O unit bends and is no longer a linear molecule. Further optimisation steps from this point on show that the O atom rotates towards the Rh centre while the H atom attached to it concurrently moves away. At the same time, the O-N bond length increases and the energy of the whole system decreases. The outcome is the formation of the Rh-OH bond and the dissociation of the N\textsubscript{2} molecule. To illustrate this, a series of snapshots from the BP(86)/SV(P) optimisation have been depicted (Figure 33). The interaction of a N\textsubscript{2}O molecule with the \textit{Trop\textsubscript{2}}NH-RhH-carbene complex is energetically favoured at the three levels of theory employed. In all cases the formation of the Rh-OH bond and the release of N\textsubscript{2} is the preferred reaction path.
Figure 33: Snap shots at the BP(86)/SV(P) level of theory for the interaction between [RhH(trop$_2$NH)(TMIY)]$^{94}$ and a N$_2$O molecule. For clarity, all non-relevant H atoms have been removed. Important bond lengths (pm) are shown. Rh atom grey, N atoms blue, Oxygen atom red, H atoms white, C atoms black.

Confirmation of this observation is seen on similar reactions of hydrogen atoms and N$_2$O to produce N$_2$ and OH,$^{132}$ reaction of H$_2$ and N$_2$O on palladium to produce N$_2$ and H$_2$O,$^{133}$ reaction of H$_2$ and N$_2$O on silver,$^{134}$ quantum chemical calculations on the reaction of N$_2$O, H$_2$ and a palladium-di-phosphane complex,$^{138}$ the detection of molecular nitrogen by GC-MS and the formation of the carboxylates (under conditions 2) by the dehydrogenative coupling reaction of the intermediately produced aldehyde with water released from the hydroxo complex 96.

The final step of the catalytic cycle (Scheme 40, reaction (iii)) at the PBE0/TZVPP level of theory is $+ 36$ kJ mol$^{-1}$ (Table 30) and at the B2-PLYP/TZVPP level is only $+ 1$ kJ mol$^{-1}$ (Table 30). Experimentally the equilibrium between the hydroxo complex 96 and the amido complex 95 + H$_2$O was confirmed (see chapters 3.2 and 5.4).

The high activation energy for the splitting of N$_2$O (158 kJ mol$^{-1}$, see Scheme 42) corresponds very well to the fact that for this reaction higher reaction temperatures ($50$ °C) are needed in order to reach high conversion. In comparison, other reported dehydrogenative coupling
reactions with [Rh(trop_2N)(L_A)] type complexes gave high conversion even at room temperature (see also chapters 3.3.2 and 4).
5.4 Synthesis and analysis of the intermediate complexes of the catalytic cycle

The amido complex 95 was already characterised *in-situ* by NMR\textsuperscript{[6a]} at low temperature. At room temperature 95 slowly decomposed. Due to the extreme insolubility of the obtained material it was not possible to characterise the decomposed material though it is assumed that rhodium attacks one of the methyl group of the carbene ligand. The internal reaction of [Rh(trop\textsubscript{2}N)(L\textsubscript{A})] type complexes with an NHC ligand bearing larger substituents at the nitrogen atoms are well documented.\textsuperscript{[139]}

However a way to prepare 95 in pure form was found accidentally by an attempt to prepare the hydroxo complex 96 (see Scheme 43). While drying the obtained yellow powder of 96 under high vacuum, the colour change to green, the typical colour of [Rh(trop\textsubscript{2}N)(L\textsubscript{A})] type complexes. Analysis by low temperature NMR of the obtained green powder proved that it is identical to the *in-situ* generated 95.\textsuperscript{[6a]}

![Scheme 43: Synthesis of the amido complex 95 by first generating *in-situ* the hydroxo complex 96, then applying high vacuum.](image)

The amido complex [Rh(trop\textsubscript{2}N)(P(p-BuPh)\textsubscript{3})] 86 (see chapter 3.4) showed a similar behaviour; when adding water to a green solution of 86 the yellow hydroxo complex 88 was obtained *in-situ*. After removing the solvent and drying the yellow powder under high vacuum, the starting green amido complex 86 was obtained.

Similarly crystals of 95 suitable for X-ray analysis (see Figure 34) are grown from a solution of *in-situ* generated hydroxo complex 96 and slow vacuum application.

This experimental evidence gives proof to the proposed catalytic cycle (Scheme 41) and the assumed equilibrium described in Scheme 40, reaction (iii).
Figure 34: Ortep plot (at 50% probability) of the structure of [Rh(trop$_2$N)(TMIY)] 95. The hydrogen atoms are omitted for clarity. Atoms labelled with an asterisk are symmetry generated. Selected bond lengths [Å] and angles [°] (ct1 = centroid C4=C5, ct1* = centroid C4*=C5*): Rh1-N1 2.046(4), Rh1-C16 2.015(5), Rh1-ct1 2.053(3), Rh1-C4 2.161(3), Rh1-C5 2.182(4), C4=C5 1.412(5), C16-Rh1-N1 174.6(2), ct1-Rh1-ct1* 151.1(1).

In Table 13 selected bond lengths and angles of [Rh(trop$_2$N)(TMIY)] 95 are compared to the ones of [Rh(trop$_2$NH)(TMIY)]OTf 8$^{[6a]}$ and [Rh(trop$_2$N)(PPh$_2$Tol)]$^{[6d, 6e]}$ and the calculated bond lengths and angles of 95 at the PBE0/TZVPP level of theory. The calculated bond lengths resemble the measured ones very well; however the bond angles are smaller than the experimental ones.

Comparing 95 to the other amido complex [Rh(trop$_2$N)(PPh$_2$Tol)] gave a similar picture. The relevant bond lengths are approximately of the same size, but the two bond angles are much smaller for the phosphane amido complex.

Compared to the OTf-complex 8 the N1-Rh1 bond of the amido complex 95 is considerable smaller. This indicates that the Rh-N interaction of the neutral amido complex 95 is stronger than in the cationic OTf-complex 8. The other bond lengths and angles differ only slightly.
Table 32: Comparison of selected bond lengths and angles of [Rh(trop2N)(TMIY)] 95, [Rh(trop2NH)(TMIY)]OTf 8, [Rh(trop2N)(PPh2Tol)].[^6d, ^6e] [a] Calculated values at PBE0/TZVPP level of theory; [b] Rh1-ct1* bond length; [c] C4*=C5* bond length; [d] ct1-Rh1-ct1* bond angle; [e] Rh1-P1 bond length; [f] N1-Rh1-P1 bond angle.

<table>
<thead>
<tr>
<th>Complex</th>
<th>95</th>
<th>95[^a]</th>
<th>8[^6a]</th>
<th>[Rh(trop2N)(PPh2Tol)][^6d, ^6e]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh1-N1</td>
<td>2.046(4)</td>
<td>2.020</td>
<td>2.130(4)</td>
<td>2.007(1)</td>
</tr>
<tr>
<td>Rh1-C16</td>
<td>2.015(5)</td>
<td>2.041</td>
<td>1.993(5)</td>
<td>2.316(1)[^e]</td>
</tr>
<tr>
<td>Rh1-ct1</td>
<td>2.053(3)</td>
<td>2.046</td>
<td>2.059(5)</td>
<td>2.058(2)</td>
</tr>
<tr>
<td>Rh1-ct2</td>
<td>2.053(3)[^b]</td>
<td>2.046</td>
<td>2.033(5)</td>
<td>2.070(2)</td>
</tr>
<tr>
<td>C4=C5</td>
<td>1.412(5)[^c]</td>
<td>1.413</td>
<td>1.408(6)</td>
<td>1.423(3)</td>
</tr>
<tr>
<td>C19=C20</td>
<td>1.412(5)[^c]</td>
<td>1.413</td>
<td>1.393(5)</td>
<td>1.407(3)</td>
</tr>
<tr>
<td>N1-Rh1-C16</td>
<td>174.6(2)</td>
<td>169.5</td>
<td>176.2(2)</td>
<td>166.18(5)[^f]</td>
</tr>
<tr>
<td>ct1-Rh1-ct2</td>
<td>151.1(1)[^d]</td>
<td>146.5</td>
<td>149.4(2)</td>
<td>135.8(7)</td>
</tr>
</tbody>
</table>

Table 33: Comparison of selected ¹H-NMR and ¹³C-NMR shifts of the amido complexes [Rh(trop2N)(TMIY)] 95, [Rh(trop2N)(PPh₃)] 1[^6a] [Rh(trop2N)(P(p-BuPh)₃)] 86, the amine hydride complexes [RhH(trop2NH)(TMIY)] 94, [RhH(trop2NH)(PPh₃)] 2[^6a] [RhH(trop2NH)(P(p-BuPh)₃)] 87 and the hydroxo complexes [Rh(OH)(trop2NH)(TMIY)] 96, [Rh(OH)(trop2NH)(PPh₃)] 63, [Rh(OH)(trop2NH)(P(p-BuPh)₃)] 88.

<table>
<thead>
<tr>
<th>Amido complexes</th>
<th>95</th>
<th>95[^a]</th>
<th>8[^6a]</th>
<th>96[^a]</th>
<th>63</th>
<th>88</th>
</tr>
</thead>
<tbody>
<tr>
<td>CΗشق [ppm]</td>
<td>4.78; 6.02</td>
<td>4.77</td>
<td>75.7; 81.3</td>
<td>76.6; 80.2</td>
<td>76.3; 66.4</td>
<td>70.9</td>
</tr>
<tr>
<td>CΗشف [ppm]</td>
<td>4.69; 5.62</td>
<td>4.92</td>
<td>76.2; 84.5</td>
<td>63.9; 65.9</td>
<td>63.3; 66.4</td>
<td>70.8</td>
</tr>
<tr>
<td>8[^6a]</td>
<td>4.70; 5.63</td>
<td>4.93</td>
<td>75.8; 83.8</td>
<td>63.3; 66.4</td>
<td>63.3; 66.4</td>
<td>70.8</td>
</tr>
<tr>
<td>Hydride complexes</td>
<td>94</td>
<td>3.29; 3.79</td>
<td>4.38</td>
<td>52.3; 54.1</td>
<td>71.1</td>
<td></td>
</tr>
<tr>
<td>2[^6a]</td>
<td>3.55; 3.91</td>
<td>4.56</td>
<td>57.8; 60.6</td>
<td>72.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>87</td>
<td>3.62; 3.94</td>
<td>4.51</td>
<td>57.2; 60.3</td>
<td>72.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydroxo complexes</td>
<td>96</td>
<td>4.99; 6.18</td>
<td>5.31</td>
<td>76.6; 80.2</td>
<td>71.6</td>
<td></td>
</tr>
<tr>
<td>63</td>
<td>4.53; 4.65</td>
<td>5.00</td>
<td>63.9; 65.9</td>
<td>70.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>88</td>
<td>4.55; 4.60</td>
<td>4.99</td>
<td>63.3; 66.4</td>
<td>70.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The amino hydride complex [RhH(trop2NH)(TMIY)] and the hydroxo complex [Rh(OH)(trop2NH)(TMIY)] were both prepared in-situ by reacting the amido complex with hydrogen gas and water respectively then analysed by NMR.

In Table 33 the $^1$H and $^{13}$C-NMR shifts of the olefinic and benzylic proton and carbon atoms were compared for the amido, the amine hydride and the hydroxo complexes with TMIY, PPh$_3$ and P(p-BuPh)$_3$ as axial ligand. It is not surprising that the chemical shifts of the complexes with the different phosphane ligands do only slightly differ since the P(p-BuPh)$_3$ complexes were designed to resemble the PPh$_3$ analogues as much as possible around the metal centre (see chapter 3.4). It is though remarkable that the chemical shifts of the carbene complexes are mostly similar to the phosphane complexes, furthermore the trends are almost equal: Going from the amido complexes to the amine hydride complexes the olefinic protons are shifted by approximately 1.2 and 2.0 ppm to lower frequencies, whereas the olefinic carbons are shifted by approximately 20 and 25 ppm to lower frequencies. For the hydroxo complexes the shifts of the olefinic protons and carbons are quite close to the ones measured for the corresponding amido complex, whereas the benzylic carbon shifts do only slightly differ from the ones of the amino hydride complex. The largest difference between the carbene and the phosphane complexes are the chemical shifts of the olefinic protons and carbons, which are shifted to lower frequencies by approximately 0.5 ppm and 14 ppm respectively.

In conclusion N$_2$O was successfully applied as hydrogen acceptor in the dehydrogenative coupling reaction of alcohols yielding acids and ester depending on the chosen conditions. A possible reaction mechanism was studied by quantum chemical calculations and the calculated intermediates were either isolated or characterised in-situ by NMR. Further efforts will be made in order to use cheap non-noble metal complexes to catalytically harvest the oxidative power of N$_2$O.
6 Nitrosobenzene as a hydrogen acceptor in rhodium catalysed dehydrogenation reactions of alcohols:
Synthesis of aldehydes and azoxybenzenes
6.1 Introduction

The very efficient transfer hydrogenation catalyst \([\text{Rh(trop}_2\text{N})(\text{PPh}_3)]\) \(1\) is also known to catalyse the dehydrogenative coupling reactions (DHC’s) of primary alcohols with water, methanol and amines, yielding the corresponding acids, methyl esters and amides.\(^{[24]}\) This reaction however requires the use of a hydrogen acceptor such as cyclohexanone or methyl methacrylate (MMA) in excess which lowers the atom efficiency of this reaction.

Up to now cyclohexanone or MMA were successfully substituted by oxygen from air (see chapter 4) or \(\text{N}_2\text{O}\) (see chapter 5), which is an industrial waste product. The advantages of oxygen and \(\text{N}_2\text{O}\) as hydrogen acceptor are that they are inexpensive and are transformed into non-toxic products such as water or molecular nitrogen. However, in the case of oxygen as hydrogen acceptor, the phosphane ligand of the catalyst can easily be oxygenated. Furthermore, it was found that \(\text{N}_2\text{O}\) reacts only slowly with the amino hydride complex \([\text{RhH(trop}_2\text{NH})(\text{PPh}_3)]\) \(2\) (see chapter 5.2.1) and heating is not recommended due to accelerated isomerisation of \(2\) to form the inactive but more stable axial hydride complex \(10\)\(^{[6a]}\). These side reactions severely decrease the conversion. By exchanging the phosphane ligand with the carbene ligand TMIY, a more stable catalytic system was obtained and full conversion was achieved using oxygen or \(\text{N}_2\text{O}\) as hydrogen acceptor.

Unfortunately the carbene complex \([\text{Rh(trop}_2\text{N})(\text{TMIY})]\) \(95\) is known to be a much less active catalyst in the transfer hydrogenation reactions than its phosphane analogue \(1\)\(^{[6a]}\). Therefore a 10-fold higher catalyst loading was necessary to achieve full conversion using the system \(95/\text{O}_2\) or \(\text{N}_2\text{O}\) compared to \(1/\text{cyclohexanone or MMA}\). Computations and experimental evidence\(^{[6a, 24]}\) (see also chapter 5.3) indicate that the catalytic dehydrogenative coupling of a primary alcohol, \(\text{R-CH}_2\text{-OH}\), with \(\text{HX (X = OH, OMe, NHR')}\) in presence of an hydrogen acceptor \(\text{A}\), proceeds stepwise (see Eq. 17 and Eq. 18).

\[
\begin{align*}
\text{R-CH}_2\text{-OH} + \text{A} & \rightarrow \text{R-CH}=\text{O} + \text{AH}_2 \\
\text{R-CH}=\text{O} + \text{HX} + \text{A} & \rightarrow \text{RC}(=\text{O})\text{X} + \text{AH}_2
\end{align*}
\] (Eq. 17) (Eq. 18)

If this scheme is correct, aldehydes must be intermediates which are formed in an alcohol dehydrogenation reaction promoted by the amido complexes \(1\) or \(95\). However only the very electron rich substrate 4-(hydroxymethyl)-2-methoxyphenol afforded the corresponding aldehyde to be isolated in pure form.\(^{[6a, 24]}\) (see also chapters 4.2.2 and 5.2.2)
In order to find conditions which tolerate phosphane ligands on the catalyst and furthermore allow the isolation of the aldehydes as the product, the search for alternative hydrogen acceptors was continued.

Nitrosobenzene is a versatile reagent which undergoes a large variety of reactions. Among them the reactions with metal complexes, the facile reduction of nitrosobenzene by many reagents, such as diborane and trialkylborane, hydrazine derivatives, NADH, NADPH and especially metal hydride (for an example see Scheme 44) and the facile hydrogenation of nitrosobenzene are the most important ones. Therefore nitrosobenzene promises to be a viable candidate as an alternative hydrogen acceptor.

Scheme 44: Reaction of nitrosobenzene with a metal hydride (M = Ru, Rh, Ir) to azoxybenzene.

6.2 Results and discussion

6.2.1 Optimisation of the catalytic conditions

Preliminary experiments were performed using 1 mol% of the deep green and air-sensitive Rh amido complex \([\text{Rh(trop}_2\text{N)(PPh}_3])\) 1, benzyl alcohol and 1.5 equivalents of nitrosobenzene. Almost 75% of the benzyl alcohol was converted to benzaldehyde, whereas the nitrosobenzene was fully converted to azoxybenzene as confirmed by GC-MS. If 2.1 equivalents of nitrosobenzene were used, the benzyl alcohol was fully converted to benzaldehyde.

Scheme 45: Rhodium catalysed dehydrogenation of benzyl alcohol to yield benzaldehyde using nitrosobenzene as hydrogen acceptor.
Samples of this reaction were taken after different reaction times and analysed by GC. It was found that per 1 equivalent of formed benzaldehyde, 2 equivalents of nitrosobenzene were consumed and 1 equivalent of azoxybenzene was obtained (Scheme 45).

In order to simplify the reaction conditions, we used the cationic air-stable orange complex \([\text{Rh}(\text{trop}_2\text{NH})(\text{PPh}_3)]\text{OTf} \, 9\) as catalyst precursor, which, together with \(\text{K}_2\text{CO}_3\), completely converted benzyl alcohol to the corresponding aldehyde. Here, \(\text{K}_2\text{CO}_3\) acts as heterogeneous base and converts \(9\) into the active catalyst \(1\) (Eq. 19; see also Scheme 46 below):

\[
[\text{Rh}(\text{trop}_2\text{NH})(\text{PPh}_3)]\text{OTf} \, 9 + \text{K}_2\text{CO}_3 \rightarrow [\text{Rh}(\text{trop}_2\text{N})(\text{PPh}_3)] \, 1 + \text{KOTf} + \text{KHCO}_3 \quad \text{(Eq. 19)}
\]

After these very encouraging results obtained in the preliminary experiments, a series of complexes was tested as catalysts (0.1 mol\%) for the dehydrogenation reaction of benzyl alcohol using nitrosobenzene as hydrogen acceptor (Table 34).

**Table 34:** Achieved conversion of benzyl alcohol to benzaldehyde using different catalysts.
Conditions: 1.25 mmol benzyl alcohol, 0.1 mol\% catalyst (specified below), 2.2 eq. nitrosobenzene, 2 mol\% \(\text{K}_2\text{CO}_3\), 2 ml THF. [a] conversion determined by GC.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion[^{[%]}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>([\text{Rh}(\text{trop}_2\text{NH})(\text{PPh}_3)]\text{OTf} , 9)[6a]</td>
<td>93</td>
</tr>
<tr>
<td>2</td>
<td>([\text{Ir}(\text{trop}_2\text{NH})(\text{PPh}_3)]\text{OTf}, 6\text{a}]</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>([\text{Rh}(\text{trop}_2\text{NH})(\text{OPh}_3)]\text{OTf}, 6\text{a}]</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>([\text{Rh}(\text{trop}_2\text{NH})(\text{TPP})]\text{OTf}, 6\text{a}]</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>([\text{Rh}(\text{trop}_2\text{NH})(\text{Bu}_3)]\text{OTf}, 6\text{a}]</td>
<td>73</td>
</tr>
<tr>
<td>6</td>
<td>([\text{Rh}(\text{trop}_2\text{NH})(\text{TMIIY})]\text{OTf} , 8)[6a]</td>
<td>11</td>
</tr>
<tr>
<td>7</td>
<td>([\text{Rh}(\text{trop(NH}t\text{ropPhPPh}_2)]\text{OTf} , 3\text{d}]</td>
<td>54</td>
</tr>
<tr>
<td>8</td>
<td>([\text{Rh}(\text{trop(NHCH}_2\text{StilbPPh}_2)]\text{OTf} , 5\</td>
<td>16</td>
</tr>
<tr>
<td>9</td>
<td>([\text{Rh}(\text{trop}<em>2\text{NH})(\text{PPh}(</em>{di-3,5-CF}_3\text{Ph})_2)]\text{OTf} , 8\text{d}</td>
<td>35</td>
</tr>
<tr>
<td>10</td>
<td>([\text{Rh}(\text{OHCM}_2\text{StilbPPh}_2)]\text{OTf} , 5\text{f}</td>
<td>3</td>
</tr>
<tr>
<td>11</td>
<td>([\text{Rh}(\text{OHtropPhPPh}_2)]\text{OTf} , 6\text{f}</td>
<td>2</td>
</tr>
</tbody>
</table>

The initially used complex \([\text{Rh}(\text{trop}_2\text{NH})(\text{PPh}_3)]\text{OTf} \, 9\) (entry 1) proved to be the best catalyst among the tested complexes. Substituting rhodium for iridium (entry 2), the conversion dropped by over 50\%. Acceptable conversions were obtained when the \(\text{PPh}_3\) ligand is substituted with \(\text{P(Bu}_3\) or TPP (entries 4 and 5), however only moderate conversion was obtained employing complex \(8\text{d}\) (entry 9) bearing the rather electron deficient...
PPh(di-3,4-CF₃Ph)₂ ligand. Furthermore rhodium complexes with tetradentate ligands (entries 7 and 8: see chapter 2.3) gave considerably lower conversions compared to 9. Only traces of the desired products were observed using the Rh-phosphane olefin alcohol complexes 59 and 60 (entries 10 and 11) or the rhodium complex with P(OPh)₃ or TMIY as axial ligand (entries 3 and 6).

After the phosphane complex 9 had been determined to be the best catalyst precursor the question arose whether it might be possible to use the produced azoxybenzene as hydrogen acceptor, which would consequently allow to apply less nitrosobenzene.

It was found in the literature that azoxybenzene is reduced by hexamethylsilane to azobenzene catalysed by tetrabutyl ammonium fluoride (TBAF).\(^{[147]}\) Therefore the effects of TBAF as co-catalyst were studied. Indeed small amounts of azobenzene were found by GC-MS analysis, however most of the nitrosobenzene was still converted to azoxybenzene and the amount of azobenzene did not increase even after prolonged reaction time.

Surprisingly, TBAF had a strong accelerating effect on the original reaction as described in Scheme 45. When 1 mol% of the catalyst precursor 9 was used together with 2.2 equivalents of nitrosobenzene full conversion was achieved after only one minute when 10 mol% TBAF was added. Full conversion of the analogous reaction without TBAF was only reached after one hour.

Not only did TBAF accelerate the desired catalytic reaction, it also quickens the decomposition of the catalyst. Using 0.1 mol% of 9 only 53% conversion was achieved in the presence of TBAF. Without TBAF 93% of benzyl alcohol was converted to benzaldehyde (see Table 34, entry 1). Other fluoride sources besides TBAF, such as LiF, were used, however no difference was found compared to the catalytic reaction without the fluoride source.

Furthermore, it was found that TBAF also catalyses the dehydrogenation of benzyl alcohol with nitrosobenzene as hydrogen acceptor. The reaction was however found to be much slower compared to the reaction with the rhodium catalyst 9 and TBAF. After 5 minutes only 2% conversion was achieved using only TBAF as catalyst; after 20 hours 42% of benzyl alcohol was converted to benzaldehyde. Together with 9 after only 1 minute full conversion was achieved.

Since TBAF was not able to activate azoxybenzene in a way that would allow its utilisation as hydrogen acceptor and enhanced the catalyst decomposition, the catalytic dehydrogenation of alcohols with nitrosobenzene was further studied without TBAF as co-catalyst.
6.2.2 Dehydrogenation reaction of various alcohols as substrate with nitrosobenzene as hydrogen acceptor

Table 35: Isolated yields for various alcohols dehydrogenated by \([\text{Rh(trop}_2\text{NH)(PPh}_3\text{)}]\text{OTf} \, \text{9}\) and base using nitrosobenzene as hydrogen acceptor. [a]: Conditions for S/C = 1000: 2.50 mmol alcohol, 5.12 mmol nitrosobenzene, 2.5 \(\mu\text{mol}\) \([\text{Rh(trop}_2\text{NH)(PPh}_3\text{)}]\text{OTf} \, \text{9}\), 0.125 mmol \(\text{K}_2\text{CO}_3\), 5 mL THF, RT, stirred overnight; Conditions for S/C = 200: 1.25 mmol alcohol, 2.56 mmol nitrosobenzene, 6.0 \(\mu\text{mol}\) \([\text{Rh(trop}_2\text{NH)(PPh}_3\text{)}]\text{OTf} \, \text{9}\), 60 \(\mu\text{mol}\) \(\text{K}_2\text{CO}_3\), 2.5 mL THF, RT, stirred overnight; [b]: Conversion determined by GC as given by the ratio of aldehyde to not reacted alcohol; [c]: \(\text{t-BuOK}\) was used as base instead of \(\text{K}_2\text{CO}_3\).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alcohol</th>
<th>S/C</th>
<th>Yield([a])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Image" /></td>
<td>1000</td>
<td>91%</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2" alt="Image" /></td>
<td>1000</td>
<td>96%</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3" alt="Image" /></td>
<td>200</td>
<td>23%</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4" alt="Image" /></td>
<td>1000</td>
<td>93%</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5" alt="Image" /></td>
<td>200</td>
<td>97%</td>
</tr>
<tr>
<td>6</td>
<td><img src="image6" alt="Image" /></td>
<td>200</td>
<td>37%</td>
</tr>
<tr>
<td>7</td>
<td><img src="image7" alt="Image" /></td>
<td>200</td>
<td>52%</td>
</tr>
<tr>
<td>8</td>
<td><img src="image8" alt="Image" /></td>
<td>1000</td>
<td>93%</td>
</tr>
<tr>
<td>9</td>
<td><img src="image9" alt="Image" /></td>
<td>200</td>
<td>5%([b])</td>
</tr>
<tr>
<td>10</td>
<td><img src="image10" alt="Image" /></td>
<td>200</td>
<td>97%</td>
</tr>
<tr>
<td>11</td>
<td><img src="image11" alt="Image" /></td>
<td>200</td>
<td>11%([b])</td>
</tr>
<tr>
<td>12</td>
<td><img src="image12" alt="Image" /></td>
<td>200</td>
<td>61%([c])</td>
</tr>
</tbody>
</table>
In the next step, this catalytic system was tested with a variety of alcohols as substrates (Table 35). The catalytic protocol worked best when applied to benzyl alcohol and benzyl alcohol derivatives with electron donating substituents. These substrates were smoothly converted with low catalyst loading in high yields to the corresponding benzaldehyde derivatives (Table 35, entries 1, 2 and 4). (4-(methylthio)phenyl) methanol (entry 5) demanded a higher catalyst loading but could also be quantitatively converted to 4-methylthiobenzaldehyde. This could be attributed to the thioether function competing with the substrate in binding to the metal catalyst hence reducing its activity.

Also allylic alcohol derivatives, like furfuryl alcohol (entry 7), geraniol (entry 10), and the secondary alcohol 1-phenyl ethanol (entry 12) could be converted to the corresponding aldehydes in moderate to high yields although a higher catalyst loading was needed. On the other hand, benzyl alcohol substrates bearing an electron withdrawing group on the aromatic ring were converted to the corresponding aldehydes in rather low yields (about 20%). The conversion of aliphatic alcohols is very low and even with catalyst loadings up to 5 mol% only 5% conversion of 1-octanol to octanal was reached. 95% of unreacted 1-octanol was observed by GC (see also the discussion in chapter 6.2.3). 31P-NMR analysis of the reaction mixture revealed catalyst decomposition to P(O)Ph3 and other not identified products.

This is the first catalytic system which allow the clean formation of aldehydes from primary alcohols employing [Rh(trop:2N)(L)] as dehydrogenation catalyst. Hitherto aldehydes were assumed to be primary intermediates of the dehydrogenation reaction, which were irreversibly coupled with water, alcohols or amines to the corresponding acids, esters or amides.[6a, 24] The only observed exception was with the very electron rich alcohol 4-(hydroxymethyl)-2-methoxyphenol (entry 8), which was also converted to the aldehyde under the previously applied reaction conditions with cyclohexanone, MMA,[6a, 24] O2 and N2O as hydrogen acceptors (see chapters 4.2.2 and 5.2.2). In this case, it is likely that the aromatic hydroxyl group is deprotonated and the corresponding phenolate lowers the electrophilicity of the aldehyde group in para-position to such an extent that the conversion to the hemiacetal followed by a second dehydrogenation to the carboxylic acid derivative does not take place.
6.2.3 Transfer hydrogenative coupling of nitrosobenzene derivates to azoxybenzene

Azoxyarenes bearing alkyl- or alkoxy-substituents in \( p, p' \)-position exhibit interesting properties as liquid crystals.\(^{148}\) This type of compound is usually prepared by oxidation of anilines with hydrogen peroxide under harsh conditions.\(^{149}\) If different substituents on the phenyl ring are required they can be prepared by the condensation of the corresponding \( N \)-arylhydroxylamines and nitrosoarenes.\(^{150}\)

The mild and clean formation of azoxybenzene, the other product in the catalytic reaction discussed above, provides an alternative synthetic approach to symmetrically substituted azoxyarenes. In order to investigate the tolerance of the catalytic reaction with respect to different functional groups, a series of \( p \)-substituted nitrosobenzenes were synthesised and reacted in an ethanol/THF mixture as solvent using 0.1 mol\% of the catalyst precursor \([\text{Rh(trop2NH)}(\text{PPh}_3)]\text{OTf} \) 9. Under these conditions, ethanol, which is present in large excess, serves as hydrogen donor whereas THF was added to improve the solubility of the nitrosobenzene derivatives.

Table 36: Results of the transfer hydrogenative coupling of nitrosobenzene derivates to symmetric azoxyarene. \([a]\): Conditions: 2.19 mmol substrate, 2.2 \( \mu \)mol \([\text{Rh(trop2NH)}(\text{PPh}_3)]\text{OTf} \) 9, 0.11 mmol \( K_2\text{CO}_3 \), 2 mL ethanol, 1 mL THF, RT, 2 hours reaction time; \([b]\): 1-octanol as hydrogen donor; conditions: 0.48 mmol nitrosobenzene, 2.4 \( \mu \)mol \([\text{Rh(trop2NH)}(\text{PPh}_3)]\text{OTf} \) 9, 0.38 mL 1-octanol, 0.12 mmol \( K_2\text{CO}_3 \), 2 mL THF, RT, 2 hours reaction time, conversion determined by GC; \([c]\): 4 hours reaction time.

<table>
<thead>
<tr>
<th>Entry</th>
<th>( p )-substituent</th>
<th>Yield([a])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>97%</td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>99.7%([b])</td>
</tr>
<tr>
<td>3</td>
<td>Me</td>
<td>95%</td>
</tr>
<tr>
<td>4</td>
<td>OMe</td>
<td>92%</td>
</tr>
<tr>
<td>5</td>
<td>F</td>
<td>98%</td>
</tr>
<tr>
<td>6</td>
<td>Cl</td>
<td>93%([c])</td>
</tr>
<tr>
<td>7</td>
<td>CO(_2)Me</td>
<td>69%([c])</td>
</tr>
</tbody>
</table>
As shown in Table 36 the azoxybenzene derivatives were formed in high yields (> 90%) after a reaction time of 2-4 hours. The only exception is the 4-methyl ester substituted nitrosobenzene derivative (entry 7) which was converted in moderate yield (about 70%) to the corresponding azoxybenzene compound.

It may seem inconsistent that the reductive coupling reaction of nitrosoarenes to symmetric azoxyarenes using ethanol as reductant (hydrogen donor) proceeds especially smoothly, whilst alkyl alcohols are inefficiently converted to the corresponding aldehydes (see the poor conversion of 1-octanol to octanal in Table 35, entry 9). Note however, that the coupling of the nitroso derivatives proceeds in presence of a large excess of ethanol which acts as a co-solvent in this catalytic system. Indeed, when 1-octanol was employed in excess as hydrogen donor (5 equivalents with respect to nitrosobenzene) with 0.5 mol% catalyst nitrosobenzene is completely converted to azoxybenzene (Table 36, entry 2). An explanation for this observation may be that in the presence of larger amounts of alcohol the equilibrium (Eq. 20) lies far to the side of the amino hydride complex 2 which is not decomposed to a catalytically inactive species (see discussion below).

\[
[Rh(trop_2N)(PPh_3)] + RCH_2OH \rightleftharpoons [Rh(H)(trop_2NH)(PPh_3)] + RCHO \quad \text{(Eq. 20)}
\]

The amido complex \([Rh(trop_2N)(PPh_3)]\) 1, however, is sensitive and the addition of nitrosobenzene leads to irreversible decomposition and deactivation of the catalyst via phosphane oxidation. Also the product azoxybenzene reacts with the amido complex 1. A new penta-coordinated complex \([Rh(trop_2N)(eq\text{-}PPh_3)(ax\text{-}PhN=N(O)Ph)]\) 97 is formed in which the triphenylphosphane ligand occupies the equatorial position (indicated by the low frequency of the \(^{31}\text{P} \) resonance \(\delta = 7.9 \) ppm and the small coupling constant \(J_{RhP} = 118.8 \) Hz) and azoxybenzene an axial position in a trigonal bipyramidal structure. 97 is still an active catalyst for the standard transfer hydrogenation reaction of acetophenone. However, when a solution of 97 was left at room temperature for a few days, the oxygen atom from azoxybenzene is transferred to the phosphane ligand forming triphenylphosphane oxide, azobenzene and further decomposition products which were not identified.

Consequently, the equilibrium concentration of free amido complex 1 should be as small as possible in order to establish a sustainable catalytic system, which can be achieved with high alcohol concentrations. Under these conditions, equilibrium Eq. 20 lies far to the side of the amino hydride complex 2, which is part of the catalytic cycle.
6.2.4 Mechanistic investigations

In order to examine the mechanism of the discussed catalytic reaction a number of separate stoichiometric experiments were performed, which are summarised in Scheme 46, steps iii - v. First, the amino hydride complex 2 was reacted with one equivalent nitrosobenzene (Scheme 46, step iii). In a fast reaction, a new complex 98 was formed which precipitated from the reaction mixture and was isolated by filtration.

![Scheme 46](image)

Scheme 46: a) Proposed catalytic cycle for the dehydrogenation of alcohols and formation of azoxybenzene based on individually performed reaction steps i - v. b) It cannot be excluded that azoxybenzene is also produced by a simple non-catalysed condensation reaction between N-phenyl hydroxylamine and nitrosobenzene (step vi).

The same complex 98 was also obtained in the reaction of the amido complex 1 with N-phenyl hydroxylamine. 98 was thoroughly characterised by NMR spectroscopy; selected chemical shifts and the $^{1}J_{RhP}$ coupling constant are compared to the other complexes (see Table 37) shown in Scheme 46.
Table 37: Selected $^1$H, $^{13}$C, $^{31}$P and $^{103}$Rh chemical shifts and the rhodium phosphorus coupling constant of the new synthesised complex 98 compared to [Rh(trop$_2$NH)(PPh$_3$)]OTf 9, [RhH(trop$_2$NH)(PPh$_3$)] 2 and [Rh(OH)(trop$_2$NH)(PPh$_3$)] 63. [a]: The chemical shift of the NH proton of 63 could not be determined because it is in a fast equilibrium with the present H$_2$O.

<table>
<thead>
<tr>
<th>Complex</th>
<th>98</th>
<th>9$^{[6a, 6e, 28a]}$</th>
<th>2$^{[6a, 6e, 28a]}$</th>
<th>63</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH δ [ppm]</td>
<td>4.59</td>
<td>5.66</td>
<td>5.56</td>
<td>n. d.$^{[a]}$</td>
</tr>
<tr>
<td>CH$^{\text{olef}}$ δ [ppm]</td>
<td>4.80; 4.87</td>
<td>4.94; 5.43</td>
<td>3.55; 3.91</td>
<td>4.53; 4.65</td>
</tr>
<tr>
<td>CH$^{\text{benzyl}}$ δ [ppm]</td>
<td>4.67</td>
<td>4.91</td>
<td>4.56</td>
<td>5.00</td>
</tr>
<tr>
<td>CH$^{\text{olef}}$ δ [ppm]</td>
<td>67.4; 69.7</td>
<td>74.0; 74.2</td>
<td>57.8; 60.6</td>
<td>63.9; 65.9</td>
</tr>
<tr>
<td>CH$^{\text{benzyl}}$ δ [ppm]</td>
<td>73.0</td>
<td>72.7</td>
<td>72.2</td>
<td>70.8</td>
</tr>
<tr>
<td>$^{31}$P δ [ppm]</td>
<td>43.1</td>
<td>40.6</td>
<td>65.4</td>
<td>41.1</td>
</tr>
<tr>
<td>$^1$$J_{\text{RhP}}$ [Hz]</td>
<td>135.0</td>
<td>137.7</td>
<td>144.0</td>
<td>134.3</td>
</tr>
<tr>
<td>$^{103}$Rh δ [ppm]</td>
<td>-7147</td>
<td>-6797</td>
<td>-8476</td>
<td>-7109</td>
</tr>
</tbody>
</table>

The differences between 98 and the hydroxo complex 63 (see chapter 3.2) are the smallest expect for the chemical shift of the benzylic proton and carbon. Particularly the difference of the rhodium phosphorus coupling constant and the chemical shift of the $^{103}$Rh-NMR resonance between these two complexes is very small thus indicating a similar coordination sphere for 98 with an oxygen donor as fifth ligand in the equatorial position and the phosphane in the axial position of a trigonal bipyramidal structure (indicated by a high frequency shifted $^{31}$P resonance δ = 43.1 ppm and a larger $^1$$J_{\text{RhP}} = 135.0$ Hz).

Furthermore, the $^1$H-NMR exhibits two distinct signals (8.20 ppm and 8.35 ppm) for the ortho-protons of the phenyl group in N-phenyl hydroxylamine, indicating that the rotation of the phenyl ring is frozen on the NMR time scale. The $^{13}$C-NMR spectrum confirmed this finding and six distinct signals (122.8, 125.9, 129.1, 129.2, 130.0 and 132.0 ppm) for the same phenyl ring were observed. These results indicate that the amino hydride complex 2 transfers hydrogen to nitrosobenzene to give N-phenyl hydroxylamine and the amido complex 1. Subsequently, the hydroxylamine adds across the Rh-N bond of 1 to give 98.

The hydroxylamine complex 98 reacts with an excess of a primary alcohol to the amino hydride complex 2 and aniline which was unequivocally identified directly by GC-MS and by first reacting it with acetic anhydride. The formation of acetanilide was then confirmed by GC-MS analysis. This reaction (Scheme 46, step ⅳ) is relatively slow and requires several minutes.
In order to test whether N-phenyl hydroxylamine and aniline are also formed as intermediates in the course of the catalysis an excess of acetic anhydride was added to the catalytic reaction. Since alcohols also react with the trapping reagent hydrogen gas was used as hydrogen donor. In fact some of the aniline and N-phenyl hydroxylamine was trapped as acetonilide and N,O-diacetylphenyl hydroxylamine and could be identified by GC-MS. The latter compound is known to be formed by the reaction of N-phenyl hydroxylamine with an excess of acetic anhydride.\[^{[151]}\]

Remarkably in the presence of the amido complex 1, aniline reacts rapidly with nitrosobenzene to azoxybenzene; the amino hydride complex 2 was formed in this reaction (Scheme 46, step v) and in the presence of an excess of nitrosobenzene 2 was converted to [Rh(ONHPh)(trop2NH)(PPh3)] 98. To our knowledge, this is the first time azoxybenzene instead of azobenzene is produced from aniline and nitrosobenzene.

In Scheme 46, these individual reactions are combined to propose a catalytic cycle which is also consistent with earlier findings and computations for transfer hydrogenations\[^{[6a-c]}\] promoted by [Rh(trop2N)(L)] complexes as catalysts. In the first step (i), the catalyst precursor 9 is deprotonated to the catalytically active amido complex 1 which in (ii) dehydrogenates the alcohol to the aldehyde compound forming the amino hydride complex 2 (which was isolated and fully characterised including an X-ray diffraction study).\[^{[6a-c, 24]}\] The amino hydride complex 2 transfers hydrogen to nitrosobenzene in step (iii) to give N-phenyl hydroxylamine, which immediately reacts with the amido complex 1 to form [Rh(ONHPh)(trop2NH)(PPh3)] 98. In step (iv), 98 reacts slowly with the alcohol to form aniline, aldehyde, and water. Finally in step (v), aniline reacts with nitrosobenzene in the presence of the amido complex 1 in a fast reaction to azoxybenzene; 1 is converted to the amino hydride complex 2. Because free N-phenyl hydroxylamine was detected as intermediate of the catalytic reactions, partial formation of azoxybenzene in a non-metal catalysed condensation reaction (vi) cannot be excluded.

The formation of aldehydes and the absence of carboxylates as dehydrogenative coupling products between aldehydes and water\[^{[6a, 24]}\] (see also chapter 4.2.2 and 5.2.2) can be explained as follows: a) Water formed in reactions (iv) and eventually (vi) is present in very small amounts and moreover it is captured by heterogeneously suspended K2CO3. b) The equilibrium concentration of the amido complex 1 is always very low because it is intercepted by alcohol or N-hydroxylamine to give 2 or 98 respectively. This prevents water addition across the Rh-N bond in amide 1 to give the hydroxo complex [Rh(OH)(trop2NH)(PPh3)] 63.
which is the active species to convert aldehydes to the corresponding hemiacetals and then further to carboxylates (see chapter 3.2). Indeed, even when 10 equivalents of water are added to a mixture of benzyl alcohol and nitrosobenzene, benzaldehyde remains the main product while benzoate is formed in about 30% yield only. c) Note that under the given reaction conditions, aniline is not dehydrogenatively coupled with aldehydes to amides as previously observed for primary alkyl amines[6a, 24] but is irreversibly and rapidly converted to azoxybenzene.

On the other hand if a primary alkyl amine such as butylamine is added to the catalytic reaction some of the formed benzaldehyde is dehydrogenatively coupled with the amine to N-butylbenzamide. Also the condensation product N-benzylidenebutan-1-amine was detected by GC-MS.

The formation of an unsymmetrically substituted azoxyarene was attempted by using a 1:1 mixture of 1-methoxy-4-nitrosobenzene and 4-nitrosobenzoate as substrate for the transfer hydrogenative coupling reaction of the nitrosoarene. Although the methoxy substituted nitrosoarene has proven to react the fastest, all four possible products were observed by 1H-NMR analysis.

It was also attempted to produce an unsymmetrically substituted azoxyarene by adding aniline to the catalytic transfer hydrogenative coupling reaction of 1-methoxy-4-nitrosobenzene. However the doubly substituted 4,4′-dimethoxyazoxybenzene was the only product observed. In an attempt to use N-phenyl hydroxylamine as hydrogen acceptor, most of the benzyl alcohol was not reacted; minor quantities of benzaldehyde and N-benzylideneaniline were observed by GC-MS. The N-phenyl hydroxylamine however was disproportionated by the catalyst to nitrosobenzene and aniline. Most of the intermediately produced nitrosobenzene was consumed to form azoxybenzene. The fact that small quantities of nitrosobenzene were detected and consequently the disproportion of N-phenyl hydroxylamine was observed indicates that the hydrogenation of nitrosobenzene (Scheme 46, step iii) is reversible.

### 6.3 Conclusion

A novel catalytic system could be successfully developed which allows the efficient dehydrogenation of activated alcohols to the corresponding aldehydes using a Rh\(^{1}\) amido olefin complex 1 as catalyst (up to 0.1 mol%) and nitrosobenzene as hydrogen acceptor. Although not all steps involved in this reaction are fully understood, a simplified mechanism for the formation of aldehydes can be proposed. The formation of the corresponding
carboxylic acids by the dehydrogenative coupling of the aldehydes with the formed water is suppressed. As such, this reaction complements the previously reported protocols with [Rh(trop$_2$N)(L)] catalysts leading exactly to these products, that is carboxylic acids, esters and amides$^{[6a, 24]}$ (see also chapter 4.2.2 and 5.2.2). The findings reported here imply that aldehydes are also formed in these reactions as primary intermediates (see Eq. 20) which are subsequently dehydrogenatively coupled to a carboxylic acid derivative in an irreversible reaction. In the reactions we report here, a nitrosoarene as hydrogen acceptor is first converted to an N-arenyl hydroxylamine. Under the catalytic conditions, this reacts further with a molecule of alcohol in the presence of the catalyst to give an aniline derivative and the aldehyde. The exact mechanism of this reaction is not known yet. Employing ethanol as an inexpensive and readily available “reductant” (hydrogen donor), this catalytic reaction can be used to prepare azoxyarenes in very good yields. To our knowledge a catalytic dehydrogenative coupling reaction, under the formation of N-N bonds, is a new reaction and as such might be useful for the preparation of functionalised azoxyarenes under very mild conditions or inspire further catalysed coupling reactions. Future work will focus also on more robust – phosphane-free – catalysts – ideally with low-cost, non-noble metals – which shall also allow the efficient conversion of alkyl alcohols to the corresponding alkyl aldehydes and/or the synthesis of unsymmetrical azoxyarenes.
7 Experimental section
7.1 General comments

7.1.1 General techniques
If not stated otherwise all experiments were performed under an inert atmosphere of Ar using standard Schlenk and vacuum line techniques or in a glove box (M Braun: lab master 130). The argon was provided by PANGAS and further purified with an MBraun 100 HP gas purification system. Glassware was flame dried under high vacuum or dried at 120 °C overnight prior to use. Solvents were distilled under argon from sodium/benzophenone (THF, diethyl ether, toluene), sodium/benzophenone/tetraglyme (n-hexane), sodium/diethyl phthalate (ethanol), magnesium (methanol), or calcium hydride (DCM) then stored under Ar over 3 Å molecular sieves. Deuterated solvents were purchased from Eurisotop, degassed and distilled from the proper drying agent, and stored over 3 Å molecular sieves.

7.1.2 Chemicals
Basic chemicals were purchased from ABCR, Acros, Aldrich, Fluka, Lancaster or STREM. Chemicals used for catalysis were either used as received or purified as described in the corresponding section. The following organic compounds and metal complexes were prepared by literature methods: (2-(1,3-dioxolan-2-yl)phenyl)methanol,[38] (2-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)methanol,[38, 50] 2-(2-bromophenyl)-1,3-dioxolane,[35c] 5H-dibenzo[a,d]cycloheptene-5-amine (tropNH2),[36] [Rh2(μ2-Cl)2(COD)2],[152] tert-butyl (2-(bromomethyl)phenyl)carbamate,[56] tris(3,5-dimethylphenyl)phosphate,[85b] 5H-dibenzo[a,d]cycloheptene-5-one, [42b, 44] [Rh2(μ2-Cl)2(trop2NH)2]61, 60, 6d, 6e [Rh(trop2NH)(PPh3)(TMY)],[61] [Rh(trop2NH)(P(Ph3)3)OTf]9, [6a, 6d, 6e] [Rh(trop2N)(PPh3)]1, [6a, 6d, 6e] [Rh(trop2N)(PPh3)]OTf, [6a, 6d, 6e] tris(3,5-dimethylphenyl)phosphane, [85f] tris(3,5-bis(trifluoromethyl)phenyl)phosphane, [85d] 1-bromo-3,5-di-tert-butylbenzene, [153] tris(3,5-di-tert-butylphenyl)phosphane, [85e] 1-bromo-3,5-diisopropylbenzene, [154] bis(3,5-dimethylphenyl)(phenyl)phosphane, [85b] bis(3,5-bis(trifluoromethyl)phenyl)(phenyl)phosphane, [155] 5-phenyl-5H-dibenzophosphole (DBP), [156] tri(pyridin-2-yl)phosphane, [85a] tris(4-butylphenyl)phosphane, [85c] triethyl ammonium triflate, 1,3,4,5 tetramethyleimidazol-2-ylidene (TMY), [157] [RhCl(trop2NH)(TMY)],[93, 6a, 51] [Rh(trop2NH)(TMY)OTf]8, [6a, 51] [Ir(trop2NH)(PPh3)OTf],[6a] [Rh(trop2NH)(P(Ph3)3)OTf],[6a] [Rh(trop2NH)(P(Bu3)3)OTf],[6a, 51] [Rh(trop2NH)(TPP)]OTf,[6a, 51] N-phenyl hydroxylamine.[158]
7.1.3 NMR spectra
NMR spectra were recorded on *Bruker Avance 700, 500, 400, 300, 250 and 200* spectrometers. The chemical shifts (δ) are measured according to IUPAC[159] and expressed in ppm relative to Si(CH₃)₄, CD₃NO₂, CFCl₃, H₃PO₄, and Rh(acac)₃ for ¹H, ²H, ¹³C, ¹⁵N, ¹⁹F, ³¹P and ¹⁰³Rh respectively. Coupling constants J are given in Hertz [Hz] as absolute values. The multiplicity of the signals is indicated as s, d, t, q, or m for singlets, doublets, triplets, quartets, or multiplets, respectively. The abbreviation br. is given for broadened signals. Quaternary carbon atoms are indicated as C⁴ quat, aromatic units as CH⁴ ar and CH⁴ ar if not noted otherwise. The olefinic protons and ¹³C atoms are indicated as CH⁴ olefin and CH⁴ olefin. The benzylic protons and ¹³C atoms in the central seven-membered ring of the trop-unit are indicated as CH⁴ benzyl and CH⁴ benzyl.

7.1.4 IR spectra
IR spectra were recorded on a *Perkin-Elmer-Spectrum 2000* FT-IR-Raman spectrometer with KBr beam splitter (range 500-4000 cm⁻¹); the ATR technique was applied. The absorption bands are described as follows: strong (s), middle (m), weak (w), or broad (br).

7.1.5 Gas chromatography (GC)
Gas chromatography was performed on a *Hewlett Packard HP 6890 Series* GC system equipped with an EPC split/splitless injector. If not stated otherwise the measurements were done with an inlet pressure of 4.88 psi, a 50:1 split resulting in a slit flow of 108 mL/min and a HP-5 Crosslinked 5% PH ME Siloxane column (30 m x 0.32 mm, film thickness 0.25 μm), flow rate 27.2 mL/min at 4.88 psi. and temperature program: initial temperature 80 °C (hold 1 min), increased to 180 °C at a rate of 4 °C/min and hold for 40 min.

7.1.6 GC-MS
GC-MS analysis was done with a *Trace GC Ultra* and a *Polaris Q* device both from *Thermo Finnigan*. Columns: Zebron ZB-5MS: 5% phenyl arylene, 95% dimethylpolysiloxane (30 m x 0.25 mm x 0.25 μm); J&W Scientific GS-GASPRO 113-4362: 5 Å molecular sieves (60 m, 0.32 mm). Ion source: EI; Mass analyser: ion trap.

7.1.7 High resolution MALDI MS (HiRes MS) and ESI MS
High resolution MALDI MS and ESI MS were measured by the mass spectroscopy service of ETH Zürich.

7.1.8 Elemental Analysis
Elemental analyses were performed by the microanalytical laboratory of the ETH Zürich.
7.1.9 X-Ray diffraction
X-Ray diffraction was measured on a Bruker SMART Apex diffractometer with CCD area detector; MoKα radiation (0.71073 Å). The structures were solved (SHELX 6.14 8/6/00) by direct methods and successive interpretation of the difference Fourier maps, followed by least-squares refinement against full matrix (versus $F^2$) with SHELXTL (ver. 6.12) and SHELXL-97. All non-hydrogen atoms were refined anisotropically. The contribution of some hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Some others were located in the difference Fourier map and refined freely. Empirical absorption correction was done, SADABS-2008/1 (Bruker).

7.1.10 Computational Methods
The optimization of the molecules was performed at the BP(86)/SV(P), BP(86)/TZVPP and PBE0/TZVPP levels of theory with the program TURBOMOLE Version 6.0.2mpi or 6.3.1mpi. All calculated species are true minima on the energy hyper-surface as shown by the absence of imaginary frequencies. For the B2-PLYP/TZVPP level of theory, a single point energy calculation on the optimised (PBE0/TZVPP) structure was performed. For the corresponding literature of the basis sets see ftp://ftp.chemie.uni-karlsruhe.de/pub/basen. The transition states were found at the B3PW91/lanl2dz level of theory using the program Gaussian09, Revision A.02. Once the transition states were found, as indicated by the presence of 1 imaginary frequency, the x,y,z coordinates were taken and used in TURBOMOLE. An optimization and frequency calculation at the PBE0/TZVPP level of theory were performed. All transition states show only one negative frequency vector identical to the reaction coordinates of either the H₂ splitting and addition to the complex or N₂O splitting and addition to the hydride complex. NBO analysis was performed at the B3PW91/lanl2dz level of theory using the program Gaussian09, Revision A.02.

7.1.11 Electrochemical experiments
The electrochemical experiments were done by our collaborators Bianchini et al. at the Institute of Chemistry of Organometallic Compounds ICCOM-CNR.

7.1.12 Electron microscopy
The Electron microscopy measurements were performed at the Electron Microscopy Center ETH Zurich (EMEZ)
7.2 Catalysis

7.2.1 Synthesised rhodium complexes tested in standard transferhydrogenation catalysis

7.2.1.1 Purification of the substrates

Acetophenone and cyclohexanone were distilled from molecular sieves. Benzyl alcohol, 1-octanol, methyl geranate and ethyl cinnamate were distilled under reduced pressure. Benzalacetone was recrystallised from hot hexane and benzophenone was recrystallised from hot ethanol.

7.2.1.2 Transferhydrogenation reactions

Transferhydrogenation reactions of the synthesised rhodium complexes with the tetradentate ligands.

To a solution of $[\text{Rh(tropNHCH}_2\text{StilbPPh}_2\text{)}]\text{OTf}$ 5 (1.2 mg, 1.3 µmol, $10^{-4}$ eq.) and acetophenone (1.51 mL, 1.55 g, 12.9 mmol, 1 eq.) in ethanol (6.5 mL) $\text{K}_2\text{CO}_3$ (17.9 mg, 0.129 mmol, 0.01 eq.) was added. The reaction mixture was stirred at room temperature and several samples were taken after a certain reaction time. The conversion was calculated by the ratio of the integrals of the methyl-group of acetophenone (2.63 (s)) and 1-phenyl ethanol (1.52 (d, $^3J_{HH} = 6.3$ Hz)).

To a solution of $[\text{Rh(tropNHtropPhPPh}_2\text{)}]\text{OTf}$ 34 (2 isomers) or 6 (single isomer) (2.0 mg, 2.2 µmol, $10^{-4}$ eq.) and acetophenone (2.56 mL, 2.64 g, 22.0 mmol, 1 eq.) in ethanol (11 mL) $\text{K}_2\text{CO}_3$ (30.4 mg, 0.22 mmol, 0.01 eq.) was added. The reaction mixture was stirred at room temperature and several samples were taken after a certain reaction time. The conversion was calculated by the ratio of the integrals of the methyl-group of acetophenone (2.63 (s)) and 1-phenyl ethanol (1.52 (d, $^3J_{HH} = 6.3$ Hz)).

To a solution of acetophenone (1.22 mL, 1.32 g, 22.0 mmol, 1 eq.) in ethanol (10 mL) a solution of $[\text{Rh(tropNHCH}_2\text{StilbPPh}_2\text{)}]\text{OTf}$ 5 (1.0 mL, 2.2·$10^{-4}$ M in ethanol, 0.2 mg, 0.22 µmol, $10^{-5}$ eq.) was added. The resulting solution was degased for 30 minutes then $\text{K}_2\text{CO}_3$ (30 mg, 0.22 mmol, 0.01 eq.) was added. The reaction mixture was stirred for 1 day then a sample was analysed by $^1\text{H}$ NMR. The conversion was calculated by the ratio of the integrals of the methyl-group of acetophenone (2.63 (s)) and 1-phenyl ethanol (1.52 (d, $^3J_{HH} = 6.3$ Hz)).

To a solution of acetophenone (6.99 mL, 7.19 g, 59.9 mmol, 1 eq.) in ethanol (30 mL) a solution of $[\text{Rh(tropNHCH}_2\text{StilbPPh}_2\text{)}]\text{OTf}$ 5 (0.27 mL, 2.2·$10^{-4}$ M in ethanol, 54 µg, 60 nmol, $10^{-6}$ eq.) was added. The resulting solution was degased for 30 minutes then $\text{K}_2\text{CO}_3$ (83 mg, 0.60 mmol, 0.01 eq.) was added. The reaction mixture was stirred for 2 days then a
sample was analysed by $^1$H NMR. The conversion was calculated by the ratio of the integrals of the methyl-group of acetophenone (2.63 (s)) and 1-phenyl ethanol (1.52 (d, $^3J_{HH} = 6.3$ Hz)).

To a solution of acetophenone (6.41 mL, 6.60 g, 55.0 mmol, 1 eq.) in ethanol (27.5 mL) a solution of [Rh(tropNHtropPhPPh$_2$)]OTf 34 (2 isomers) or 6 (single isomer) (0.125 mL, 4.4·10$^{-4}$ M in ethanol, 50 μg, 55 nmol, 10$^{-6}$ eq.) was added. The resulting solution was degased for 30 minutes then K$_2$CO$_3$ (76 mg, 0.55 mmol, 0.01 eq.) was added. The reaction mixture was stirred for 2 days then a sample was analysed by $^1$H NMR. The conversion was calculated by the ratio of the integrals of the methyl-group of acetophenone (2.63 (s)) and 1-phenyl ethanol (1.52 (d, $^3J_{HH} = 6.3$ Hz)).

To a solution of [Rh(tropNHCH$_2$StilbPPh$_2$)]OTf 5 (4.5 mg, 5.0 μmol, 10$^{-3}$ eq.) and a substrate (5.0 mmol, 1 eq.) in ethanol (2.5 mL) K$_2$CO$_3$ (6.9 mg, 50 μmol, 0.01 eq.) was added. The reaction mixture was stirred at room temperature and several samples were taken after a certain reaction time. The conversion was determined by GC (Measured retention time: ethyl cinnamate 16.74 min; ethyl 3-phenylpropanoate 12.96 min; (E)-methyl geranate 12.19 min; (Z)-methyl geranate 10.87 min; methyl 3,7-dimethyloct-6-enoate 10.25 min; (E)-methyl geranate 14.36 min; (Z)-ethyl geranate 13.03 min; ethyl 3,7-dimethyloct-6-enoate 12.38 min; benzalacetone 13.26 min; 4-Phenylbutan-2-one 9.84 min; 4-Phenylbut-3-en-2-ol 12.25 min; 4-Phenylbutan-2-ol 10.28 min; benzophenone 21.46 min, diphenylmethanol 21.81 min).

To a solution of [Rh(tropNHtropPhPPh$_2$)]OTf 34 (2 isomers) or 6 (single isomer) (4.5 mg, 5.0 μmol, 10$^{-3}$ eq.) and a substrate (5.0 mmol, 1 eq.) in ethanol (2.5 mL) K$_2$CO$_3$ (6.9 mg, 50 μmol, 0.01 eq.) was added. The reaction mixture was stirred at room temperature and several samples were taken after a certain reaction times. The conversion was determined by GC.

**General procedure for the transfer hydrogenation of acetophenone with ethanol to test the synthesised rhodium$^1$trop$_2$NH complexes with different phosphanes as catalysts.**

To a solution of the catalyst (1.7 μmol, 10$^{-4}$ eq.) and acetophenone (2.01 mL, 2.06 g, 17.2 mmol, 1 eq.) in ethanol (6 mL) K$_2$CO$_3$ (23.7 mg, 0.17 mmol, 0.01 eq.) was added. The reaction mixture was stirred overnight then a sample was analysed by $^1$H-NMR. The conversion was determined by the integration of the methyl-group of acetophenone (2.63 (s)) and 1-phenyl ethanol (1.52 (d, $^3J_{HH} = 6.3$ Hz)).
7.2.1.3 Dehydrogenative coupling reaction to acids

Dehydrogenative coupling reaction to acids of the synthesised rhodium complexes with the tetradeionate ligands.

A two phasic solution of H2O (6.5 mL, 6.5 g, 362 mmol, 66 eq.), NaOH (263 mg, 6.60 mmol, 1.2 eq.), benzyl alcohol (0.57 mL, 595 mg, 5.50 mmol, 1 eq.) and cyclohexanone (2.80 mL, 2.70 g, 27.5 mmol, 5 eq.) was degased for 30 minutes then [Rh(tropNHtropPhPPh2)]OTf 5 (5.0 mg, 5.5 μmol, 10^−3 eq.) was added. The reaction mixture was stirred overnight then all volatiles were removed. The residue was dissolved in water and washed with a small portion of Et2O. The aqueous phase was acidified with HCl (pH < 2) then extracted 3 times with small portions of Et2O. The combined organic phases were washed with brine, dried over Na2SO4 and filtered then the solvent was removed under reduced pressure. Yield: 538 mg, 80%.

A two phasic solution of H2O (6.5 mL, 6.5 g, 362 mmol, 66 eq.), NaOH (263 mg, 6.60 mmol, 1.2 eq.), 1-octanol (0.87 mL, 716 mg, 5.50 mmol, 1 eq.) and cyclohexanone (2.80 mL, 2.70 g, 27.5 mmol, 5 eq.) was degased for 30 minutes, then [Rh(tropNHCH2StilbPPh2)]OTf 5 (5.0 mg, 5.5 μmol, 10^−3 eq.) was added. The reaction mixture was stirred overnight then all volatiles were removed. The residue was dissolved in water and washed with a small portion of Et2O. The aqueous phase was acidified with HCl (pH < 2) then extracted 3 times with small portions of Et2O. The combined organic phases were washed with brine, dried over Na2SO4 and filtered then the solvent was removed under reduced pressure. Yield: 584 mg, 74%.

A two phasic solution of H2O (13 mL, 13 g, 725 mmol, 66 eq.), NaOH (526 mg, 13.2 mmol, 1.2 eq.), benzyl alcohol (1.14 mL, 1.19 g, 11 mmol, 1 eq.) and cyclohexanone (1.40 mL, 1.30 g, 13.7 mmol, 5 eq.) was degased for 30 minutes then [Rh(tropNHCH2StilbPPh2)]OTf 5 (2.0 mg, 2.2 μmol, 2·10^−4 eq.) was added. The reaction mixture was stirred overnight then all volatiles were removed. The residue was dissolved in water and washed with a small portion of Et2O. The aqueous phase was acidified with HCl (pH < 2) then extracted 3 times with small portions of Et2O. The combined organic phases were washed with brine, dried over Na2SO4 and filtered then the solvent was removed under reduced pressure. Yield: 725 mg, 43%.

A two phasic solution of H2O (6.5 mL, 6.5 g, 362 mmol, 66 eq.), NaOH (263 mg, 6.60 mmol, 1.2 eq.), benzyl alcohol (0.57 mL, 595 mg, 5.50 mmol, 1 eq.) and cyclohexanone (2.80 mL, 2.70 g, 27.5 mmol, 5 eq.) was degased for 30 minutes then Rh(tropNHtropPhPPh2)]OTf 34 (5.0 mg, 5.5 μmol, 10^−3 eq.) was added. The reaction mixture was stirred overnight then all volatiles were removed. The residue was dissolved in water and washed with a small portion of Et2O. The aqueous phase was acidified with HCl (pH < 2) then extracted 3 times with small portions of Et2O. The combined organic phases were washed with brine, dried over Na2SO4 and filtered then the solvent was removed under reduced pressure. Yield: 540 mg, 81%.
A two phasic solution of H$_2$O (6.5 mL, 6.5 g, 362 mmol, 66 eq.), NaOH (263 mg, 6.60 mmol, 1.2 eq.), 1-octanol (0.87 mL, 716 mg, 5.50 mmol, 1 eq.) and cyclohexanone (2.80 mL, 2.70 g, 27.5 mmol, 5 eq.) was degased for 30 minutes then Rh(tropNHtropPhPPh$_2$)OTf $^{34}$ (5.0 mg, 5.5 $\mu$mol, 10$^{-3}$ eq.) was added. The reaction mixture was stirred overnight then all volatiles were removed. The residue was dissolved in water and washed with a small portion of Et$_2$O. The aqueous phase was acidified with HCl (pH < 2) then extracted 3 times with small portions of Et$_2$O. The combined organic phases were washed with brine, dried over Na$_2$SO$_4$ and filtered then the solvent was removed under reduced pressure. Yield: 730 mg, 92%.

A two phasic solution of H$_2$O (6.5 mL, 6.5 g, 362 mmol, 66 eq.), NaOH (263 mg, 6.60 mmol, 1.2 eq.), 1-octanol (0.87 mL, 716 mg, 5.50 mmol, 1 eq.) and cyclohexanone (2.80 mL, 2.70 g, 27.5 mmol, 5 eq.) was degased for 30 minutes then Rh(tropNHtropPhPPh$_2$)OTf $^{34}$ (1.0 mg, 1.1 $\mu$mol, 2$\cdot$10$^{-4}$ eq.) was added. The reaction mixture was stirred overnight then all volatiles were removed. The residue was dissolved in water and washed with a small portion of Et$_2$O. The aqueous phase was acidified with HCl (pH < 2) then extracted 3 times with small portions of Et$_2$O. The combined organic phases were washed with brine, dried over Na$_2$SO$_4$ and filtered then the solvent was removed under reduced pressure. Yield: 725 mg, 43%.

General procedure for the dehydrogenative coupling of benzyl alcohol with water to benzoic acid to test the synthesised Rh$^1$ trop$_2$NH complexes with different phosphanes as catalysts.

A two phasic solution of H$_2$O (6.29 mL, 6.29 g, 349 mmol, 66 eq.), NaOH (254 mg, 6.35 mmol, 1.2 eq.), benzyl alcohol (0.55 mL, 572 mg, 5.29 mmol, 1 eq.) and cyclohexanone (2.74 mL, 2.60 g, 26.5 mmol, 5 eq.) was degased for 30 minutes then the catalyst (5.3 $\mu$mol, 10$^{-3}$ eq.) was added. The reaction mixture was stirred overnight then all volatiles were removed. The residue was dissolved in water and washed with a small portion of Et$_2$O. The aqueous phase was acidified with HCl (pH < 2) then extracted 3 times with small portions of Et$_2$O. The combined organic phases were washed with brine, dried over Na$_2$SO$_4$ and filtered then the solvent was removed under reduced pressure. The residue was analysed by NMR.

NMR-data of benzoic acid:
$^1$H-NMR (250.13 MHz, CDCl$_3$, 298 K): $\delta$ = 7.52 (dd, $^3$$J_{HH}$ = 7.7 Hz, $^3$$J_{HH}$ = 7.3 Hz 2H, CH$_2^a$), 7.66 (dd, $^3$$J_{HH}$ = 7.4 Hz, $^3$$J_{HH}$ = 7.3 Hz 1H, CH$_3^a$), 8.15 (d, $^3$$J_{HH}$ = 7.7 Hz, 2H, CH$_2^b$); $^{13}$C{$^1$H}-NMR (62.90 MHz, CDCl$_3$, 298 K): $\delta$ = 128.5 (s, 2C, CH$_2^b$), 129.3 (s, 1C, C$_{quat}$), 130.2 (s, 2C, CH$_2^b$), 133.8 (s, 1C, CH$_2^b$), 172.2 (s, 1C, COOH).

NMR-data of octanoic acid:
$^1$H NMR (300.13 MHz, CDCl$_3$, 298 K): $\delta$ = 0.88-0.90 (m, 3H, CH$_3$), 1.30-1.32 (m, 8H, CH$_2$), 1.60-1.68 (m, 2H, CH$_2$), 2.37 (t, $^3$$J_{HH}$ = 7.5 Hz, CH$_2$COOH), 10.92 (s, 1H, COOH); $^{13}$C{$^1$H}-NMR (75.48 MHz, CDCl$_3$, 298 K): $\delta$ = 14.0 (s, 1C, CH$_3$), 22.6 (s, 1C, CH$_2$), 24.7 (s, 1C, CH$_2$), 28.9 (s, 1C, CH$_2$), 29.0 (s, 1C, CH$_2$), 31.6 (s, 1C, CH$_2$), 34.1 (s, 1C, CH$_2$), 180.5 (s, 1C, COOH).
7.2.1.4 Dehydrogenative coupling reaction to methyl ester

Dehydrogenative coupling reaction to methyl ester of the synthesised rhodium complexes with the tetradeutate ligands.

To a solution of [Rh(tropNHCH₂StilbPPh₂)]OTf 5 (5.0 mg, 5.5 µmol, 10⁻³ eq.), benzyl alcohol (0.57 mL, 595 mg, 5.50 mmol, 1 eq.) and cyclohexanone (2.8 mL, 2.7 g, 28 mmol, 5 eq.) in methanol (2.2 mL, 1.7 g, 54 mmol, 10 eq.) K₂CO₃ (37.6 mg, 0.271 mmol, 0.05 eq.) was added. The reaction mixture was stirred for 4 hours then all volatiles were removed under reduced pressure. The residue was dissolved in ethyl acetate and washed with a small portion of aqueous NH₄Cl. The organic phase was dried over Na₂SO₄ concentrated and the residue was purified by column chromatography (Eluent: PET:EtOAc 20:1). Yield: 532 mg, 71%.

¹H-NMR (250.13 MHz, CDCl₃, 298 K): δ = 3.95 (s, 3H, CH₃), 7.47 (dd, ³J_HH = 7.8 Hz, ³J_HH = 7.3 Hz, 2H, CH₃), 7.59 (dd, ³J_HH = 7.5 Hz, ³J_HH = 7.3 Hz, 1H, CH₃), 8.07 (d, ³J_HH = 7.5 Hz, 2H, CH₃).

¹³C{¹H}-NMR (62.90 MHz, CDCl₃, 298 K): δ = 52.1 (s, 1C, CH₃), 128.4 (s, 2C, CH₃), 129.6 (s, 2C, CH₃), 130.2 (s, 1C, CH₃), 132.9 (s, 1C, CH₃), 167.1 (s, 1C, COOMe).

To a solution of [Rh(tropNHtropPhPPh₂)]OTf 34 (2 isomers) or 6 (single isomer) (5.0 mg, 5.5 µmol, 10⁻³ eq.), benzyl alcohol (0.57 mL, 595 mg, 5.50 mmol, 1 eq.) and cyclohexanone (2.8 mL, 2.7 g, 28 mmol, 5 eq.) in methanol (2.2 mL, 1.7 g, 54 mmol, 10 eq.) K₂CO₃ (37.6 mg, 0.271 mmol, 0.05 eq.) was added. The reaction mixture was stirred for 4 hours then analysed by GC. (Measured retention time: benzyl alcohol 4.82 min; benzoic acid 3.68 min; methyl benzoate 6.05 min, benzyl benzoate 25.41 min).

To a solution of [Rh(tropNHCH₂StilbPPh₂)]OTf 5 (0.5 mg, 0.55 µmol, 10⁻⁴ eq.), benzyl alcohol (0.57 mL, 595 mg, 5.50 mmol, 1 eq.) and cyclohexanone (2.8 mL, 2.7 g, 28 mmol, 5 eq.) in methanol (2.2 mL, 1.7 g, 54 mmol, 10 eq.) K₂CO₃ (37.6 mg, 0.271 mmol, 0.05 eq.) was added. The reaction mixture was stirred overnight then analysed by GC.

To a solution of [Rh(tropNHtropPhPPh₂)]OTf 34 (0.5 mg, 0.55 µmol, 10⁻⁴ eq.), benzyl alcohol (0.57 mL, 595 mg, 5.50 mmol, 1 eq.) and cyclohexanone (2.8 mL, 2.7 g, 28 mmol, 5 eq.) in methanol (2.2 mL, 1.7 g, 54 mmol, 10 eq.) K₂CO₃ (37.6 mg, 0.271 mmol, 0.05 eq.) was added. The reaction mixture was stirred overnight then analysed by GC.

To a solution of Rh(tropNHCH₂StilbPPh₂)]OTf 5 (2.7 mg, 3.2 µmol, 10⁻³ eq.), 1-octanol (0.50 mL, 413 mg, 3.17 mmol, 1 eq.) and cyclohexanone (1.6 mL, 1.6 g, 16 mmol, 5 eq.) in methanol (1.3 mL, 1.0 g, 32 mmol, 10 eq.) K₂CO₃ (21.9 mg, 0.158 mmol, 0.05 eq.) was added. The reaction mixture was stirred for 4 hours then analysed by GC. (Measured retention time: 1-octanol 5.43 min; octanal 4.20 min; methyl octanoate 6.55 min; octyl octanoate 25.60 min).
To a solution of [Rh(tropNHtropPhPPh₂)]OTf 34 (2.9 mg, 3.2 μmol, 10⁻³ eq.), 1-octanol (0.50 mL, 413 mg, 3.17 mmol, 1 eq.) and cyclohexanone (1.6 mL, 1.6 g, 16 mmol, 5 eq.) in methanol (1.3 mL, 1.0 g, 32 mmol, 10 eq.) K₂CO₃ (21.9 mg, 0.158 mmol, 0.05 eq.) was added. The reaction mixture was stirred for 4 hours then analysed by GC.

**General procedure for the dehydrogenative coupling of benzyl alcohol with methanol to methyl benzoate to test the synthesised Rh¹ trop₂NH complexes with different phosphanes as catalysts.**

To a solution of the catalyst (5.3 μmol, 10⁻³ eq.), benzyl alcohol (0.55 mL, 572 mg, 5.29 mmol, 1 eq.) and cyclohexanone (2.74 mL, 2.60 g, 26.5 mmol, 5 eq.) in methanol (2.14 mL, 1.69 g, 52.9 mmol, 10 eq.) K₂CO₃ (36.6 mg, 0.264 mmol, 0.05 eq.) was added. The reaction mixture was stirred overnight then the conversion was determined by GC (Measured retention time: benzaldehyde: 3.66 min; benzyl alcohol: 4.79 min; methyl benzoate: 6.05 min).
7.2.2 Aerobic oxidation of primary alcohols

7.2.2.1 Other oxygen acceptors

To a mixture of [Rh(trop₂NH)(TMIY)]OTf 8 (2.0 mg, 2.6 μmol, 0.01 eq.) and NaOH (12.5 mg, 0.31 mmol, 1.2 eq.) in H₂O (0.83 mL) and THF (1.67 mL) in an open vessel a previously prepared 1-octanol/octadecane solution (15:1, 46 μL, 33.9 mg, 0.26 mmol, 1 eq.) and an oxygen acceptor (thioanisole or PPh₃) were added. In order to avoid excessive evaporation of THF a balloon filled with air was put over the top of the vessel. The reaction mixture was stirred overnight then n-hexane (2 mL) was added. The mixture was stirred for 10 min then a sample of the apolar phase was analysed by GC (Measured retention time: 1-octanol 5.43 min; octyl octanoate 25.60 min; octadecane 26.17 min).

With PPh₃ as oxygen acceptor the formed triphenylphosphane oxide could be detected by $^{31}$P{$^1$H}-NMR (121.49 MHz, CDCl₃, 298 K): $\delta = 29.6$ (s).

7.2.2.2 Blind experiments

No catalyst: To a solution of NaOH (12.5 mg, 0.31 mmol, 1.2 eq.) in H₂O (0.83 mL) and DMSO (1.67 mL) in an open vessel a previously prepared 1-octanol/octadecane solution (15:1, 46 μL, 33.9 mg, 0.26 mmol, 1 eq.) was added. The reaction mixture was stirred overnight then n-hexane (2 ml) was added The mixture was stirred for 10 min then a sample of the n-hexane phase was analysed by GC (Measured retention time: 1-octanol 5.43 min; octadecane 26.17 min). No conversion was observed.

Exclusion of O₂: To a degased solution of [Rh(trop₂NH)(TMIY)]OTf 8 (2.0 mg, 2.6 μmol, 0.01 eq.) and NaOH (12.5 mg, 0.31 mmol, 1.2 eq.) in H₂O (0.83 mL) and DMSO (1.67 mL) under argon atmosphere a previously prepared 1-octanol/octadecane solution (15:1, 46 μL, 33.9 mg, 0.26 mmol, 1 eq.) was added. The reaction mixture was stirred overnight then n-hexane (2 ml) was added The mixture was stirred for 10 min then a sample of the n-hexane phase was analysed by GC (Measured retention time: 1-octanol 5.43 min; octadecane 26.17 min). No conversion was observed.

7.2.2.3 Different additives

To a mixture of [Rh(trop₂NH)(TMIY)]OTf 8 (2.0 mg, 2.6 μmol, 0.01 eq.), NaOH (12.5 mg, 0.31 mmol, 1.2 eq.) and an additive in H₂O/DMSO (total volume 2.5 mL) in an open vessel a previously prepared 1-octanol/octadecane solution (15:1, 46 μL, 33.9 mg, 0.26 mmol, 1 eq.) was added. The reaction mixture was stirred overnight then n-hexane (2 ml) was added The mixture was stirred for 10 min then a sample of the n-hexane phase was analysed by GC (Measured retention time: 1-octanol 5.43 min; octyl octanoate 25.60 min; octadecane 26.17 min).
7.2.2.4 Aerobic dehydrogenative coupling of various primary alcohols

NaOH (63 mg, 1.6 mmol, 1.2 eq.), [Rh(trop2NH)(TMIY)]OTf 8 (10 mg, 0.013 mmol, 0.01 eq.), water (3.1 mL), DMSO (9.4 mL), THF (1 mL) and a primary alcohol (1.3 mmol, 1 eq.) were put in an open round bottom flask under aerobic conditions at room temperature and stirred overnight. Then all volatiles were removed under reduced pressure and, if not stated otherwise, the residue was suspended in water (15 mL) and the aqueous phase extracted with Et2O (5 mL). The aqueous phase was acidified by addition of 1 M hydrochloric acid and the product was extracted 3 times from the aqueous phase with small portions of Et2O (5 mL). The organic phases were combined, washed with brine and dried with Na2SO4. The solvent was removed under reduced pressure and the obtained product analysed by NMR.

octanoic acid: from 1-octanol. Yield: 121 mg, 64%.

1H-NMR (300.13 MHz, CDCl3, 298 K): δ = 0.88-0.90 (m, 3H, CH3), 1.30-1.32 (m, 8H, CH2), 1.60-1.68 (m, 2H, CH2), 2.37 (t, 3JHH = 7.5 Hz, CH2COOH), 10.92 (s, 1H, COOH).

13C{1H}-NMR (75.48 MHz, CDCl3, 298 K): δ = 14.0 (s, 1C, CH3), 22.6 (s, 1C, CH2), 24.7 (s, 1C, CH2), 28.9 (s, 1C, CH2), 29.0 (s, 1C, CH2), 31.6 (s, 1C, CH2), 34.1 (s, 1C, CH2), 180.5 (s, 1C, COOH).

benzoic acid: from benzyl alcohol. Yield: 125 mg, 79%.

1H-NMR (300.13 MHz, CDCl3, 298 K): δ = 4.80 (s, 1H, COOH), 7.51 (dd, 3JHH = 7.5 Hz, 3JHH = 7.2 Hz 2H, CHar), 7.65 (dd, 3JHH = 7.5 Hz, 3JHH = 7.2 Hz 1H, CHar), 8.15 (d, 3JHH = 7.5 Hz, 2H, CHar).

13C{1H}-NMR (75.48 MHz, CDCl3, 298 K): δ = 128.5 (s, 2C, CHar), 129.4 (s, 1C, Cquat), 130.2 (s, 2C, CHar), 133.8 (s, 1C, CHar), 172.1 (s, 1C, COOH).

geranic acid: from geraniol. Yield: 175 mg, 81%.

1H-NMR (300.13 MHz, CDCl3, 298 K): δ = 1.63 (s, 3H, CH3), 1.71 (s, 3H, CH3), 2.18-2.20 (m, 7H, CH2, CH3), 5.10 (br, 1H, CH=CMε2), 5.71 (br, 1H, CHCOOH).

13C{1H}-NMR (75.48 MHz, CDCl3, 298 K): δ = 17.7 (s, 1C, CH3), 19.1 (s, 1C, CH3), 25.6 (s, 1C, CH3), 26.0 (s, 1C, CH2), 41.2 (s, 1C, CH2), 114.9 (s, 1C, CHCOOH), 122.7 (s, 1C, CH=CMε2), 132.7 (s, 1C, CMε2), 163.3 (s, 1C, C=CHCOOH), 171.7 (s, 1C, COOH).

citronellic acid: from citronellol. Yield: 140 mg, 64%.

1H-NMR (250.13 MHz, CDCl3, 298 K): δ = 1.00 (d, 3JHH = 6.5 Hz, 3H, CH3), 1.34-1.44 (m, 2H, CH2), 1.62 (s, 3H, CH3), 1.70 (s, 3H, CH3), 1.97-2.03 (m, 3H, CH2, CH), 2.13-2.19 (m, 1H, CH2), 2.43-2.35 (m, 1H, CH2), 5.12 (m, 1H, CH=CMε2).

13C{1H}-NMR (62.90 MHz, CDCl3, 298 K): δ = 17.6 (s, 1C, CH3), 19.6 (s, 1C, CH2), 25.4 (s, 1C, CH2), 25.7 (s, 1C, CH3), 29.8 (s, 1C, CH3), 36.7 (s, 1C CH2), 41.5 (s, 1C, CH), 124.2 (s, 1C, CH=CMε2), 131.7 (s, 1C, CMε2), 179.1 (s, 1C, COOH).
4-(hydroxymethyl)benzoic acid: from 1,4-phenylenedimethanol. After removing the solvent, the residue was dissolved in water (15 ml) and the aqueous phase extracted with Et₂O (5 ml). The aqueous phase was acidified by addition of 1 M hydrochloric acid and the precipitated product collected by filtration. Yield: 53 mg, 27%.

\[ ^1\text{H-NMR} \ (300.13 \text{ MHz, CDCl}_3, \ 298 \text{ K}): \delta = 8.10 \ (d, \ J = 7.8 \text{ Hz, 2H, } C\text{H}^\text{ar}), \ 7.49 \ (d, \ J = 8.5 \text{ Hz, 2H, } C\text{H}^\text{ar}), \ 4.82 \ (s, \ 2H, C\text{H}_2\text{OH}). \]

4-methoxybenzoic acid: from (4-methoxyphenyl)methanol. After removing the solvent, the residue was dissolved in water (15 mL) and the aqueous phase extracted with CH₂Cl₂ (5 mL). The aqueous phase was acidified by addition of 1 M hydrochloric acid and the product was extracted 3 times from the aqueous phase with small portions of CH₂Cl₂ (5 mL). The organic phases were combined, washed with brine and dried with Na₂SO₄. The solvent was removed under reduced pressure and the obtained product analysed by NMR. Yield: 124 mg, 63%.

\[ ^1\text{H-NMR} \ (300.13 \text{ MHz, CDCl}_3, \ 298 \text{ K}): \delta = 3.90 \ (s, \ 3H, C\text{H}_3), \ 6.97 \ (d, \ J_{HH} = 8.8 \text{ Hz, 2H, } C\text{H}^\text{ar}), \ 8.08 \ (d, \ J_{HH} = 8.8 \text{ Hz, 2H, } C\text{H}^\text{ar}). \]

\[ ^{13}\text{C\{}^1\text{H}\text{-NMR} \ (75.48 \text{ MHz, CDCl}_3, \ 298 \text{ K}): \delta = 14.8 \ (s, \ 1C, C\text{H}_3), \ 124.9 \ (s, \ 2C, C\text{H}^\text{ar}), \ 126.9 \ (s, \ 1C, C\text{H}^\text{quat}), \ 130.5 \ (s, \ 2C, C\text{H}^\text{ar}), \ 146.8 \ (s, \ 1C, C\text{H}^\text{quat}), \ 171.4 \ (s, \ 1C, C\text{OOH}). \]

4-(methylthio)benzoic acid: from (4-(methylthio)phenyl)methanol. Yield: 131 mg, 60%.

\[ ^1\text{H-NMR} \ (300.13 \text{ MHz, CDCl}_3, \ 298 \text{ K}): \delta = 2.55 \ (s, \ 3H, C\text{H}_3), \ 7.30 \ (d, \ J_{HH} = 8.5 \text{ Hz, 2H, } C\text{H}^\text{ar}), \ 8.03 \ (d, \ J_{HH} = 8.4 \text{ Hz, 2H, } C\text{H}^\text{ar}). \]

\[ ^{13}\text{C\{}^1\text{H}\text{-NMR} \ (75.48 \text{ MHz, CDCl}_3, \ 298 \text{ K}): \delta = 14.8 \ (s, \ 1C, C\text{H}_3), \ 124.9 \ (s, \ 2C, C\text{H}^\text{ar}), \ 126.9 \ (s, \ 1C, C\text{H}^\text{quat}), \ 130.5 \ (s, \ 2C, C\text{H}^\text{ar}), \ 146.8 \ (s, \ 1C, C\text{H}^\text{quat}), \ 171.4 \ (s, \ 1C, C\text{OOH}). \]

4-isopropylbenzoic acid: from (4-isopropylphenyl)methanol. Yield: 163 mg, 77%.

\[ ^1\text{H NMR} \ (300.13 \text{ MHz, CDCl}_3, \ 298 \text{ K}): \delta = 8.08 \ (d, \ J_{HH} = 8.3 \text{ Hz, 2H, } C\text{H}^\text{ar}), \ 7.36 \ (d, \ J_{HH} = 8.2 \text{ Hz, 2H, } C\text{H}^\text{ar}), \ 3.02 \ (\text{sept, } J_{HH} = 6.85 \text{ Hz, 1H, } C\text{H}^\text{quat}), \ 1.31 \ (d, \ J_{HH} = 6.85 \text{ Hz, 6H, } C\text{H}_3). \]

\[ ^{13}\text{C\{}^1\text{H}\text{-NMR} \ (75.48 \text{ MHz, CDCl}_3, \ 298 \text{ K}): \delta = 172.2 \ (s, \ 1C, C\text{OOH}), \ 155.4 \ (s, \ 1C, C\text{quat}), \ 130.4 \ (s, \ 2C, C\text{H}^\text{ar}), \ 126.9 \ (s, \ 1C, C\text{H}^\text{quat}), \ 126.6 \ (s, \ 2C, C\text{H}^\text{ar}), \ 34.3 \ (s, \ 1C, C\text{H}), \ 23.7 \ (s, \ 2C, C\text{H}_3). \]

4-hydroxy-3-methoxybenzaldehyde: from 4-(hydroxylmethyl)-2-methoxyphenol: Yield: 70 mg, 36%.

\[ ^1\text{H-NMR} \ (300.13 \text{ MHz, CDCl}_3, \ 298 \text{ K}): \delta = 3.92 \ (s, \ 3H, C\text{H}_3), \ 5.68 \ (s, \ Ar\text{O}H), \ 6.91 \ (m, \ 1H, C\text{H}^\text{ar}), \ 7.06 \ (m, \ 1H, C\text{H}^\text{ar}), \ 7.44 \ (m, \ 1H, C\text{H}^\text{ar}), \ 9.84 \ (s, \ 1H, C\text{HO}). \]

\[ ^{13}\text{C\{}^1\text{H}\text{-NMR} \ (75.48 \text{ MHz, CDCl}_3, \ 298 \text{ K}): \delta = 55.9 \ (s, \ 1C, C\text{H}_3), \ 108.8 \ (s, \ 1C, C\text{H}^\text{ar}), \ 114.3 \ (s, \ 1C, C\text{H}^\text{quat}), \ 127.5 \ (s, \ 1C, C\text{H}^\text{ar}), \ 129.9 \ (s, \ 1C, C\text{H}^\text{quat}), \ 147.2 \ (s, \ 1C, C\text{quat}), \ 151.7 \ (s, \ 1C, C\text{quat}), \ 190.9 \ (s, \ 1C, C\text{HO}). \]
**furan-2-carboxylic acid**: from furan-2-ylmethanol Yield: 94 mg, 65%.

$^1$H-NMR (250.13 MHz, CDCl$_3$, 298 K): $\delta = 6.60$ (dd, $J = 3.54$ Hz, $J = 1.7$ Hz, 1H, CH), 7.37 (d, $J = 3.5$ Hz, 1H, CH), 7.68 (d, $J = 1.7$ Hz, 1H, CH).

$^{13}$C{$^1$H}-NMR (62.90 MHz, CDCl$_3$, 298 K): $\delta = 112.3$ (s, 1C, CH), 120.0 (s, 1C, CH), 142.6 (s, 1C, $C^{\text{quat}}$), 147.4 (s, 1C, CH), 162.9 (s, 1C, COOH).
7.2.3 Dehydrogenation of alcohols with N₂O as hydrogen acceptor

7.2.3.1 Preliminary remarks

Liquid alcohol substrates were distilled from CaH₂ and cinnamyl alcohol was recrystallised from hot hexane. The other solid substrates were used as received. Nitrous oxide was provided from PanGas with a purity of 99.995% and used without further purification.

7.2.3.2 Optimisation of the catalytic conditions

Preliminary experiment

\( t\)-BuOK (2.8 mg, 25 \( \mu \)mol, 0.1 eq.) was added to a mixture of benzyl alcohol (26 \( \mu \)L, 27 mg, 250 \( \mu \)mol, 1 eq.), 4 Å molecular sieves (100 mg) and THF (3 mL) in a 100 mL Schlenk-tube. The resulting suspension was cooled to -78 °C then \([\text{Rh(trop}₂\text{NH})(\text{PPh₃})\text{OTf}] \) (2.3 mg, 2.5 \( \mu \)mol, 0.01 eq.) was added. The flask was evacuated and filled with \( \text{N}_₂\text{O} \) (100 mL, 1 bar, 8 eq.) then it was warmed to room temperature while attached to an overpressure vessel. The mixture was stirred overnight. GC-analysis showed 18% conversion to a 1:10 mixture of benzaldehyde and benzyl benzoate (Measured retention time: benzyl alcohol 4.82 min; benzaldehyde; 3.53 min; benzyl benzoate 25.41 min).

Solvent evaluation

\( t\)-BuOK (2.8 mg, 25 \( \mu \)mol, 0.1 eq.) was added to a mixture of benzyl alcohol (26 \( \mu \)L, 27 mg, 250 \( \mu \)mol, 1 eq.), 4 Å molecular sieves (100 mg) in the solvent (THF, DMF, DMSO, toluene, THF:toluene 1:1 or 1:2; total volume 3 mL) in a 100 mL Schlenk-tube. The resulting suspension was cooled to -78 °C then \([\text{Rh(trop}₂\text{NH})(\text{PPh₃})\text{OTf}] \) (2.3 mg, 2.5 \( \mu \)mol, 0.01 eq.) was added. The flask was evacuated and filled with \( \text{N}_₂\text{O} \) (100 mL, 1 bar, 8 eq.) then it was warmed to room temperature while attached to an overpressure vessel. The mixture was stirred overnight then analysed by GC.

Catalyst evaluation

\( t\)-BuOK (2.8 mg, 25 \( \mu \)mol, 0.1 eq.) was added to a mixture of benzyl alcohol (26 \( \mu \)L, 27 mg, 250 \( \mu \)mol, 1 eq.), 4 Å molecular sieves (100 mg) and THF (1 mL) and toluene (2 mL) in a 100 mL Schlenk-tube. The resulting suspension was cooled to -78 °C then the catalyst (2.5 \( \mu \)mol, 0.01 eq.) was added. The flask was evacuated and filled with \( \text{N}_₂\text{O} \) (100 mL, 1 bar, 8 eq.) then it was warmed to room temperature while attached to an overpressure vessel. The mixture was stirred overnight at 50 °C then analysed by GC.

Evaluation of the role of molecular sieves

A 100 mL Schlenk flask charged with \([\text{Rh(trop}₂\text{NH})(\text{TMIY})\text{OTf}] \) (1.9 mg, 2.5 \( \mu \)mol, 0.01 eq.), \( t\)-BuOK (2.8 mg, 25 \( \mu \)mol, 0.1 eq.) and an additive (100 mg) was evacuated and filled with \( \text{N}_₂\text{O} \) (100 mL, 1 bar, 8 eq.). THF (1 mL), benzyl alcohol (26 \( \mu \)L, 27 mg, 250 \( \mu \)mol, 1 eq.) and toluene (2 mL) were added. The reaction mixture was stirred overnight at 50 °C then analysed by GC.
Double catalyst concentration

$t$-BuOK (2.8 mg, 25 µmol, 0.1 eq.) was added to a mixture of benzyl alcohol (26 µL, 27 mg, 250 µmol, 1 eq.), 4 Å molecular sieves (100 mg) and THF (3 mL) in a 100 mL Schlenk-tube. The resulting suspension was cooled to -78 °C then $[\text{Rh(trop}_2\text{NH)(TMIY)}]\text{OTf}$ 8 (3.9 mg, 5.0 µmol, 0.02 eq.) was added. The flask was evacuated and filled with N₂O (100 mL, 1 bar, 8 eq.) then it was warmed to room temperature while attached to an overpressure vessel. The mixture was stirred overnight at 50 °C. GC-analysis showed 44% conversion to a 1:100 mixture of benzaldehyde and benzyl benzoate.

Half catalyst concentration

$t$-BuOK (2.8 mg, 25 µmol, 0.1 eq.) was added to a mixture of benzyl alcohol (26 µL, 27 mg, 250 µmol, 1 eq.), 4 Å molecular sieves (100 mg) and THF (3 mL) in a 100 ml Schlenk-tube. The resulting suspension was cooled to -78 °C then $[\text{Rh(trop}_2\text{NH)(TMIY)}]\text{OTf}$ 8 (1.0 mg, 1.25 µmol, 0.005 eq.) was added. The flask was evacuated and filled with N₂O (100 mL, 1 bar, 8 eq.) then it was warmed to room temperature while attached to an overpressure vessel. The mixture was stirred overnight at 50 °C. GC-analysis showed 46% conversion to a 1:100 mixture of benzaldehyde and benzyl benzoate.

Double substrate concentration

$t$-BuOK (2.8 mg, 25 µmol, 0.05 eq.) was added to a mixture of benzyl alcohol (52 µL, 54 mg, 500 µmol, 1 eq.), 4 Å molecular sieves (100 mg) and THF (3 mL) in a 100 ml Schlenk-tube. The resulting suspension was cooled to -78 °C then $[\text{Rh(trop}_2\text{NH)(TMIY)}]\text{OTf}$ 8 (1.9 mg, 2.5 µmol, 0.005 eq.) was added. The flask was evacuated and filled with N₂O (100 mL, 1 bar, 4 eq.) then it was warmed to room temperature while attached to an overpressure vessel. The mixture was stirred overnight at 50 °C. GC-analysis showed 32% conversion to a 1:5 mixture of benzaldehyde and benzyl benzoate.

Evaluation of the role of molecular sieves

A 100 mL Schlenkflask charged with $[\text{Rh(TMIY)(trop}_2\text{NH)}]\text{OTf}$ (1.9 mg, 2.5 µmol, 0.01 eq.), $t$-BuOK (2.8 mg, 25 µmol, 0.1 eq.) and an additive (100 mg) was evacuated and filled with N₂O (100 mL, 1 bar, 8 eq.). THF (1 mL), benzyl alcohol (26 µL, 250 µmol, 1 eq.) and toluene (2 mL) were added. The reaction mixture was stirred overnight at 50 °C then analysed by GC.

Use of stoichiometric amounts of base

A 100 ml Schlenkflask charged with $[\text{Rh(trop}_2\text{NH)(TMIY)}]\text{OTf}$ 8 (1.9 mg, 2.5 µmol, 0.01 eq.) and $t$-BuOK (various amounts) was evacuated and filled with N₂O (100 ml, 1 bar, 8 eq.). THF (1 mL), benzyl alcohol (26 µL, 27 mg, 250 µmol, 1 eq.) and toluene (2 mL) were added. The reaction mixture was stirred overnight at 50 °C then hydrolysed with concentrated hydrochloric acid (0.1 mL, 37%, 1.2 mmol, 4.8 eq.). The organic phase was analysed by GC.
**Blind experiments**

A 100 ml Schlenk flask charged with $t$-BuOK (2.8 mg, 25 µmol, 0.1 eq.) and powdered 4 Å molecular sieves (300 mg) was evacuated and filled with N$_2$O (100 ml, 1 bar, 8 eq.). THF (1 mL), benzyl alcohol (26 µL, 27 mg, 250 µmol, 1 eq.) and toluene (2 mL) were added. The reaction mixture was stirred overnight at 50 °C then hydrolysed with concentrated hydrochloric acid (0.1 mL, 37%, 1.2 mmol, 4.8 eq.). GC-analysis of the organic phase showed no conversion.

A 100 mL Schlenk flask under argon atmosphere was charged with [Rh(trop$_2$NH)(TMIY)]OTf$^8$ (1.9 mg, 2.5 µmol, 0.01 eq.), $t$-BuOK (2.8 mg, 25 µmol, 0.1 eq.) and 4 Å molecular sieves (300 mg). THF (1 mL), benzyl alcohol (26 µL, 27 mg, 250 µmol, 1 eq.) and toluene (2 mL) were added. The reaction mixture was stirred overnight at 50 °C then all solvents were removed under reduced pressure and the residue analysed by $^1$H NMR. Benzyl alcohol was found to be the only component.

**Detection of N$_2$**

A 100 mL Young schlenk charged with [Rh(trop$_2$NH)(TMIY)]OTf$^8$ (1.9 mg, 2.5 µmol, 1 eq.), $t$-BuOK (2.8 mg, 25 µmol, 10 eq.), powdered 4 Å molecular sieves (300 mg), THF (1 mL) and toluene (2 mL) was evacuated then filled with N$_2$O (100 mL, 1 bar, 800 eq.). The schlenk was put in liquid nitrogen to freeze the N$_2$O then filled with H$_2$ (100 mL, 1 bar, 800 eq.). The reaction mixture was warmed to 50 °C and stirred overnight. N$_2$ was detected by analysis of the atmosphere in the Schlenk flask by GC-MS. N$_2$ was also detected in the atmosphere of the reactions run under conditions 1 and 2 (see below).

**7.2.3.3 General procedure for the dehydrogenative coupling of primary alcohols to esters with nitrous oxide as hydrogen acceptor (Condition 1)**

A 250 mL Schlenk flask charged with [Rh(trop$_2$NH)(TMIY)]OTf$^8$ (9.7 mg, 12.5 µmol, 0.01 eq.), $t$-BuOK (14.0 mg, 125 µmol, 0.1 eq.) and powdered 4 Å molecular sieves (1.5 g) was evacuated and filled with N$_2$O (250 mL, 1 bar, 8 eq.). THF (5 mL), alcohol (1.25 mmol, 1 eq.) and toluene (10 mL) were added. The reaction mixture was heated to 50 °C and stirred overnight. All volatiles were removed under reduced pressure and the residue was purified by filtration over a short column with silica gel.

**benzyl benzoate:** From benzyl alcohol. Yield: 130 mg, 98%.

$^1$H-NMR (500.23 MHz, CDCl$_3$, 298 K): $\delta = 5.41$ (s, 2H, CH$_2$), 7.38-7.40 (m, 1H, CH$_{ar}$), 7.41-7.43 (m, 2H, CH$_{ar}$), 7.45 (d, $J = 7.8$ Hz, 1H, CH$_{ar}$), 7.48-7.50 (m, 3H, CH$_{ar}$), 7.60 (dd, $J = 7.6$ Hz, $J = 7.4$ Hz, 1H, CH$_{ar}$), 8.11-8.13 (m, 2H, CH$_{ar}$).

$^{13}$C{$^1$H}-NMR (125.78 MHz, CDCl$_3$, 298 K): $\delta = 67.1$ (s, 1C, CH$_2$), 128.6 (s, 2C, CH$_{ar}$), 128.7 (s, 1C, CH$_{ar}$), 128.8 (s, 2C, CH$_{ar}$), 129.0 (s, 2C, CH$_{ar}$), 130.1 (s, 2C, CH$_{ar}$), 130.6 (s, 1C, C$_{quat}$), 133.4 (s, 1C, CH$_{ar}$), 136.5 (s, 1C, C$_{quat}$), 166.9 (s, 1C, CO$_2$CH$_2$).
4-methoxybenzyl 4-methoxybenzoate: From (4-methoxyphenyl) methanol. Yield: 161 mg, 98% (9:1 mixture of ester and aldehyde).

1H-NMR (400.13 MHz, CDCl₃, 298 K) of 4-methoxybenzyl 4-methoxybenzoate: δ = 3.84 (s, 3H, CH₃), 3.87 (s, 3H, CH₃), 5.29 (s, 2H, CH₂), 6.93 (m, 4H, CH₄), 7.41 (d, 3J_HH = 8.7 Hz, 2H, CH₄), 8.04 (d, 3J_HH = 9.1 Hz, 2H, CH₄).

13C{1H}-NMR (100.16 MHz, CDCl₃, 298 K) of 4-methoxybenzyl 4-methoxybenzoate: δ = 55.7 (s, 1C, CH₃), 55.8 (s, 1C, CH₃), 66.6 (s, 1C, CH₂), 114.0 (s, 2C, CH₃), 114.4 (s, 2C, CH₃), 123.1 (s, 1C, Cqu), 128.8 (s, 1C, Cqu), 130.4 (s, 2C, Cqu), 132.1 (s, 2C, Cqu), 160.0 (s, 1C, Cqu), 163.8 (s, 1C, Cqu), 166.7 (s, 1C, CO₂CH₂).

1H-NMR (400.13 MHz, CDCl₃, 298 K) of 4-methoxybenzaldehyde: δ = 3.91 (s, 3H, CH₃), 7.03 (d, 3J_HH = 8.8 Hz, 2H, CH₃), 7.87 (d, 3J_HH = 8.8 Hz, 2H, CH₃), 9.91 (s, 1H, CHO).

4-(methylthio)benzyl 4-(methylthio)benzoate: From (4-(methylthio)phenyl) methanol. Yield: 165 mg, 88% (50:1 mixture of ester and aldehyde).

1H-NMR (400.13 MHz, CDCl₃, 298 K) of 4-(methylthio)benzyl 4-(methylthio)benzoate: δ = 2.51 (s, 3H, CH₃), 2.53 (s, 3H, CH₃), 5.32 (s, 2H, CH₂), 7.26 (d, 3J_HH = 8.5 Hz, 2H, CH₃), 7.29 (d, 3J_HH = 8.3 Hz, 2H, CH₃), 7.39 (d, 3J_HH = 8.3 Hz, 2H, CH₃), 7.98 (d, 3J_HH = 8.51 Hz, 2H, CH₃).

13C{1H}-NMR (100.16 MHz, CDCl₃, 298 K) of 4-(methylthio)benzyl 4-(methylthio)benzoate: δ = 15.2 (s, 1C, CH₃), 16.2 (s, 1C, CH₃), 66.7 (s, 1C, CH₂), 125.3 (s, 2C, CH₃), 126.6 (s, 1C, Cqu), 127.0 (s, 2C, Cqu), 129.3 (s, 2C, CH₃), 130.4 (s, 2C, CH₃), 133.3 (s, 1C, Cqu), 144.8 (s, 1C, Cqu), 146.1 (s, 1C, Cqu), 166.6 (s, 1C, CO₂CH₂).

1H-NMR (400.13 MHz, CDCl₃, 298 K) of 4-(methylthio) benzaldehyde: δ = 2.56 (s, 3H, CH₃), 7.33-7.35 (m, 2H, CH₃), 7.80 (d, 3J_HH = 8.3 Hz, 2H, CH₃), 9.95 (s, 1H, CHO).

Piperonylic acid piperonyl ester: From piperonyl alcohol. Yield: 164 mg (87%) (25:1 mixture of ester and aldehyde).

1H-NMR (400.13 MHz, CDCl₃, 298 K) of piperonylic acid piperonyl ester: δ = 5.24 (s, 2H, CO₂CH₂), 5.99 (s, 2H, OCH₂O), 6.05 (s, 2H, OCH₂O), 6.82-6.86 (m, 2H, CH₄), 6.94 (m, 2H, CH₄), 7.50 (d, 3J_HH = 1.3 Hz, 1H, CH₄), 7.69 (dd, 3J_HH = 8.1 Hz, 1H, CH₄).

13C{1H}-NMR (100.16 MHz, CDCl₃, 298 K) of piperonylic acid piperonyl ester: δ = 67.0 (s, 1C, CO₂CH₂), 101.6 (s, 1C, OCH₂O), 102.2 (s, 1C, OCH₂O), 108.4 (s, 1C, CH₄), 108.7 (s, 1C, CH₄), 109.4 (s, 1C, CH₄), 110.0 (s, 1C, CH₄), 122.6 (s, 1C, CH₄), 124.5 (s, 1C, Cqu), 125.9 (s, 1C, CH₄), 130.3 (s, 1C, Cqu), 148.0 (s, 1C, Cqu), 148.1 (s, 1C, Cqu), 148.2 (s, 1C, Cqu), 152.1 (s, 1C, Cqu), 166.2 (s, 1C, CO₂CH₂).

1H-NMR (400.13 MHz, CDCl₃, 298 K) of piperonal: δ = 6.10 (s, 2H, OCH₂O), 6.92-6.96 (m, 1H, CH₃), 7.36 (d, 3J_HH = 1.1 Hz, 1H, CH₄), 7.44 (dd, 3J_HH = 7.96 Hz, 1H, CH₄), 9.84 (s, 1H, CHO).
**4-hydroxy-3-methoxybenzaldehyde**: From 4-(hydroxymethyl)-2-methoxyphenol. After the reaction time, the reaction mixture was filtered through celite then all volatiles were removed under reduced pressure. The residue was dissolved in aqueous NaOH (5%) and washed 2 times with small portions of Et₂O. The aqueous phase was acidified with HCl and extracted 3 times with small portions of Et₂O. The combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated. Yield: 102 mg (54%).

1H-NMR (500.23 MHz, CDCl₃, 298 K): δ = 4.00 (s, 3H, OCH₃), 6.31 (br, 1H, OH), 7.07 (d, JHH = 8.5 Hz, 1H, CH₃), 7.44-7.46 (m, 2H, CH₃), 9.85 (s, 1H, CHO).

13C{¹H}-NMR (125.78 MHz, CDCl₃, 298 K): δ = 56.5 (s, 1C, CH₃), 109.2 (s, 1C, CH₂), 114.8 (s, 1C, CH₃), 127.9 (s, 1C, CH₃), 130.3 (s, 1C, Cquat), 147.6 (s, 1C, Cquat), 152.1 (s, 1C, Cquat), 191.3 (s, 1C, CHO).

**octyl octanoate**: From 1-octanol. Yield: 130 mg, 98%.

1H-NMR (400.13 MHz, CDCl₃, 298 K): δ = 0.90 (t, JHH = 6.4 Hz, 6H, CH₃), 1.26-1.36 (m, 18H, CH₂), 1.60-1.65 (m, 4H, CH₂), 2.31 (t, JHH = 7.6 Hz, 2H, CH₂COOCH₂), 4.07 (t, JHH = 6.7 Hz, 2H, CH₂COOCH₂).

13C{¹H}-NMR (100.16 MHz, CDCl₃, 298 K): δ = 14.5 (s, 1C, CH₃), 14.5 (s, 1C, CH₃), 23.0 (s, 1C, CH₂), 23.0 (s, 1C, CH₂), 25.4 (s, 1C, CH₂), 26.3 (s, 1C, CH₂), 29.1 (s, 1C, CH₂), 29.3 (s, 1C, CH₂), 29.5 (s, 1C, CH₂), 29.6 (s, 1C, CH₂), 32.1 (s, 1C, CH₂), 32.2 (s, 1C, CH₂), 34.8 (s, 1C, CH₂), 64.8 (s, 1C, CH₂COOCH₂), 174.4 (s, 1C, CO₂CH₂).

**citronelic acid citronellylester**: From citronellol. Yield: 184 mg (95%).

1H-NMR (400.13 MHz, CDCl₃, 298 K): δ = 0.93 (d, JHH = 6.5 Hz, 3H, CHCH₃), 0.96 (d, JHH = 6.6 Hz, 3H, CHCH₃), 1.17-1.28 (m, 2H, CH₂), 1.32-1.41 (m, 2H, CH₂), 1.42-1.49 (m, 1H, CH), 1.54-1.60 (m, 1H, CH), 1.62 (s, 6H, CCH₃), 1.70 (s, 6H, CCH₃), 1.95-2.04 (m, 6H, CH₂), 2.12 (dd, JHH = 14.5 Hz, JHH = 8.2 Hz, 1H, CHCH₂CO₂), 2.32 (dd, JHH = 14.5 Hz, JHH = 5.9 Hz, 1H, CHCH₂CO₂), 4.09-4.16 (m, 2H, CO₂CH₂), 5.09-5.12 (m, 2H, CH₂). 13C{¹H}-NMR (100.16 MHz, CDCl₃, 298 K): δ = 18.0 (s, 2C, CCH₃) 19.8 (s, 1C, CHCH₃), 20.0 (s, 1C, CHCH₃), 25.8 (s, 1C, CH₂), 25.8 (s, 1C, CH₂), 26.1 (s, 2C, CCH₃), 29.9 (s, 1C, CH), 30.5 (s, 1C, CH), 35.9 (s, 1C, CH₂), 37.2 (s, 1C, CH₂) 37.4 (s, 1C, CH₂) 42.3 (s, 1C, CH₂CO₂), 63.1 (s, 1C, CO₂CH₂), 124.7 (s, 1C, CH₂), 147.6 (s, 1C, Cquat), 152.1 (s, 1C, Cquat), 131.7 (s, 1C, CH₂), 131.9 (s, 1C, CH₂), 173.7 (s, 1C, CO₂CH₂).

**geranyl geranate**: from geraniol. An inseparable mixture of products was obtained. GC-MS analysis showed 8 major products, 4 had M⁺ +1 of 307 and the other 4 had M⁺ +1 of 309.
propyl propionate: A 100 mL Schlenk flask charged with [Rh(trop2NH)(TMIY)]OTf 8 (2.3 mg, 2.9 μmol, 0.01 eq.), t-BuOK (3.3 mg, 29 μmol, 0.1 eq.) and powdered 4 Å molecular sieves (0.3 g) was evacuated and filled with N₂O (100 mL, 1 bar, 8 eq.). THF (1 mL), allyl alcohol (20 μL, 17 mg, 294 μmol, 1 eq.) and toluene (2 mL) were added. The reaction mixture was heated to 50 °C and stirred overnight. Analysis by GC-MS showed that propyl propionate was the only product.

GC-MS (EI, m/z (fragment, abundance)): 117.0 (C₆H₁₃O₂⁺; M⁺ +1, 2%), 75.0 (C₃H₇O₂⁺, 78%), 71.1 (C₄H₇O⁺, 37%), 57.0 (C₃H₅O⁺, 100%).

3-phenylpropyl 3-phenylpropanoate: From cinnamyl alcohol. Yield: 165 mg 99% (93:7 mixture of 3-phenylpropyl 3-phenylpropanoate and 3-phenylpropyl cinnamate).

¹H-NMR (300.13 MHz, CDCl₃, 298 K) of 3-phenylpropyl 3-phenylpropanoate: δ = 3.02 (s, 3H, CH₃), 2.61 (s, 3H, CH₃), 2.07 (tt, 3J_HH = 7.5 Hz, 3J_HH = 6.4 Hz, 2H, CH₂CH₂CH₂Ph), 2.78 (t, 3J_HH = 6.4 Hz, 2H, CH₂CH₂CH₂Ph), 4.26 (t, 3J_HH = 6.4 Hz, 2H, CH₂CH₂CH₂Ph), 6.48 (d, 3J_HH = 16.0 Hz, 1H, CH₂Ph), 7.32 (m, 10H, C₆H₆), 7.71 (d, 3J_HH = 16.0 Hz, 1H, CH₂Ph).

¹⁳C{¹H}-NMR (75.48 MHz, CDCl₃, 298 K): δ = 30.2 (s, 1C, C₆H₅), 31.0 (s, 1C, C₆H₅), 32.1 (s, 1C, C₆H₅), 35.9 (s, 1C, C₆H₅), 63.8 (s, 1C, C₆H₅), 126.0 (s, 1C, C₆H₅), 126.3 (s, 1C, C₆H₅), 128.3 (s, 2C, C₆H₅), 128.4 (s, 2C, C₆H₅), 128.4 (s, 2C, C₆H₅), 140.5 (s, 1C, C₆H₅), 141.2 (s, 1C, C₆H₅), 172.9 (s, 1C, C₆H₅).

acetophenone: A 250 mL Schlenk flask charged with [Rh(trop₂NH)(TMIY)]OTf 8 (5.0 mg, 6.5 μmol, 0.01 eq.), t-BuOK (7.0 mg, 64 μmol, 0.1 eq.) and powdered 4 Å molecular sieves (0.75 g) was evacuated and filled with N₂O (250 mL, 1 bar, 16 eq.). THF (2.5 mL), 1-phenylethanol (78 μL, 0.65 mmol, 1 eq.) and toluene (5 mL) were added. The reaction mixture was heated to 50 °C and stirred overnight. Then all volatiles were removed under reduced pressure and the residue was purified by filtering over a short column with silica gel. Yield: 75 mg, 97% (the same result was also obtained without using 4 Å molecular sieves).

¹H-NMR (300.13 MHz, CDCl₃, 298 K): δ = 2.61 (s, 3H, CH₃), 7.44-7.50 (m, 2H, CH₆), 7.57 (t, 3J_HH = 7.4 Hz, 1H, CH₂Ph), 7.95-7.99 (m, 2H, CH₂Ph).

¹³C{¹H}-NMR (75.48 MHz, CDCl₃, 298 K): δ = 26.6 (s, 1C, C₆H₅), 128.3 (s, 2C, C₆H₅), 128.6 (s, 2C, C₆H₅), 137.2 (s, 1C, C₆H₅), 198.1 (s, 1C, CO).
General procedure for the dehydrogenative coupling of primary alcohols with water to acids using nitrous oxide as hydrogen acceptor (Condition 2)

A 250 mL Schlenkflask charged with [Rh(trop₂NH)(TMIY)]OTf 8 (4.8 mg, 6.25 μmol, 0.01 eq.) and t-BuOK (74 mg, 0.656 mmol, 1.05 eq.) and was evacuated and filled with N₂O (250 mL, 1 bar, 16 eq.). THF (2.5 mL), alcohol (0.625 mmol, 1 eq.) and toluene (5 mL) were added. The reaction mixture was heated to 50 °C and stirred overnight. Then a 0.1 M aqueous NaOH solution was added and the phases separated. The aqueous phase was acidified with HCl (pH < 2) and extracted 3 times with small portions Et₂O. The combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated.

**Benzoic acid:** from benzyl alcohol. Yield: 73 mg, 96%.

1H-NMR (250.13 MHz, CDCl₃, 298 K): δ = 7.52 (dd, 3J_HH = 7.7 Hz, 3J_HH = 7.3 Hz 2H, CH₃), 7.66 (dd, 3J_HH = 7.4 Hz, 3J_HH = 7.3 Hz 1H, CH₃), 8.15 (d, 3J_HH = 7.7 Hz, 2H, CH₃).

13C{1H}-NMR (62.90 MHz, CDCl₃, 298 K): δ = 128.5 (s, 2C, CH₃) 129.3 (s, 1C, C̸) 130.2 (s, 2C, CH₃), 133.8 (s, 1C, CH₃), 172.2 (s, 1C, COOH).

**4-methoxybenzoic acid:** from (4-methoxyphenyl)methanol. After the reaction, a 0.1 M aqueous NaOH solution was added and the phases separated. The aqueous phase was acidified with HCl and extracted 3 times with small portions of CH₂Cl₂. The organic phases were combined, washed with brine and dried with Na₂SO₄. The solvent was removed and the obtained product analysed by NMR. Yield: 90 mg, 98%.

1H-NMR (250.13 MHz, CDCl₃, 298 K): δ = 3.91 (s, 3H, CH₃), 6.98 (d, 3J_HH = 9.0 Hz, 2H, CH₃), 8.10 (d, 3J_HH = 9.0 Hz, 2H, CH₃).

13C{1H}-NMR (62.90 MHz, CDCl₃, 298 K): δ = 55.5 (s, 1C, CH₃), 113.8 (s, 2C, CH₃), 121.9 (s, 1C, C̸), 132.4 (s, 2C, CH₃), 164.1 (s, 1C, C̸), 171.5 (s, 1C, COOH).

**4-(methylthio)benzoic acid:** from (4-(methylthio)phenyl)methanol. Yield: 90 mg, 87%.

1H-NMR (250.13 MHz, CDCl₃, 298 K): δ = 2.56 (s, 3H, CH₃), 7.30 (d, 3J_HH = 8.1 Hz, 2H, CH₃), 7.53 (d, 4J_HH = 1.3 Hz, CH₃), 7.75 (dd, 3J_HH = 8.1 Hz, 4J_HH = 1.3 Hz, CH₃).

13C{1H}-NMR (75.48 MHz, CDCl₃, 298 K): δ = 101.94 (s, 1C, CH₂), 108.11 (s, 1C, CH₃), 109.95 (s, 1C, CH₃), 122.97 (s, 1C, C̸), 126.31 (s, 1C, CH₃), 147.85 (s, 1C, C̸), 152.32 (s, 1C, C̸), 168.8 (s, 1C, COOH).

**Piperonylic acid:** from piperonyl alcohol. Yield: 94 mg, 91%.

1H-NMR (300.13 MHz, CDCl₃, 298 K): δ = 6.09 (s, 2H, CH₂), 6.89 (d, 3J_HH = 8.1 Hz, CH₃), 7.53 (d, 4J_HH = 1.3 Hz, CH₃), 7.75 (dd, 3J_HH = 8.1 Hz, 4J_HH = 1.3 Hz, CH₃).

13C{1H}-NMR (75.48 MHz, CDCl₃, 298 K): δ = 101.94 (s, 1C, CH₂), 108.11 (s, 1C, CH₃), 109.95 (s, 1C, CH₃), 122.97 (s, 1C, C̸), 126.31 (s, 1C, CH₃), 147.85 (s, 1C, C̸), 152.32 (s, 1C, C̸), 168.8 (s, 1C, COOH).
4-hydroxy-3-methoxybenzaldehyde: from 4-(hydroxymethyl)-2-methoxyphenol. After the reaction time all volatiles were removed under reduced pressure. The residue was dissolved in aqueous NaOH (5%) and washed 2 times with small portions of Et₂O. The aqueous phase was acidified with HCl and extracted 3 times with small portions of Et₂O. The combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated. Yield: 78 mg (83%).

$^1$H-NMR (500.23 MHz, CDCl₃, 298 K): $\delta = 3.99$ (s, 3H, OCH₃), 6.35 (br, 1H, OCH₂), 7.07 (d, $^3J_{HH} = 8.5$ Hz, 1H, CH⁻), 7.44-7.46 (m, 2H, CH⁻), 9.85 (s, 1H, CHO).

$^{13}$C{¹H}-NMR (125.78 MHz, CDCl₃, 298 K): $\delta = 56.5$ (s, 1C, OCH₃), 109.2 (s, 1C, CH⁻), 114.8 (s, 1C, CH⁻), 127.9 (s, 1C, CH⁻), 130.3 (s, 1C, CH⁻), 147.6 (s, 1C, CH⁻), 152.1 (s, 1C, CH⁻), 191.3 (s, 1C, CHO).

octanoic acid: from 1-octanol. Yield: 84 mg, 92%.

$^1$H-NMR (200.13 MHz, CDCl₃, 298 K): $\delta = 0.88-0.94$ (m, 3H, CH₃), 1.29-1.36 (m, 8H, CH₂), 1.59-1.75 (m, 2H, CH₂), 2.38 (t, $^3J_{HH} = 7.4$ Hz, CH₂COOH).

$^{13}$C{¹H}-NMR (50.33 MHz, CDCl₃, 298 K): $\delta = 14.0$ (s, 1C, CH₃), 22.6 (s, 1C, CH₂), 24.7 (s, 1C, CH₂), 28.9 (s, 1C, CH₂), 29.0 (s, 1C, CH₂), 31.6 (s, 1C, CH₂), 34.1 (s, 1C, CH₂), 180.2 (s, 1C, COOH).

citronellic acid: from citronellol. Yield: 94 mg, 92%.

$^1$H-NMR (250.13 MHz, CDCl₃, 298 K): $\delta = 1.01$ (d, $^3J_{HH} = 6.5$ Hz, 3H, CH₃), 1.24-1.44 (m, 2H, CH₂), 1.63 (s, 3H, CH₃), 1.71 (s, 3H, CH₃), 1.97-2.03 (m, 3H, CH₂, CH), 2.13-2.19 (m, 1H, CH₂), 2.35-2.43 (m, 1H, CH₂), 5.12 (m, 1H, CH=CMe₂).

$^{13}$C{¹H}-NMR (62.90 MHz, CDCl₃, 298 K): $\delta = 17.6$ (s, 1C, CH₃), 19.6 (s, 1C, CH₂), 25.4 (s, 1C, CH₃), 25.7 (s, 1C, CH₃), 29.8 (s, 1C, CH₂), 36.7 (s, 1C CH₂), 41.5 (s, 1C, CH), 124.2 (s, 1C, CH=CMe₂), 131.7 (s, 1C, CMe₂), 179.8 (s, 1C, COOH).

geranic acid: from geraniol. Yield: 50 mg of a mixture of geranic acid, citronellic acid and other not identified products were obtained.

propionate: A 100 mL Schlenkflask charged with [Rh(trop₂NH)(TMIY)]OTf 8 (2.3 mg, 2.9 μmol, 0.01 eq.) and t-BuOK (35 mg, 310 μmol, 1.05 eq.) was evacuated and filled with N₂O (100 mL, 1 bar, 8 eq.). THF (1 mL), allyl alcohol (20 μL, 17 mg, 294 μmol, 1 eq.) and toluene (2 mL) were added. The reaction mixture was heated to 50 °C and stirred overnight. Then a 0.1 M aqueous NaOH solution was added and the phases separated. Under reduced pressure water was removed from the aqueous phase and the residue analysed by NMR.

$^1$H-NMR (500.23 MHz, CDCl₃, 298 K): $\delta = 0.93$ (t, $^3J_{HH} = 7.6$ Hz, 3H, CH₃), 2.06 (q, $^3J_{HH} = 7.6$ Hz, 2H, CH₂); $^{13}$C{¹H}-NMR (125.78 MHz, CDCl₃, 298 K): $\delta = 10.6$ (s, 1C, CH₃), 31.1 (s, 1C, CH₂), 185.4 (s, 1C, COOH).
**3-phenylpropanoic acid:** from cinnamyl alcohol. Yield: 35 mg, 37%. (7:3 mixture of 3-phenylpropanoic acid and cinnamic acid).

$^1$H-NMR (300.13 MHz, CDCl$_3$, 298 K) of 3-phenylpropanoic acid: $\delta = 2.72$ (t, $^3J_{HH} = 7.8$ Hz, 2H, $CH_2$), 3.00 (t, $^3J_{HH} = 7.8$ Hz, 2H, $CH_2$), 7.23-7.32 (m, 4H, $CH^\text{ar}$), 7.41-7.44 (m, 1H, $CH^\text{ar}$), 8.80 (br, 1H, COO$\text{H}$).

$^{13}$C$\{^1$H$\}$-NMR (75.48 MHz, CDCl$_3$, 298 K) of 3-phenylpropanoic acid: $\delta = 30.6$ (s, 1C, $CH_2$), 35.6 (s, 1C, $CH_2$), 128.3 (s, 2C, $CH^\text{ar}$), 128.6 (s, 2C, $CH^\text{ar}$), 129.0 (s, 1C, $CH^\text{ar}$), 134.1 (s, 1C, $C^\text{quat}$), 178.7 (s, 1C, COOH).

$^1$H-NMR (300.13 MHz, CDCl$_3$, 298 K) of cinnamic acid: $\delta = 6.47$ (d, $^3J_{HH} = 16.0$ Hz, 1H, $CH^\text{olef}$), 7.33 (m, 3H, $CH^\text{ar}$), 7.58 (m, 2H, $CH^\text{ar}$), 7.81 (d, $^3J_{HH} = 16.0$ Hz, 1H, $CH^\text{olef}$), 8.80 (br, 1H, COO$\text{H}$).

$^{13}$C$\{^1$H$\}$-NMR (75.48 MHz, CDCl$_3$, 298 K) of cinnamic acid: $\delta = 117.3$ (s, 1C, $CH^\text{olef}$) 126.4 (s, 2C, $CH^\text{ar}$), 128.4 (s, 2C, $CH^\text{ar}$), 130.8 (s, 1C, $CH^\text{ar}$), 140.2 (s, 1C, $C^\text{quat}$) 147.1 (s, 1C, $CH^\text{olef}$) 172.1 (s, 1C, COOH).

**furan-2-carboxylic acid:** from furan-2-ylmethanol. Yield: 30 mg, 42%.

$^1$H-NMR (400.13 MHz, CDCl$_3$, 298 K): $\delta = 6.60$ (dd, $J = 3.5$ Hz, $J = 1.7$ Hz, 1H, $CH$), 7.37 (d, $J = 3.5$ Hz, 1H, $CH$), 7.68 (d, $J = 1.7$ Hz, 1H, $CH$).

$^{13}$C$\{^1$H$\}$-NMR (100.16 MHz, CDCl$_3$, 298 K): $\delta = 112.7$ (s, 1C, $CH$), 120.5 (s, 1C, $CH$), 142.8 (s, 1C, $C^\text{quat}$) 147.8 (s, 1C, $CH$), 163.7 (s, 1C, COOH).

**acetophenone:** A 250 mL Schlenkflask charged with [Rh(trop$_2$NH)(TMIY)]OTf 8 (5.0 mg, 6.5 µmol, 0.01 eq.) and t-BuOK (76 mg, 0.68 mmol, 1.05 eq.) was evacuated and filled with N$_2$O (250 mL, 1 bar, 16 eq.). THF (2.5 mL), 1-phenylethanol (78 µml, 0.65 mmol, 1 eq.) and toluene (5 mL) were added. The reaction mixture was heated to 50 °C and stirred overnight. Then all volatiles were removed under reduced pressure and the residue was purified by filtering over a short column with silica gel. Yield: 5 mg, 6%.

$^1$H-NMR (300.13 MHz, CDCl$_3$, 298 K) $\delta = 2.61$ (s, 3H, $CH_3$), 7.44-7.50 (m, 2H, $CH^\text{ar}$), 7.57 (tt, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.4$ Hz, 1H, $CH^\text{ar}$), 7.95-7.99 (m, 2H, $CH^\text{ar}$).

$^{13}$C$\{^1$H$\}$-NMR (75.48 MHz, CDCl$_3$, 298 K): $\delta = 26.6$ (s, 1C, $CH_3$), 128.3 (s, 2C, $CH^\text{ar}$), 128.6 (s, 2C, $CH^\text{ar}$), 133.1 (s, 1C, $CH^\text{ar}$), 137.2 (s, 1C, $C^\text{quat}$), 198.1 (s, 1C, CO).
7.2.4 Nitrosobenzene as a hydrogen acceptor in rhodium catalysed dehydrogenation reactions of alcohols: Synthesis of aldehydes and azoxybenzenes

7.2.4.1 Preliminary remarks

Liquid alcohol substrates were distilled from CaH₂; solid substrates were used as received. Nitrosobenzene was provide from Acros and sublimated before use. p-substituted nitrosobenzene derivatives were synthesised according to literature procedure from their commercially available nitro-compounds [162] and sublimated before use. Tetrabutyl ammonium fluoride solution in THF was obtained from Acros and degased prior to use.

7.2.4.2 Optimisation of the catalytic conditions

Preliminary experiment

To a solution of [Rh(trop₂N)(PPh₃)] I (1.9 mg, 2.5 μmol, 0.01 eq.) and benzyl alcohol (26 μL, 27 mg, 0.25 mmol, 1 eq.) in THF (3 mL) nitrosobenzene (40 mg, 0.38 mmol, 1.5 eq.) was added. The solution was stirred overnight and analysed by GC. (Measured retention time: benzaldehyde: 3.66 min; benzyl alcohol: 4.79 min; azoxybenzene: 27.65 min). 74% of the benzyl alcohol was converted to benzaldehyde. The formation of azoxybenzene was confirmed by GC-MS.

GC-MS (EI, m/z (fragment, abundance)): 199 (C₁₂H₁₁N₂O⁺; M⁺ +1, 14%), 198 (C₁₂H₁₀N₂O⁺; M⁺, 34%), 182 (C₁₂H₁₁N₂⁺, 10%), 169 (C₁₁H₈N₂⁺, 100%), 141 (22%), 115 (13%), 105 (C₆H₅N⁺, 23%), 91 (C₄H₄N⁺, 9%), 77 (C₆H₅⁺, 79%).

To a solution of [Rh(trop₂NH)(PPh₃)]OTf 9 (2.3 mg, 2.5 μmol, 0.01 eq.), benzyl alcohol (26 μL, 27 mg, 0.25 mmol, 1 eq.) and nitrosobenzene (59 mg, 0.55 mmol, 2.2 eq.) in THF (3 mL) K₂CO₃ (3.5 mg, 25 μmol, 0.1 eq.) was added. The resulting mixture was stirred overnight then analysed by GC. Benzyl alcohol was fully converted to benzaldehyde.

Blind experiments

To a solution of benzyl alcohol (26 μL, 27 mg, 0.25 mmol, 1 eq.) and nitrosobenzene (59 mg, 0.55 mmol, 2.2 eq.) in THF (3 mL) K₂CO₃ (3.5 mg, 25 μmol, 0.1 eq.) was added. The resulting mixture was stirred overnight then analysed by GC. Only traces (approximately 0.1%) of benzyl alcohol were converted to benzaldehyde.

To a solution of [Rh(trop₂NH)(PPh₃)]OTf 9 (2.3 mg, 2.5 μmol, 0.01 eq.) and benzyl alcohol (26 μL, 27 mg, 0.25 mmol, 1 eq.) in THF (3 mL) nitrosobenzene (59 mg, 0.55 mmol, 2.2 eq.) was added. The resulting mixture was stirred overnight then analysed by GC. 10% of benzyl alcohol was converted to benzaldehyde.
Catalyst evaluation
To a solution of a catalyst (1.3 μmol, 10⁻³ eq.), benzyl alcohol (130 μL, 135 mg, 1.25 mmol, 1 eq.) and nitrosobenzene (295 mg, 2.75 mmol, 2.2 eq.) in THF (2 mL) K₂CO₃ (3.5 mg, 25 μmol, 0.02 eq.) was added. The resulting mixture was stirred overnight then analysed by GC.

Tetrabutyl ammonium fluoride as accelerating additive
To a solution of [Rh(trop₂NH)(PPh₃)]OTf 9 (2.3 mg, 2.5 μmol, 0.01 eq.), benzyl alcohol (26 μL, 27 mg, 0.25 mmol, 1 eq.) and nitrosobenzene (35 mg, 0.33 mmol, 1.3 eq.) in THF (2 mL) K₂CO₃ (6.9 mg, 50 μmol, 0.2 eq.) and TBAF (1.0 M in THF, 25 μL, 25 μmol, 0.1 eq.) were added. The resulting mixture was stirred at room temperature. After 30 seconds the original green colour changed to yellow which indicated that the nitrosobenzene was almost completely consumed. GC analysis revealed that 68% of the benzyl alcohol was converted to benzaldehyde whereas the nitrosobenzene was converted to 97% azoxybenzene and to 3% azobenzene. (Measured retention time: azobenzene: 21.29 min) To formation of azobenzene was confirmed by GC-MS.

GC-MS (EI, m/z (fragment, abundance)): 183 (C₁₂H₁₁N₂⁺; M⁺ +1, 10%), 182 (C₁₂H₁₀N₂⁺; M⁺, 77%), 153 (19%), 152 (52%), 105 (C₆H₅N₂⁺, 36%), 77 (C₆H₅⁺, 100%).

To a solution of [Rh(trop₂NH)(PPh₃)]OTf 9 (1.1 mg, 1.2 μmol, 10⁻³ eq.), benzyl alcohol (125 μL, 130 mg, 1.20 mmol, 1 eq.) and nitrosobenzene (264 mg, 2.46 mmol, 2.05 eq.) in THF (4 mL) K₂CO₃ (8.3 mg, 60 μmol, 0.05 eq.) and TBAF (1.0 M in THF, 12 μL, 12 μmol, 0.1 eq.) were added. The resulting mixture was stirred at room temperature and after 2 hours analysed by GC. 53% of the benzyl alcohol was converted to benzaldehyde whereas the nitrosobenzene was converted in 93% to azoxybenzene and in 1% to azobenzene.

To a solution of [Rh(trop₂NH)(PPh₃)]OTf 9 (2.3 mg, 2.5 μmol, 0.01 eq.), benzyl alcohol (26 μL, 27 mg, 0.25 mmol, 1 eq.) and nitrosobenzene (59 mg, 0.55 mmol, 2.2 eq.) in THF (2 mL) K₂CO₃ (6.9 mg, 50 μmol, 0.2 eq.) and TBAF (1.0 M in THF, 25 μL, 25 μmol, 0.1 eq.) were added. The resulting mixture was stirred at room temperature. After 1 minute the original green colour changed to yellow which indicated that the nitrosobenzene was almost completely consumed. GC analysis revealed that 97% of the benzyl alcohol was converted to benzaldehyde whereas 92% nitrosobenzene was converted to azoxybenzene and 2% to azobenzene.

Blind reaction:
To a solution of benzyl alcohol (26 μL, 27 mg, 0.25 mmol, 1 eq.) and nitrosobenzene (35 mg, 0.33 mmol, 1.3 eq.) in THF (2 mL) K₂CO₃ (6.9 mg, 50 μmol, 0.2 eq.) and TBAF (1.0 M in THF, 25 μL, 25 μmol, 0.1 eq.) were added. The resulting mixture was stirred at room temperature and the reaction was analysed by GC after a certain reaction interval as indicated in Table 38.
Table 38: Measured conversion of benzyl alcohol to benzaldehyde and nitrosobenzene to azoxybenzene and azobenzene using only TBAF as catalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction time</th>
<th>Conversion of benzyl alcohol to benzaldehyde [%]</th>
<th>Conversion of nitrosobenzene to azoxybenzene [%]</th>
<th>Conversion of nitrosobenzene to azobenzene [%]</th>
</tr>
</thead>
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<td>1</td>
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<td>2</td>
<td>2</td>
<td>0.2</td>
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<tr>
<td>2</td>
<td>15 min</td>
<td>5</td>
<td>14</td>
<td>1</td>
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<td>1</td>
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<tr>
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<td>20 h</td>
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<td>2</td>
</tr>
</tbody>
</table>

7.2.4.3 Dehydrogenation of alcohols with nitrosobenzene as hydrogen acceptor

benzaldehyde: To a solution of benzyl alcohol (0.26 mL, 270 mg, 2.50 mmol, 1 eq.) and nitrosobenzene (549 mg, 5.12 mmol, 2.05 eq.) in THF (5 mL) [Rh(trop2NH)(PPh3)]OTf 9 (2.3 mg, 2.5 μmol, 10⁻³ eq.) and K₂CO₃ (17.3 mg, 125 μmol, 0.05 eq.) were added. The resulting mixture was stirred overnight at room temperature then all volatiles were removed under high vacuum at 100 °C and collected in a cooling trap. The trapped chemicals proved to be THF and benzaldehyde. The later was obtained by removing the THF under reduced pressure. Yield: 242 mg, 91%.

1H-NMR (500.23 MHz, CDCl₃, 298 K): δ = 7.55 (dd, 3JHH = 8.1 Hz, 3JHH = 7.7 Hz, 2H, CHp), 7.65 (tt, 4JHH = 7.7 Hz, 4JHH = 1.2 Hz, 1H, CHp), 7.90 (dd, 3JHH = 8.1 Hz, 4JHH = 1.2 Hz, 2H, CHp), 10.04 (s, 1H, CHO).

13C{1H}-NMR (125.78 MHz, CDCl₃, 298 K): δ = 129.4 (s, 2C, CHar), 130.1 (s, 2C, CHar), 134.9 (s, 1C, CHar), 136.8 (s, 1C, Cquat), 192.8 (s, 1C, CHO).

4-methoxybenzaldehyde: To a solution of (4-methoxyphenyl) methanol (0.31 mL, 345 mg, 2.50 mmol, 1 eq.) and nitrosobenzene (549 mg, 5.12 mmol, 2.05 eq.) in THF (5 mL) [Rh(trop2NH)(PPh₃)]OTf 9 (2.3 mg, 2.5 μmol, 10⁻³ eq.) and K₂CO₃ (17.3 mg, 125 μmol, 0.05 eq.) were added. The resulting mixture was stirred overnight at room temperature then the solvent was removed under reduced pressure and the residue purified by column chromatography (petrol ether 30/50:ethyl acetate 10:1). Yield: 326 mg, 96%.

1H-NMR (300.13 MHz, CDCl₃, 298 K): δ = 3.90 (s, 3H, OCH₃), 7.01 (d, 3JHH = 8.8 Hz, 2H, CHp), 7.85 (d, 3JHH = 8.8 Hz, 2H, CHp), 9.89 (s, 1H, CHO).

13C{1H}-NMR (75.48 MHz, CDCl₃, 298 K): δ = 55.6 (s, 1C, OCH₃), 114.3 (s, 2C, CHar), 130.0 (s, 1C, Cquat), 132.0 (s, 2C, CHar), 164.6 (s, 1C, Cquat), 190.8 (s, 1C, CHO).
4-nitrobenzaldehyde: To a solution of (4-nitrophenyl) methanol (183 mg, 1.25 mmol, 1 eq.) and nitrosobenzene (262 mg, 2.56 mmol, 2.05 eq.) in THF (2.5 mL) [Rh(trop2NH)(PPh3)]OTf 9 (5.5 mg, 6.0 μmol, 5·10⁻³ eq.) and K₂CO₃ (8.2 mg, 60 μmol, 0.05 eq.) were added. The resulting mixture was stirred overnight at room temperature then the solvent was removed under reduced pressure and the residue purified by column chromatography (petrol ether 30/50:ethyl acetate 30:1). Yield: 41 mg, 23%.

1H-NMR (500.23 MHz, CDCl₃, 298 K): δ = 8.10 (d, 3J_HH = 8.7 Hz, 2H, CH₉), 8.43 (d, 3J_HH = 8.7 Hz, 2H, CH₉), 10.19 (s, 1H, CHO).

13C{1H}-NMR (125.78 MHz, CDCl₃, 298 K): δ = 124.7 (s, 2C, CH₉), 130.9 (s, 2C, CH₉), 140.5 (s, 1C, C²⁰¹), 151.0 (s, 1C, C²⁰¹), 190.7 (s, 1 C, CHO).

3,4-(methylenedioxy)-benzaldehyde: To a solution of piperonyl alcohol (380 mg, 2.50 mmol, 1 eq.) and nitrosobenzene (549 mg, 5.12 mmol, 2.05 eq.) in THF (5 mL) [Rh(trop2NH)(PPh₃)]OTf 9 (2.3 mg, 2.5 μmol, 10⁻³ eq.) and K₂CO₃ (17.3 mg, 125 μmol, 0.05 eq.) were added. The resulting mixture was stirred overnight at room temperature then the solvent was removed under reduced pressure and the residue purified by column chromatography (petrol ether 30/50:ethyl acetate 10:1). Yield: 348 mg, 93%.

1H-NMR (300.13 MHz, CDCl₃, 298 K): δ = 6.07 (s, 2H, CH₂), 6.93 (d, 3J_HH = 8.0 Hz, 1H, CH₉), 7.33 (d, 4J_HH = 1.4 Hz, 1H, CH₉), 7.41 (dd, 3J_HH = 8.0 Hz, 4J_HH = 1.7 Hz, 1H, CH₉), 9.81 (s, 1H, CHO).

13C{1H}-NMR (75.48 MHz, CDCl₃, 298 K): δ = 102.1 (s, 1C, CH₂), 106.9 (s, 1C, CH₉), 108.3 (s, 1C, CH₉), 128.6 (s, 1C, CH₉), 131.9 (s, 1C, C²⁰¹), 148.7 (s, 1C, C²⁰¹), 153.1 (s, 1C, C²⁰¹), 190.3 (s, 1C, CHO).

4-(methylthio)benzaldehyde: To a solution of (4-(methylthio)phenyl)methanol (193 mg, 1.25 mmol, 1 eq.) and nitrosobenzene (262 mg, 2.56 mmol, 2.05 eq.) in THF (2.5 mL) [Rh(trop2NH)(PPh₃)]OTf 9 (5.5 mg, 6.0 μmol, 5·10⁻³ eq.) and K₂CO₃ (8.2 mg, 60 μmol, 0.05 eq.) were added. The resulting mixture was stirred overnight at room temperature then the solvent was removed under reduced pressure and the residue purified by column chromatography (petrol ether 30/50:ethyl acetate 10:1). Yield: 183 mg, 97%.

1H-NMR (300.13 MHz, CDCl₃, 298 K): δ = 2.54 (s, 3H, SCH₃), 7.33 (d, 3J_HH = 8.4 Hz, 2H, CH₉), 7.78 (d, 3J_HH = 8.4 Hz, 2H, CH₉), 9.93 (s, 1H, CHO).

13C{1H}-NMR (75.48 MHz, CDCl₃, 298 K): δ = 14.7 (s, 1C, SCH₃), 125.2 (s, 2C, CH₉), 130.0 (s, 2C, CH₉), 133.0 (s, 1C, C²⁰¹), 147.9 (s, 1C, C²⁰¹), 191.2 (s, 1C, CHO).
4-methoxycarbonylbenzaldehyde: To a solution of methyl 4-(hydroxymethyl)benzoate (208 mg, 1.25 mmol, 1 eq.) and nitrosobenzene (262 mg, 2.56 mmol, 2.05 eq.) in THF (2.5 mL) [Rh(tropol2NH)(PPh3)]OTf 9 (5.5 mg, 6.0 μmol, 5·10⁻³ eq.) and K₂CO₃ (8.2 mg, 60 μmol, 0.05 eq.) were added. The resulting mixture was stirred overnight at room temperature then the solvent was removed under reduced pressure and the residue purified by column chromatography (petrol ether 30/50:ethyl acetate 9:1). Yield: 76 mg, 37%.

1H-NMR (500.23 MHz, CDCl₃, 298 K): δ = 3.99 (s, 3H, CO₂C₃H₃), 7.98 (d, 3JHH = 8.5 Hz, 2H, CH₃), 8.22 (d, 3JHH = 8.5 Hz, 2H, CH₃), 10.13 (s, 1H, CHO).

13C{1H}-NMR (125.78 MHz, CDCl₃, 298 K): δ = 53.0 (s, 1C, CO₂C₃H₃), 129.9 (s, 2C, CH₃), 130.6 (s, 2C, CH₃), 135.5 (s, 1C, Cquat), 139.6 (s, 1C, Cquat), 166.5 (s, 1C, CO₂C₃H₃), 192.0 (s, 1C, CHO).

2-furan-carboxaldehyde: To a solution of furan-2-ylmethanol (0.11 mL, 123 mg, 1.25 mmol, 1 eq.) and nitrosobenzene (262 mg, 2.56 mmol, 2.05 eq.) in THF (2.5 mL) [Rh(tropol2NH)(PPh3)]OTf 9 (5.5 mg, 6.0 μmol, 5·10⁻³ eq.) and K₂CO₃ (8.2 mg, 60 μmol, 0.05 eq.) were added. The resulting mixture was stirred overnight at room temperature then the solvent was removed under reduced pressure and the residue purified by column chromatography (petrol ether 30/50:ethyl acetate 30:1). Yield: 63 mg, 52%.

1H-NMR (300.13 MHz, CDCl₃, 298 K): δ = 6.61 (dd, 3JHH = 3.6 Hz, 3JHH = 1.7 Hz, 1H, C₃H), 7.26 (dd, 3JHH = 3.64, 4JHH = 0.8 Hz, 1H, CH), 7.70 (m, 1H, C₃H), 9.67 (s, 1H, CHO).

13C{1H}-NMR (125.78 MHz, CDCl₃, 298 K): δ = 112.6 (s, 1C, CH), 120.9 (s, 1C, CH), 148.0 (s, 1C, CH), 153.0 (s, 1C, Cquat), 177.9 (s, 1C, CHO).

4-hydroxy-3-methoxybenzaldehyde: To a solution of 4-(hydroxymethyl)-2-methoxyphenol (385 mg, 2.50 mmol, 1 eq.) and nitrosobenzene (549 mg, 5.12 mmol, 2.05 eq.) in THF (5 mL) [Rh(tropol2NH)(PPh₃)]OTf 9 (2.3 mg, 2.5 μmol, 10⁻³ eq.) and K₂CO₃ (17.3 mg, 125 μmol, 0.05 eq.) were added. The resulting mixture was stirred overnight at room temperature then all volatiles were removed under reduced pressure. The residue was dissolved in aqueous NaOH (5%) and washed 2 times with small portions of Et₂O. The aqueous phase was acidified with HCl and extracted 3 times with small portions of Et₂O. The combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated. Yield: 353 mg, 93%.

1H-NMR (500.23 MHz, CDCl₃, 298 K): δ = 3.97 (s, 3H, OCH₃), 6.50 (s, br, 1H, OH), 7.06 (d, 3JHH = 8.5 Hz, 1H, CH), 7.44-7.45 (m, 2H, CH₃), 9.84 (s, 1H, CHO).

13C{1H}-NMR (125.78 MHz, CDCl₃, 298 K): δ = 147.6 (s, 1C, CH), 152.2 (s, 1C, CH), 191.4 (s, 1C, CHO).

octanal: To a solution of 1-octanol (0.20 mL, 162 mg, 1.25 mmol, 1 eq.) and nitrosobenzene (262 mg, 2.56 mmol, 2.05 eq.) in THF (2.5 mL) [Rh(tropol2NH)(PPh₃)]OTf 9 (5.5 mg, 6.0 μmol, 5·10⁻³ eq.) and K₂CO₃ (8.2 mg, 60 μmol, 0.05 eq.) were added. The resulting mixture was stirred overnight at room temperature then analysed by GC. Conversion: 5%, 95% of not reacted 1-octanol was found.

31P{1H}-NMR (101.25 MHz, [H8]THF, 298 K) δ = 29.3 (s, P(O)Ph₃).
geraniol: To a solution of geraniol (0.22 mL, 193 mg, 1.25 mmol, 1 eq.) and nitrosobenzene (262 mg, 2.56 mmol, 2.05 eq.) in THF (2.5 mL) [Rh(trop$_2$NH)(PPh$_3$)]OTf 9 (5.5 mg, 6.0 μmol, 5·10$^{-3}$ eq.) and K$_2$CO$_3$ (8.2 mg, 60 μmol, 0.05 eq.) were added. The resulting mixture was stirred overnight at room temperature then the solvent was removed under reduced pressure and the residue purified by column chromatography (petrol ether 30/50:ethyl acetate 30:1). Yield: 184 mg, 97%.

$^1$H-NMR (500.23 MHz, CDCl$_3$, 298 K): δ = 1.62 (s, 3H, CH$_3$), 1.69 (s, 3H, CH$_3$), 2.18 (s, 3H, CH$_3$), 2.20-2.25 (m, 4H, CH$_2$), 5.08 (t, $^3$J$_{HH}$ = 6.7 Hz, 1H, CH$_2^{olef}$), 5.89 (d, $^3$J$_{HH}$ = 8.0 Hz, 1H, CH$_2^{olef}$), 10.00 (d, $^3$J$_{HH}$ = 8.0 Hz, 1H, CHO).

$^{13}$C{1H}-NMR (125.78 MHz, CDCl$_3$, 298 K): δ = 18.0 (s, 1C, CH$_3$), 18.1 (s, 1C, CH$_3$), 26.0 (s, 1C, CH$_3$), 26.1 (s, 1C, CH$_2$), 41.0 (s, 1C, CH$_2$), 123.0 (s, 1C, CH$_2^{olef}$), 127.8 (s, 1C, CH$_2^{olef}$), 133.3 (s, 1C, C$_{olef}$), 164.2 (s, 1C, C$_{olef}$), 191.7 (s, 1C, CHO).

citronellol: To a solution of citronellol (0.23 mL, 196 mg, 1.25 mmol, 1 eq.) and nitrosobenzene (262 mg, 2.56 mmol, 2.05 eq.) in THF (2.5 mL) [Rh(trop$_2$NH)(PPh$_3$)]OTf 9 (5.5 mg, 6.0 μmol, 5·10$^{-3}$ eq.) and K$_2$CO$_3$ (8.2 mg, 60 μmol, 0.05 eq.) were added. The resulting mixture was stirred overnight at room temperature then analysed by GC. Conversion: 11%.

acetophenone: To a solution of 1-phenylethanol (0.15 mL, 153 mg, 1.25 mmol, 1 eq.) and nitrosobenzene (262 mg, 2.56 mmol, 2.05 eq.) in THF (2.5 mL) [Rh(trop$_2$NH)(PPh$_3$)]OTf 9 (5.5 mg, 6.0 μmol, 5·10$^{-3}$ eq.) and t-BuOK (6.8 mg, 60 μmol, 0.05 eq.) were added. The resulting mixture was stirred overnight at room temperature then the solvent was removed under reduced pressure and the residue purified by column chromatography (petrol ether 30/50:ethyl acetate 50:1, then 10:1). Yield: 92 mg, 61%.

$^1$H-NMR (300.13 MHz, CDCl$_3$, 298 K): δ = 2.61 (s, 3H, CH$_3$), 7.44-7.50 (m, 2H, CH$_2^{ar}$), 7.57 (tt, $^3$J$_{HH}$ = 7.4 Hz, $^4$J$_{HH}$ = 1.4 Hz, 1H, CH$_2^{ar}$), 7.95-7.99 (m, 2H, CH$_2^{ar}$).

$^{13}$C{1H}-NMR (125.78 MHz, CDCl$_3$, 298 K): δ = 26.6 (s, 1C, CH$_3$), 128.3 (s, 2C, CH$_2^{ar}$), 128.6 (s, 2C, CH$_2^{ar}$), 133.1 (s, 1C, CH$_3^{ar}$), 137.2 (s, 1C, C$_{olef}^{ar}$), 198.1 (s, 1C, CO).

7.2.4.4 General procedure for the transferhydrogenative reductive dimerization of nitrosobenzene derivatives to the corresponding azoxybenzene-compounds

To a solution of a nitrosobenzene derivative (2.19 mmol, 1 eq.) and [Rh(trop$_2$NH)(PPh$_3$)]OTf 9 (2.0 mg, 2.2 μmol, 10$^{-3}$ eq.) in ethanol (2 mL) and THF (1 mL) K$_2$CO$_3$ (15 mg, 0.11 mmol, 0.05 eq.) was added. The resulting mixture was stirred for 2 hours then all volatiles were removed and the residue was purified by column chromatography.
4,4'-dimethyl-azoxybenzene: from 1-methyl-4-nitrosobenzene. Yield: 240 mg, 95%.

1H-NMR (500.23 MHz, CDCl3, 298 K): δ = 2.45 (s, 3H, CH3), 2.48 (s, 3H, CH3), 7.31-7.33 (m, 4H, CHar), 8.15 (d, 3JHH = 8.5 Hz, 2H, CHar), 8.22 (d, 3JHH = 8.5 Hz, 2H, CHar).

13C{1H}-NMR (125.78 MHz, CDCl3, 298 K): δ = 21.7 (s, 1C, CH3), 21.9 (s, 1C, CH3), 122.6 (s, 2C, CHar), 126.1 (s, 2C, CHar), 129.7 (s, 4C, CHar), 140.4 (s, 1C, Cquat), 142.3 (s, 2C, Cquat), 146.7 (s, 1C, Cquat).

4,4'-difluoroazoxybenzene: from 4-fluoro-nitrosobenzene. Yield: 248 mg, 98%.

1H-NMR (300.13 MHz, CDCl3, 298 K): δ = 7.14-7.24 (m, 4H, CHar), 8.24-8.37 (m, 4H, CHar).

13C{1H}-NMR (75.48 MHz, CDCl3, 298 K): δ = 115.5 (d, 3JCF = 3.5 Hz, 2C, CHar), 115.8 (d, 2JCF = 4.4 Hz, 2C, CHar), 124.5 (d, 3JCF = 9.3 Hz, 2C, CHar), 128.0 (d, 3JCF = 8.5 Hz, 2C, CHar), 140.3 (d, 4JCF = 3.2 Hz, 1C, Cquat), 144.3 (br, 1C, Cquat), 162.6 (d, 1JCF = 252.5 Hz, 1C, Cquat), 164.5 (d, 1JCF = 252.9 Hz, 1C, Cquat).

19F-NMR (188.31 MHz, CDCl3, 298 K): δ = -108.62 - -108.48 (m, 1F), -108.06 - -107.92 (m, 1F).

4,4'-dichloro-azoxybenzene: To a solution of a 4-chloro-nitrosobenzene (310 mg 2.19 mmol, 1 eq.) and [Rh(trop2NH)(PPh3)]OTf 9 (2.0 mg, 2.2 µmol, 10⁻³ eq.) in ethanol (6 ml) and THF (6 ml) K2CO3 (15 mg, 110 µmol, 0.05 eq.) was added. The resulting mixture was stirred for 4 hours then all volatiles were removed and the residue was purified by column chromatography. Yield: 273 mg, 93%.

1H-NMR (300.13 MHz, CDCl3, 298 K): δ = 7.46 (d, 3JHH = 9.3 Hz, 2H, CHar), 7.50 (d, 3JHH = 9.3 Hz, 2H, CHar), 8.17 (d, 3JHH = 8.9 Hz, 2H CHar), 8.27 (d, 3JHH = 8.9 Hz, 2H, CHar).

13C{1H}-NMR (75.48 MHz, CDCl3, 298 K): δ = 123.7 (s, 2C, CHar), 127.1 (s, 2C, CHar), 129.0 (s, 2C, CHar), 135.3 (s, 1C, Cquat), 138.1 (s, 1C, Cquat), 142.2 (s, 1C, Cquat), 146.6 (s, 1C, Cquat).
4,4'-azoxybenzoic acid dimethyl ester: To a solution of a methyl 4-nitrosobenzoate (190 mg 1.15 mmol, 1 eq.) and [Rh(trop₂NH)(PPh₃)]OTf 9 (1.1 mg, 1.2 μmol, 10⁻³ eq.) in ethanol (4 ml) and THF (4 ml) K₂CO₃ (8.0 mg, 58 μmol, 0.05 eq.) was added. The resulting mixture was stirred for 4 hours then all volatiles were removed and the residue was purified by column chromatography. Yield: 124 mg, 69%.

¹H-NMR (250.13 MHz, CDCl₃, 298 K): δ = 1H 3.97 (s, 3H, CH₃), 3.99 (s, 3H, CH₃), 8.18-8.19 (m, 4H, CH₅), 8.21-8.23 (m, 2H, CH₅), 8.39-8.42 (m, 2H, CH₅).

¹³C{¹H}-NMR (62.90 MHz, CDCl₃, 298 K): δ = 52.3 (s, 1C, CH₃), 52.6 (s, 1C, CH₃), 122.6 (s, 2C, CH₅), 125.3 (s, 2C, CH₅), 130.2 (s, 2C, CH₅), 130.4 (s, 2C, CH₅), 130.7 (s, 1C, C₄₅), 133.3 (s, 1C, C₄₅), 147.0 (s, 1C, C₄₅), 150.9 (s, 1C, C₄₅), 165.7 (s, 1C, CO₂Me), 166.2 (s, 1C, CO₂Me).
7.3 Miscellaneous experiments

7.3.1 Determination of the equilibrium constant of \([\text{Rh(eq-OH)}(\text{trop}_{2}\text{NH})(\text{PPh}_3)]\) 63 in [D8]THF at 213 K

The following samples were prepared and analysed by \(^{31}\text{P}\{^{1}\text{H}\}\) NMR (202.50 MHz, [D8]THF, 213 K):

1. \([\text{Rh(trop}_2\text{N})(\text{PPh}_3)] 1\) (10.0 mg) (natural line width, \(\nu_\frac{1}{2} = 3.2\) Hz);
2. \([\text{Rh(eq-OH)}(\text{trop}_2\text{NH})(\text{PPh}_3)]\) 63 (10.0 mg) in presence of excess water (approximately 100 eq.). (natural line width, \(\nu_\frac{1}{2} = 6.7\) Hz);
3. \([\text{Rh(eq-OH)}(\text{trop}_2\text{NH})(\text{PPh}_3)]\) 63 (10.0 mg) (natural line width, \(\nu_\frac{1}{2} = 6.7\) Hz);
4. \([\text{Rh(eq-OH)}(\text{trop}_2\text{NH})(\text{PPh}_3)]\) 63 (7.0 mg) and \([\text{Rh(trop}_2\text{N})(\text{PPh}_3)] 1\) (3.0 mg) (natural line width, \(\nu_\frac{1}{2} = 4.7\) Hz).

7.3.2 Reactions of the hydroxide-complex 63 with alcohols and aldehydes

7.3.2.1 Reaction with acetaldehyde

To a solution of \([\text{Rh(eq-OH)}(\text{trop}_2\text{NH})(\text{PPh}_3)]\) 63 (10 mg, 0.013 mmol) in [D8]THF (0.5 ml) was added a drop of acetaldehyde (about 10 eq. determined by \(^1\text{H}\)-NMR). The greenish solution turned yellow immediately.

\(^1\text{H}\)-NMR (500.23 MHz, [D8]THF, 298 K) \(\delta = 1.28\) (s, 3H, \(\text{CH}_3\), 7), 1.46 (t, \(3\nu_{\text{HH}} = 7.0\) Hz, 3H, \(\text{CH}_3\text{CH}_2\text{OH}\)), 3.55 (t, \(3\nu_{\text{HH}} = 7.0\) Hz, 2H, \(\text{CH}_3\text{CH}_2\text{OH}\)), 4.80-4.82 (m, 4H, \(\text{CH}^\text{olefin}, \text{CH}^\text{Phenyl}, 7\)), 4.88-4.90 (m, 2H, \(\text{CH}^\text{olefin}, 7\)), 6.54 (d, \(J = 7.6\) Hz, 2H, \(\text{CH}^\text{ar}, 7\)), 6.63 (t, \(J = 7.5\) Hz, 2H, \(\text{CH}^\text{ar}, 7\)), 6.77 (t, \(J = 7.5\) Hz, 2H, \(\text{CH}^\text{ar}, 7\)), 6.83 (d, \(J = 7.4\) Hz, 2H, \(\text{CH}^\text{ar}, 7\)), 7.02 (t, \(J = 7.4\) Hz, 2H, \(\text{CH}^\text{ar}, 7\)), 7.08 (t, \(J = 7.4\) Hz, 2H, \(\text{CH}^\text{ar}, 7\)), 7.14-7.17 (m, 4H, \(\text{CH}^\text{ar}, 7\)), 7.52-7.60 (m, 9H, \(\text{CH}^\text{ar}, 7\)), 8.01 (t, \(J = 8.0\) Hz, 6H, \(\text{CH}^\text{ar}, 7\)), 11.09 (d, \(J = 6.2\) Hz, 1H, \(\text{NH}, 7\)); The ratio of ethanol and the acetato complex 7 was determined to be 1:1 by integration.

\(^{31}\text{P}\{^{1}\text{H}\}\)-NMR (202.50 MHz, [D8]THF, 298 K) \(\delta = 38.9\) (d, \(1\nu_{\text{RhP}} = 131.2\) Hz, \([\text{Rh(OAc)}(\text{trop}_2\text{NH})(\text{PPh}_3)] 7\)).
7.3.2.2 Reaction with ethanol

To a solution of \([\text{Rh(eq-OH)(trop}_2\text{NH}(\text{PPh}_3)] \text{63 (10 mg, 0.013 mmol, 1 eq.) in [D8]THF (0.5 ml)} was added ethanol (3.7 µl, 0.13 mmol, 10 eq.). The greenish solution turned yellow immediately.

\[^1H\text{-NMR} \ (500.23 \text{ MHz}, \ [\text{D8}]\text{THF}, \ 298 \text{ K}) \ \delta = 1.28 \ (s, \ 3H, CH_3, \ 7), \ 3.54-3.56 \ (m, \ 2H, CH^\text{olefin}, \ 2), \ 3.97 \ (dd, \ J = 9.2 \text{ Hz, } J = 4.6 \text{ Hz, } CH^\text{olefin}, \ 2), \ 4.54 \ (d, \ J = 8.0 \text{ Hz, } CH^\text{benzyl}, \ 2), \ 4.80-4.81 \ (m, \ 4H, CH^\text{olefin}, CH^\text{benzyl}, \ 7), \ 4.88-4.90 \ (m, \ 2H, CH^\text{olefin}, \ 7), \ 5.11 \ (d, \ J = 4.4 \text{ Hz, NH, } 2), \ 11.06 \ (d, \ J = 6.2 \text{ Hz, 1H, NH, } 7); \ The \ ratio \ of \ amine \ hydride \ complex \ 2 \ and \ the \ acetato \ complex \ 7 \ was \ determined \ to \ be \ 2:1 \ by \ integration. \ Note \ that \ the \ [^1H\text{-NMR} \ spectrum \ (at \ 500 \text{ MHz}) \ does \ not \ show \ any \ traces \ of \ other \ products \ like \ MeCHO, \ MeCOOH, \ and/or \ H_2.\]

7.3.2.3 Reaction with octanal

To a solution of \([\text{Rh(eq-OH)(trop}_2\text{NH}(\text{PPh}_3)] \text{63 (5.0 mg, 0.013 mmol, 1 eq.) in THF (0.6 ml)} was added octanal (20 µL, 17 mg, 0.13 mmol, 10 eq.). The greenish solution turned yellow immediately.

\[^{31}P\{^1H\}\text{-NMR} \ (121.49 \text{ MHz}, \ [\text{H8}]\text{THF}, \ 298 \text{ K}) \ \delta = 36.7 \ (d, \ J_{RHP} = 131.6 \text{ Hz, } \text{[Rh(C}_{8}H_{15}O_2)(trop}_2\text{NH}(\text{PPh}_3)]); \ GC: \ 4.19 \ (relative \ intensity: \ 100\%, \ octanal), \ 5.38 \ (relative \ intensity: \ 18\%, \ 1-octanol), \ 8.04 \ (relative \ intensity: \ 7\%, \ octanoic \ acid).\]

7.3.2.4 Reactions with 1-octanol

To a solution of \([\text{Rh(eq-OH)(trop}_2\text{NH}(\text{PPh}_3)] \text{63 (5.0 mg, 0.013 mmol, 1 eq.) in THF (0.6 ml)} was added 1-octanol (21 µL, 17 mg, 0.13 mmol, 10 eq.). The greenish solution turned yellow immediately.

\[^{31}P\{^1H\}\text{-NMR} \ (121.49 \text{ MHz}, \ [\text{H8}]\text{THF}, \ 298 \text{ K}) \ \delta = 37.7 \ (d, \ J_{RHP} = 131.5 \text{ Hz, } \text{[Rh(C}_{8}H_{15}O_2)(trop}_2\text{NH}(\text{PPh}_3)], \ 62.8 \ (d, \ J_{RHP} = 145.7 \text{ Hz, } \text{[RhH(trop}_2\text{NH}(\text{PPh}_3)] \ 2); \ ratio \ approximately \ 1:2 \ GC: \ 4.12 \ (relative \ intensity: \ 0.7\%, \ octanal), \ 5.40 \ (relative \ intensity: \ 100\%, \ 1-octanol).\]

7.3.3 Miscellaneous reactions for chapter 4

7.3.3.1 Detection of the formed dimethyl sulfone

Benzyl alcohol (0.14 mL, 140 mg, 1.29 mmol, 1 eq.) was added to a solution of \([\text{Rh(trop}_2\text{NH)(TMiY)}\text{OTf} \text{8 (10 mg, 0.013 mmol, 0.01 eq.) and NaOH (62 mg, 1.55 mmol, 1.2 eq.) in DMSO (8.3 mL) and water (4.2 mL). The resulting solution was stirred overnight then all volatiles were removed and the residue analysed by NMR.

\[^1H\text{-NMR} \ (300.13 \text{ MHz, D}_2\text{O, 298 K}) \ : \ \delta = 3.06 \ (s, \ 6H).\]

\[^{13}C\{^1H\}\text{-NMR} \ (75.48 \text{ MHz, D}_2\text{O, 298 K}) \ : \ \delta = 41.6 \ (s, \ 2C).\]
7.3.3.2 Cannizaro type disproportion of octanal

Octanal (20 μL, 16 mg, 0.13 mmol, 1 eq.) was added to a mixture of [Rh(trop2NH)(TMIY)]OTf 8 (1.0 mg, 1.3 μmol, 0.01 eq.) and NaOH (7.0 mg, 0.15 mmol, 1.2 eq.) in [D6]DMSO (0.5 mL), D2O (0.5 mL) and [D8THF](0.1 ml) in a NMR-tube under air. The reaction mixture was placed in an ultrasonic bath for 5 minutes then analysed by ¹H-NMR.

¹H-NMR (250.13 MHz, [D6]DMSO, D 2O, [D8]THF, 298 K): δ = 1.93 (t, 3 J_HH = 7.5 Hz, 2H, C6H13COONa), 2.04 (t, 3 J_HH = 8.0 Hz, 2H, C6H13CH2COOC8H17), 3.28 (t, 3 J_HH = 6.4 Hz, 2H, C7H15CH2OD), 3.36 (t, 3 J_HH = 6.6 Hz, 2H, C7H15CH2OH), 3.81 (t, 3 J_HH = 6.6 Hz, 2H, C7H15COOC8H17C7H15).

The original aldehyde could not be found anymore. By integration of the above mentioned signals the conversion of octanal to the three specified products was determined: sodium octanoate 53%, 1-octanol 42%, octyl octanoate 5%.

7.3.3.3 NMR-Experiment: Hydrogen- and oxygen-driven interconversion between the amide-complex 95 and the hydride-complex 94

A sample of the hydride complex 94 was prepared in situ in a young-NMR tube in [D6]DMSO. [Rh(trop2NH)(TMIY)]OTf (10 mg, 0.013 mmol, 1 eq.) dissolved in [D6]DMSO (0.5 mL) were deprotonated by addition of LiHDM (2.3 mg, 0.014 mmol, 1.05 eq.). The resulting dark green solution was frozen in liquid nitrogen the NMR tube was evacuated and was repeatedly filled with 2 bar of dihydrogen gas and shacked until a yellow solution was obtained. The young-NMR-tube was evacuated and opened to air. The ¹H-NMR showed a 3:2 mixture of the amide-complex 95 and amine-complex 8. (8 was probably formed by protonation of 95 by water, which was formed as by-product in the reaction.) The hydride complex 94 was no longer present. The air was removed from the NMR-tube by three pump-freeze-thaw cycles then the NMR-tube was refilled with 2 bar dihydrogen gas. The ¹H-NMR showed the reformation of the hydride complex 94. After evacuation and floating with air the hydride complex 94 disappeared again.

7.3.4 Miscellaneous reactions for chapter 6

To a solution of benzyl alcohol (26 μL, 27 mg, 0.25 mmol, 1 eq.) and nitrosobenzene (55 mg, 0.51 mmol, 2.05 eq.) in THF (1 mL) was added [Rh(trop2NH)(PPh3)]OTF 9 (2.3 mg, 2.5 μmol, 0.01 eq.) and K2CO3 (3.5 mg, 25 μmol, 0.01 eq.). The resulting mixture was stirred overnight at room temperature then analysed by NMR.

³¹P{¹H}-NMR (202.5 MHz, [H8]THF, 298 K) δ = 25.6 (s, P(O)Ph3).
A solution of [Rh(trop2N)(eq-PPh3)(ax-PhN=N(O)Ph)] 97 (10 mg, 10 \( \mu \text{mol} \)) in THF (0.5 mL) was left for 2 days at room temperature, the complex was partially decomposed to triphenyl phosphane oxide, azobenzene and other not identified products.

\(^{31}\)P\(_{\text{1H}}\)-NMR (101.25 MHz, \([\text{H8}]\text{THF}, 298 \text{ K}\) \( \delta = 29.3 \) (s, P(O)Ph3).

GC-MS (EI, m/z (fragment, abundance)): 183 (C\(_{12}\)H\(_{11}\)N\(_{2}\)^{+}; M\(^{+}+1\), 10%), 182 (C\(_{12}\)H\(_{10}\)N\(_{2}\)^{+}; M\(^{+}\), 77%), 153 (19%), 152 (52%), 105 (C\(_{6}\)H\(_{5}\)N\(_{2}\)^{+}, 36%), 77 (C\(_{6}\)H\(_{5}\)^{+}, 100%): azobenzene; 278 (C\(_{18}\)H\(_{13}\)OP\(^{+}\); M\(^{+}\), 26%), 277 (C\(_{18}\)H\(_{12}\)OP\(^{+}\); M\(^{+} -1\), 100%), 201 (C\(_{12}\)H\(_{10}\)OP\(^{+}\), 12%), 199 (C\(_{12}\)H\(_{8}\)OP\(^{+}\), 34%), 183 (C\(_{12}\)H\(_{8}\)P\(^{+}\), 14%), 152 (18%): P(O)Ph3.

To a solution of [Rh(trop2N)(PPh3)] 1 (10 mg, 13 \( \mu \text{mol}, 1 \text{ eq.} \)) in THF (0.5 mL) was added nitrosobenzene (14 mg, 0.13 mmol, 10 eq.). The solution turned dark red within 10 seconds.

\(^{31}\)P\(_{\text{1H}}\)-NMR (202.50 MHz, \([\text{H8}]\text{THF}, 298 \text{ K}\) \( \delta = 25.7 \) (s, OPPh3).

[RhH(trop2NH)(PPh3)] 2 was generated in-situ by reacting a solution of [Rh(trop2N)(PPh3)] 1 (10 mg, 13 \( \mu \text{mol}, 1 \text{ eq.} \)) in THF (0.5 mL) with hydrogen gas. To this solution nitrosobenzene (2.1 mg, 20 \( \mu \text{mol}, 1.5 \text{ eq.} \)) was added. After a short reaction time (less than 10 seconds) the solution turned dark yellow and a precipitate formed.

\(^{31}\)P\(_{\text{1H}}\)-NMR (101.25 MHz, \([\text{H8}]\text{THF}, 298 \text{ K}\) \( \delta = 24.6 \) (s, OPPh3), 39.9 (d, \( ^1J_{\text{RhP}} = 134.9, 98 \)).

A suspension of [Rh(trop2NH)(PPh3)(ONHPh)] 98 (5.0 mg, 5.7 \( \mu \text{mol}, 1 \text{ eq.} \)) in THF (0.5 mL) was treated overnight with hydrogen gas then analysed by \(^{31}\)P\(_{\text{1H}}\)-NMR and GC-MS.

A suspension of [Rh(trop2NH)(PPh3)(ONHPh)] 98 (5.0 mg, 5.7 \( \mu \text{mol}, 1 \text{ eq.} \)) in THF (0.5 mL) was treated overnight with ethanol (30 \( \mu \text{L}, 24 \text{ mg}, 520 \mu \text{mol, 90 eq.} \))

1H-NMR (250.13 MHz, \([\text{D8}]\text{THF}, 298 \text{ K}\) \( \delta = 10.99 \) (s, PhCHO).

[\( ^{1}H\)-NMR (101.25 MHz, \([\text{D8}]\text{THF}, 298 \text{ K}\) \( \delta = 65.2 \) (d, \( ^1J_{\text{RhP}} = 145.3 \text{ Hz, 2})

GC-MS (EI, m/z (fragment, abundance)): 106 (C\(_{7}\)H\(_{6}\)O\(^{+}\); M\(^{+}\), 16%), 105 (C\(_{7}\)H\(_{5}\)O\(^{+}\); M\(^{+} -1\), 100%), 77 (C\(_{5}\)H\(_{5}\)^{+}, 47%): benzaldehyde; 94 (C\(_{6}\)H\(_{8}\)N\(^{+}\); M\(^{+} +1\), 10%), 93 (C\(_{6}\)H\(_{7}\)N\(^{+}\); M\(^{+}\), 100%), 66 (C\(_{5}\)H\(_{6}\)^{+}, 43%): aniline; 183 (C\(_{12}\)H\(_{11}\)N\(_{2}\)^{+}; M\(^{+} +1\), 6%), 182 (C\(_{12}\)H\(_{10}\)N\(_{2}\)^{+}; M\(^{+}\), 34%), 153 (8%), 152 (14%), 105 (C\(_{6}\)H\(_{5}\)N\(_{2}\)^{+}, 31%), 77 (C\(_{6}\)H\(_{5}\)^{+}, 100%): azobenzene; 181 (C\(_{13}\)H\(_{11}\)N\(^{+}\); M\(^{+}\), 85%), 180 (C\(_{13}\)H\(_{10}\)N\(^{+}\); M\(^{+} -1\), 100%), 152 (6%), 77 (C\(_{6}\)H\(_{5}\), 28%): N-benzylideneaniline;
212 (C$_{14}$H$_{12}$O$_2^+$; M$^+$, 35%), 194 (C$_{14}$H$_{10}$O$_2^+$, 89%), 167 (37%), 105 (C$_7$H$_3$O$_2^+$, 100%), 91 (C$_7$H$_7^+$, 61%); 77 (C$_6$H$_5^+$, 52%): benzyl benzoate.

A suspension of [Rh(trop$_2$NH)(PPh$_3$)(ONHPh)] 98 (5.0 mg, 5.7 µmol, 1 eq.) in THF (0.5 mL) was treated overnight with benzyl alcohol (10 µL, 10 mg, 96 µmol, 17 eq.) then acetic anhydride (30 µL, 32 mg, 318 µmol, 56 eq.) was added and after 10 minutes the mixture was analysed by GC-MS.

GC-MS (EI, m/z (fragment, abundance)): 106 (C$_7$H$_6$O$^+$; M$^+$, 13%), 105 (C$_7$H$_5$O$^+$; M$^+$ -1, 100%), 77 (C$_6$H$_5^+$, 60%): benzyaldehyde;
151 (C$_9$H$_{11}$O$_2^+$; M$^+$ +1, 8%), 150 (C$_9$H$_{10}$O$_2^+$; M$^+$, 11%), 108 (C$_7$H$_8$O$_2^+$, 100%), 91 (C$_7$H$_7^+$, 77%), 79 (63%), 77 (C$_6$H$_5^+$, 35%): benzyl acetate;
135 (C$_8$H$_{10}$NO$^+$; M$^+$, 15%), 108 (C$_7$H$_9$N$^+$, 45%), 93 (C$_6$H$_7$N$^+$, 100%), 79 (68%), 66 (C$_5$H$_6^+$, 27%): N-phenyl acetonitrile;
194 (C$_{10}$H$_{12}$NO$_3^+$; M$^+$ +1, 1%), 193 (C$_{10}$H$_{11}$NO$_3^+$; M$^+$, 1%), 151 (C$_8$H$_9$NO$_2^+$, 46%), 136 (C$_8$H$_{10}$NO$^+$, 2%), 134 (C$_6$H$_8$NO$_2^+$, 2%), 118 (C$_6$H$_8$NO$_3^+$, 2%), 109 (C$_6$H$_8$NO$_4^+$, 100%), 91 (63%), 79 (19%), 77 (C$_6$H$_5^+$, 11%), 65 (26%), 63 (21%): N$_2$O-diacylphenyl hydroxylamine;
212 (C$_{14}$H$_{12}$O$_2^+$; M$^+$, 33%), 194 (C$_{14}$H$_{10}$O$_2^+$, 86%), 167 (36%), 105 (C$_7$H$_3$O$_2^+$, 100%), 91 (C$_7$H$_7^+$, 60%); 77 (C$_6$H$_5^+$, 51%): benzyl benzoate;
199 (C$_{12}$H$_{11}$N$_2$O$_2^+$; M$^+$ +1, 14%), 198 (C$_{12}$H$_{10}$N$_2$O$_2^+$; M$^+$, 35%), 182 (C$_{11}$H$_9$N$_2$O$_2^+$, 100%), 141 (23%), 115 (13%), 105 (C$_6$H$_5$N$_2$O$_2^+$, 25%), 91 (C$_6$H$_5$N$^+$, 9%), 77 (C$_6$H$_5^+$, 82%): azoxybenzene.

To a suspension of [Rh(trop$_2$NH)(PPh$_3$)(ONHPh)] 98 (2.0 mg, 2.3 µmol, 1 eq.) in THF (1.5 mL) benzaldehyde (23 µL, 24 mg, 0.23 mmol, 100 eq.) was added. Even after 90 minutes of stirring no reaction was observed by NMR.

A 100 mL Schlenk flask was charged with [Rh(trop$_2$NH)(PPh$_3$)]OTf 9 (2.1 mg, 2.3 µmol, 10$^{-2}$ eq.), nitrosobenzene (25 mg, 0.23 mmol, 1 eq.) and K$_2$CO$_3$ (64 mg, 0.46 mmol, 2 eq.) then evacuated and filled with hydrogen gas. THF (1 mL) and acetic anhydride (0.11 mL, 120 mg, 1.2 mmol, 5 eq.) was added via syringe and the reaction mixture was stirred for 2 hours then analysed by GC-MS.

GC-MS (EI, m/z (fragment, abundance)): 135 (C$_6$H$_9$NO$^+$; M$^+$, 15%), 108 (C$_7$H$_9$N$^+$, 45%), 93 (C$_6$H$_7$N$^+$, 100%), 79 (68%), 66 (C$_5$H$_6^+$, 26%): N-phenyl acetamide;
194 (C$_{10}$H$_{12}$NO$_3^+$; M$^+$ +1, 1%), 193 (C$_{10}$H$_{11}$NO$_3^+$; M$^+$, 1%), 151 (C$_8$H$_9$NO$_2^+$, 46%), 136 (C$_8$H$_{10}$NO$^+$, 2%), 134 (C$_6$H$_8$NO$_2^+$, 2%), 118 (C$_6$H$_8$NO$_3^+$, 2%), 109 (C$_6$H$_8$NO$_4^+$, 100%), 91 (48%), 91 (60%), 79 (11%), 77 (C$_6$H$_5^+$, 13%), 65 (23%), 63 (20%): N$_2$O-diacylphenyl hydroxylamine;
199 (C$_{12}$H$_{11}$N$_2$O$_2^+$; M$^+$ +1, 14%), 198 (C$_{12}$H$_{10}$N$_2$O$_2^+$; M$^+$, 35%), 182 (C$_{11}$H$_9$N$_2$O$_2^+$, 100%), 141 (23%), 115 (13%), 105 (C$_6$H$_5$N$_2$O$_2^+$, 25%), 91 (C$_6$H$_5$N$^+$, 9%), 77 (C$_6$H$_5^+$, 82%): azoxybenzene.
To a solution of [Rh(trop2N)(PPh3)] 1 (44 mg, 58 μmol, 1 eq.) and aniline (21 μL, 22 mg, 0.23 mmol, 5 eq.) in THF (2 mL) was added nitrosobenzene (25 mg, 0.23 mmol, 5 eq.). The reaction mixture was stirred for 10 minutes then analysed.

$^{31}$P{$^1$H}-NMR (101.25 MHz, [H8]THF, 298 K) δ = 21.2 (s, OPPh3), 38.4 (d, 1 $^3$J$^{Rh}$P = 134.7, 98).

GC-MS (EI, m/z (fragment, abundance)): 183 (C$_{12}$H$_{11}$N$_2$+; M$^+$ +1, 6%), 182 (C$_{12}$H$_{10}$N$_2$+; M$^+$, 42%), 153 (4%), 152 (16%), 105 (C$_6$H$_5$N$_2$+, 34%), 77 (C$_6$H$_5$+, 100%): azobenzene; 199 (C$_{12}$H$_{11}$N$_2$O+; M$^+$ +1, 6%), 198 (C$_{12}$H$_{10}$N$_2$O+; M$^+$, 37%), 182 (C$_{12}$H$_{11}$N$_2$+, 5%), 169 (C$_{11}$H$_9$N$_2$+, 89%), 141 (25%), 115 (18%), 105 (C$_6$H$_5$N$_2$+, 14%), 91 (C$_6$H$_3$N+, 12%), 77 (C$_6$H$_5$+, 100%): azoxybenzene.

The ratio between azobenzene and azoxybenzene was determined to approximately 1:50.

To a solution of benzyl alcohol (26 μl, 27 mg, 0.25 mmol, 1 eq.), [Rh(trop2NH)(PPh3)]OTf 9 (2.3 mg, 2.5 μmol, 0.01 eq.) and nitrosobenzene (59 mg, 0.55 mmol, 2.2 eq.) in THF (2 ml) was added H$_2$O (50 μL, 50mg, 2.8 mmol, 11 eq.) and K$_2$CO$_3$ (6.9 mg, 50 μmol, 0.2 eq.). The reaction mixture was stirred for 2 hours then acidified with 5% HCl and analysed by GC. 75% of the benzyl alcohol was converted to a 2:1 mixture of benzaldehyde and benzoic acid. (Measured retention time: benzyl alcohol 4.86 min; benzaldehyde 3.69 min; benzoic acid 8.16 min)

Addition of up to 2.2 eq. cyclohexanone did not change the result.

To a solution of 1-methoxy-4-nitrosobenzene (150 mg, 1.09 mmol, 1 eq.), methyl 4-nitrosobenzoate (181 mg, 1.09 mmol, 1 eq.) and [Rh(trop2NH)(PPh3)]OTf 9 (2.0 mg, 2.2 μmol, 10$^{-3}$ eq.) in ethanol (2 mL) and THF (1 mL) K$_2$CO$_3$ (7.6 mg, 55 μmol, 0.05 eq.) was added. The reaction mixture was stirred for 2 hours then filtered over silica gel. The solvent was removed under reduced pressure and the residue analysed by NMR.

$^1$H-NMR (300.13 MHz, CDCl$_3$, 298 K) δ = 3.81 (s, OCH$_3$), 3.81 (s, OCH$_3$), 3.82 (s, OCH$_3$), 3.83 (s, OCH$_3$), 3.87 (s, CO$_2$CH$_3$), 3.88 (s, CO$_2$CH$_3$), 3.90 (s, CO$_2$CH$_3$), 3.91 (s, CO$_2$CH$_3$). (aromatic protons are not listed.)

$^{13}$C{$^1$H}-NMR (75.48 MHz, CDCl$_3$, 298 K) δ = 52.4 (s, OCH$_3$), 52.6 (s, OCH$_3$), 52.8 (s, OCH$_3$), 55.5 (s, CO$_2$CH$_3$), 55.6 (s, CO$_2$CH$_3$), 55.7 (s, CO$_2$CH$_3$), 160.2 (s, CO$_2$CH$_3$), 161.9 (s, CO$_2$CH$_3$). (aromatic protons are not listed; due to low abundance of two products the corresponding carbon signals were not resolved.)

To a solution of 1-methoxy-4-nitrosobenzene (100 mg, 0.73 mmol, 1 eq.), aniline (66 μL, 68 mg, 0.73 mmol, 1 eq.), MMA (0.39 mL, 370 mg, 3.7 mmol, 5 eq.) and [Rh(trop2NH)(PPh$_3$)]OTf 9 (6.7 mg, 7.3 μmol, 0.01 eq.) in THF (2 mL) K$_2$CO$_3$ (5.0 mg, 36 μmol, 0.05 eq.) was added. The reaction mixture was stirred for 2 hours then analysed by GC-MS.

GC-MS (EI, m/z (fragment, abundance)): 258 (C$_{14}$H$_{14}$N$_2$O$_3$+; M$^+$, 100%), 242 (C$_{13}$H$_{11}$N$_2$O$_3$+, 11%), 227 (6%), 215 (20%), 198 (12%), 187 (14%), 137 (C$_6$H$_5$N$_2$O$^-$, 12%), 137 (C$_7$H$_7$N$_2$O$^-$, 19%), 121 (C$_7$H$_7$NO$^-$, 29%), 107 (C$_6$H$_5$O$^+$, 49%), 77 (C$_6$H$_5$+, 78%): 4,4'-dimethoxyazoxybenzene.
To a solution of benzyl alcohol (26 µL, 27 mg, 0.25 mmol, 1 eq.), N-phenyl hydroxylamine (55 mg, 0.50 mmol, 2 eq.) and Rh(trop2NH)(PPh3)OTf 9 (2.3 mg, 2.5 µmol, 0.01 eq.) in THF (2 mL) was added K2CO3 (3.5 mg, 25 µmol, 0.1 eq.). The reaction mixture was stirred for 2 hours then analysed by GC-MS.

GC-MS (EI, m/z (fragment, abundance)): 108 (C6H6NO+; M+ +1, 42%), 107 (C6H5NO+; M+, 100%), 77 (C6H5+, 96%): nitrosobenzene; 94 (C6H3N+; M+ +1, 14%), 93 (C6H3N+; M+, 100%), 66 (C5H6+, 26%): aniline; 106 (C7H6O+; M+, 15%), 105 (C7H5O+; M+ -1, 100%), 77 (C6H5+, 54%): benzaldehyde; 181 (C13H11N+; M+, 85%), 180 (C13H10N+; M+ -1, 100%), 152 (6%), 77 (C6H5+, 92%): N-benzylideneaniline; 199 (C12H11N2O+; M+ +1, 7%), 198 (C12H10N2O+; M+, 32%), 182 (C12H11N2+, 5%), 169 (C11H9N2+, 100%), 141 (28%), 115 (19%), 105 (C6H3N2+, 5%), 91 (C6H3N+, 23%), 77 (C6H5+, 92%): azoxybenzene.

To a solution of nitrosobenzene (50 mg, 0.47 mmol, 1 eq.), n-butylamine (69 µL, 51 mg, 0.70 mmol, 1.5 eq.), benzyl alcohol (24 µL, 25 mg, 0.23 mmol, 0.5 eq.) and Rh(trop2NH)(PPh3)OTf 9 (4.3 mg, 4.7 µmol, 0.01 eq.) K2CO3 (3.2 mg, 23 µmol, 0.05 eq.) was added. The reaction mixture was stirred for 2 hours then analysed by GC-MS.

GC-MS (EI, m/z (fragment, abundance)): 106 (C7H6O+; M+, 25%), 105 (C7H5O+; M+ -1, 100%), 77 (C6H5+, 46%): benzaldehyde; 162 (C11H16N+; M+ +1, 73%), 160 (C11H14N+; M+ -1, 33%), 132 (C9H10N+, 27%), 118 (C8H8N+, 69%), 104 (C7H6N+, 21%), 91 (C7H5+, 100%), 77 (C6H5+, 12%): N-benzylidenebutan-1-amine; 178 (C11H16NO+; M+ +1, 3%), 177 (C11H15NO+; M+, 4%), 176 (C11H14NO+; M+ -1, 4%), 148 (C9H10NO+, 8%), 105 (C7H5O+, 100%), 77 (C6H5+, 59%): N-butylbenzamide; 199 (C12H11N2O+; M+ +1, 25%), 198 (C12H10N2O+; M+, 38%), 182 (C12H11N2+, 13%), 169 (C11H9N2+, 100%), 141 (25%), 115 (15%), 105 (C6H3N2+, 18%), 91 (C6H3N+, 13%), 77 (C6H5+, 75%): azoxybenzene.

To a solution of acetophenone (0.60 mL, 630 mg, 5.2 mmol, 1 eq.) and [Rh(trop2N)(eq-PPh3)(ax-PhN=N(O)Ph)] 97 (5.0 mg, 5.2 µmol, 10⁻³ eq.) in ethanol (2.5 mL) K2CO3 (7.2 mg, 52 µmol, 0.01 eq.) was added. The reaction mixture was stirred overnight then a sample was analysed by ¹H-NMR. The absence of the resonance of the methyl group of acetophenone at 2.63 ppm indicated complete conversion.
7.4 Synthesis of tetradeionate ligands

2-(2-(bromomethyl)phenyl)-1,3-dioxolane (14)

MF = C_{10}H_{11}BrO_{2}

MW = 243.10 g/mol

MP: 28-29 °C

Air stable

To a solution of PPh₃ (882 mg, 3.36 mmol, 1.2 eq.) in DCM (20 mL) bromine (0.17 mL, 537 mg, 3.36 mmol, 1.2 eq) was added at -10 °C. The resulting mixture was stirred for 20 minutes then pyridine (0.34 mL, 333 mg, 3.75 mmol, 1.5 eq.) was added. Stirring was continued for another 20 minutes then (2-(1,3-dioxolan-2-yl)phenyl)methanol 15 (0.36 mL, 500 mg, 2.8 mmol, 1 eq.) was added. The resulting solution was allowed to warm to room temperature and stirred for 1.5 hours. Water was added and stirring was continued for 10 minutes. The aqueous phase was extracted three times with small portions of DCM, the combined organic phases were washed with aqueous Na₂S₂O₃ and brine, dried with Na₂SO₄ and concentrated under reduced pressure. n-hexane was added and the formed precipitate was filtered off and washed with n-hexane. The solvent was removed in vacuum and the product was purified by column chromatography (Eluent: DCM). Yield: 567 mg, 84%.

¹H-NMR (250.13 MHz, CDCl₃, 298 K): δ = 4.07-4.21 (m, 4H, OCH₂CH₂O), 4.73 (s, 2H, CH₂Br), 6.17 (s, 1H, CH₂ methine), 7.34-7.44 (m, 3H, CH₃ ar), 7.60-7.65 (m, 1H, CH₃ ar).

¹³C{¹H}-NMR (62.90 MHz, CDCl₃, 298 K): δ = 30.6 (s, 1C, CH₂Br), 65.3 (s, 2C, OCH₂CH₂O), 101.1 (s, 1C, CH₂methine), 126.6 (s, 1C, CH₃ ar), 128.7 (s, 1C, CH₃ ar), 129.5 (s, 1C, CH₃ ar), 130.9 (s, 1C, CH₃ ar), 135.9 (s, 1C, C² quat), 136.1 (s, 1C, C³ quat).

ATR IR (v in cm⁻¹): 2888 (w), 2116 (w), 1697 (w), 1459 (w), 1395 (m), 1347 (w), 1290 (w), 1232 (m), 1214 (m), 1187 (w), 1141 (w), 1094 (m), 1065 (s), 1037 (m), 970 (m), 941 (s), 884 (w), 847 (w), 811 (w), 769 (s), 749 (m), 723 (w), 664 (w), 630 (w), 607 (s).
Diethyl-2-(1,3-dioxolane-2-yl) benzylphosphonate (16)

MF = C_{14}H_{21}O_{5}P

MW = 300.29 g/mol

Air stable

A solution of 2-(2-(bromomethyl)phenyl)-1,3-dioxolane 14 (1.00 g, 4.14 mmol, 1 eq.) and P(OEt)_3 (1.74 mL, 1.72 g, 10.34 mmol, 2.5 eq.) was refluxed for 3 hours then all volatiles were removed under reduced pressure. The title compound was obtained as yellowish oil. Yield: 1.35 g, 100%.

^1^H-NMR (250.13 MHz, CDCl_3, 298 K): \( \delta = 1.26 \) (t, \( ^3J_{HH} = 7.1 \) Hz, 6H, CH\_2CH\_3), 3.43 (d, \( ^2J_{PH} = 21.8 \) Hz, 2H, CH\_2P), 3.96-4.18 (m, 8H, CH\_2CH\_3, OCH\_2CH\_2O), 6.19 (s, 1H, CH^methine), 7.31-7.39 (m, 3H, CH^ar), 7.61-7.65 (m, 1H, CH^ar).

\(^{13}\text{C}\{^1\text{H}\}\)-NMR (62.90 MHz, CDCl\_3, 298 K): \( \delta = 16.3 \) (d, \( ^3J_{PC} = 6.1 \) Hz, 2C, CH\_2CH\_2), 30.2 (d, \( ^1J_{PC} = 137.6 \) Hz, 1C, CH\_2P), 62.2 (d, \( ^2J_{PC} = 7 \) Hz, 2C, CH\_2CH\_3), 65.2 (s, 2C, OCH\_2CH\_2O), 101.5 (d, \( ^4J_{PC} = 1.4 \) Hz, 1C, CH^methine), 126.1 (d, \( J_{PC} = 3.1 \) Hz, 1C, CH\^ar), 127.1 (d, \( J_{PC} = 3.4 \) Hz, 1C, CH\^ar), 129.0 (d, \( J_{PC} = 3.5 \) Hz, 1C, CH^ar), 130.2 (d, \( J = 9.0 \) Hz, 1C, C\^quat), 131.2 (d, \( J_{PC} = 5.5 \) Hz, 1C, CH\^ar), 132.0 (d, \( J = 6.9 \) Hz, 1C, C\^quat).

\(^{31}\text{P}\{^1\text{H}\}\)-NMR (101.25 MHz, CDCl\_3, 298 K) \( \delta = 26.4 \) (s).

ATR IR (\( \nu \) in cm\(^{-1}\)): 2951 (w), 2854 (w), 1584 (w), 1472 (w), 1459 (m), 1395 (m), 1362 (w), 1339 (w), 1314 (w), 1289 (w), 1231 (m), 1214 (m), 1184 (w), 1136 (w), 1095 (s), 1076 (m), 1034 (s), 1012 (s), 989 (s), 969 (s), 953 (s), 930 (s), 889 (w), 876 (w), 845 (w), 816 (w), 785 (w), 772 (m), 761 (s), 659 (m), 638 (w).
2-(2-(bromomethyl)phenyl)-5,5-dimethyl-1,3-dioxane (99)

MF = C\textsubscript{13}H\textsubscript{17}BrO\textsubscript{2}  
MW = 285.18 g/mol

MP: 38-39 °C

Air stable

To a solution of PPh\textsubscript{3} (1.42 g, 5.43 mmol, 1.2 eq.) in DCM (10 mL) was added bromine (0.28 mL, 0.867 g, 5.43 mmol, 1.2 eq) at -10 °C. The resulting mixture was stirred for 20 minutes then pyridine (0.55 mL, 0.536 g, 6.78 mmol, 1.5 eq.) was added. Stirring was continued for another 20 minutes then (2-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)methanol \textbf{26} (0.36 mL, 500 mg, 2.8 mmol, 1 eq.) was added. The resulting solution was allowed to warm to room temperature and stirred for 1.5 hours. Water was added and stirring was continued for 10 minutes. The aquatic phase was extracted three times with small portions of DCM, the combined organic phases were washed with aqueous Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}, water and brine, dried with Na\textsubscript{2}SO\textsubscript{4} and concentrated under reduced pressure. \textit{n}-hexane was added and the formed precipitate was filtered off and washed with \textit{n}-hexane. The solvent was removed under reduced pressure and the was product purified by column chromatography (Eluent: PET : EtOAc 10 : 1). Yield: 1.13 g, 88%.

\textbf{1}H-NMR (300.13 MHz, CDCl\textsubscript{3}, 298 K): \(\delta = 0.85\) (s, 3H, CCH\textsubscript{3}), 1.33 (s, 3H, CCH\textsubscript{3}), 3.74 (d, \(^2J\text{HH} = 10.8\) Hz, 2H, CH\textsubscript{2}CMe\textsubscript{2}), 3.83 (d, \(^2J\text{HH} = 10.8\) Hz, 2H, CH\textsubscript{2}CMe\textsubscript{2}), 5.73 (s, 1H, CH\textsubscript{methine}), 7.33-7.41 (m, 3H, CH\textsubscript{ar}), 7.70-7.72 (m, 1H, CH\textsuperscript{ar}).

\textbf{13}C{\textsuperscript{1}H}-NMR (75.48 MHz, CDCl\textsubscript{3}, 298 K): \(\delta = 21.9\) (s, 1C, CCH\textsubscript{3}), 23.2 (s, 1C, CCH\textsubscript{3}), 30.3 (s, 1C, CMe\textsubscript{2}), 30.7 (s, 1C, CH\textsubscript{2}Br), 77.9 (s, 2C, CH\textsubscript{2}CMe\textsubscript{2}), 99.3 (s, 1C, CH\textsuperscript{methine}), 126.8 (s, 1C, CH\textsuperscript{ar}), 128.9 (s, 1C, CH\textsuperscript{ar}), 129.3 (s, 1C, CH\textsuperscript{ar}), 130.7 (s, 1C, CH\textsuperscript{ar}), 135.2 (s, 1C, C\textsuperscript{quat}), 136.6 (s, 1C, C\textsuperscript{quat}).

ATR IR (\(v\) in cm\textsuperscript{-1}): 3057 (w), 2951 (w), 2854 (w), 1736 (w), 1584 (w), 1496 (w), 1472 (w), 1460 (m), 1395 (m), 1361 (w), 1339 (w), 1314 (w), 1289 (w), 1231 (m), 1214 (m), 1184 (w), 1136 (w), 1093 (s), 1075 (s), 1034 (m), 1011 (s), 989 (m), 969 (s), 953 (m), 930 (m), 910 (w), 889 (w), 876 (w), 816 (w), 785 (w), 772 (m), 762 (s), 750 (m), 659 (m), 638 (w).

EA found\% (calc\%) for C\textsubscript{13}H\textsubscript{17}BrO\textsubscript{2}: C: 54.83 (54.75), H: 5.93 (6.01).
Diethyl 2-(5,5-dimethyl-1,3-dioxan-2-yl) benzylphosphonate \((27)\)

\[
\text{MF} = \text{C}_{17}\text{H}_{27}\text{O}_{5}\text{P}
\]

\[
\text{MW} = 342.37 \text{ g/mol}
\]

Air stable

A solution of 2-(2-(bromomethyl)phenyl)-5,5-dimethyl-1,3-dioxane \((99)\) (1.00 g, 3.52 mmol, 1 eq.) and \(\text{P(OEt)}_3\) (1.48 mL, 1.46 g, 8.80 mmol, 2.5 eq.) was refluxed for 3 hours then all volatiles were removed under reduced pressure. The title compound was obtained as colourless oil. Yield: 1.24 g, 100%.

\(^1\text{H}-\text{NMR} (300.13 \text{ MHz, CDCl}_3, 298 \text{ K})\): \(\delta = 0.82 \text{ (s, 3H, CCH}_3\), 1.52 \text{ (t, }^3J_{\text{HH}} = 6.9 \text{ Hz, 6H, CH}_2\text{CH}_3\), 1.32 \text{ (s, 3H, CCH}_3\), 3.62 \text{ (d, }^2J_{\text{PH}} = 21.6 \text{ Hz, 2H, CH}_2\text{P}, \text{= 3.72 (d, } ^2J_{\text{HH}} = 10.8 \text{ Hz, CCH}_2\text{CMe}_2\), 3.79 \text{ (d, } ^2J_{\text{HH}} = 10.8 \text{ Hz, CH}_2\text{CMe}_2\), 3.95-4.07 \text{ (m, 4H, CH}_2\text{CH}_3\), 5.77 \text{ (s, 1H, CH}^\text{methine}\), 7.30-7.33 \text{ (m, 3H, CH}^\text{ar}\), 7.72-7.74 \text{ (m, 1H, CH}^\text{ar}\).

\(^{13}\text{C}{^1\text{H}}\)-NMR (75.48 MHz, CDCl\(_3\), 298 K): \(\delta = 16.4 \text{ (d, } ^3J_{\text{PC}} = 6.1 \text{ Hz, 2C, CH}_2\text{CH}_3\), 21.9 \text{ (s, 1C, CCH}_3\), 23.2 \text{ (s, 1C, CCH}_3\), 30.2 \text{ (s, 1C, CMe}_2\), 30.4 \text{ (d, } ^1J_{\text{PC}} = 137.8 \text{ Hz, 1C, CH}_2\text{P), 62.2 \text{ (d, } ^2J_{\text{PC}} = 6.9 \text{ Hz, 2C, CH}_2\text{CH}_3\), 77.8 \text{ (s, 2C, CH}_2\text{CMe}_2\), 99.5 \text{ (d, } ^4J_{\text{PC}} = 1.4 \text{ Hz, 1C, CH}^\text{methine}\), 126.4 \text{ (d, } J_{\text{PC}} = 3.2 \text{ Hz, 1C, CH}^\text{ar}\), 127.2 \text{ (d, } J_{\text{PC}} = 3.7 \text{ Hz, 1C, CH}^\text{ar}\), 128.8 \text{ (d, } J_{\text{PC}} = 3.5 \text{ Hz, 1C, CH}^\text{ar}\), 129.3 \text{ (d, } ^2J_{\text{PC}} = 9.1 \text{ Hz, 1C, CH}^\text{quat}\), 131.1 \text{ (d, } J_{\text{PC}} = 5.6 \text{ Hz, 1C, CH}^\text{quat}\), 137.0 \text{ (d, } ^3J_{\text{PC}} = 6.9 \text{ Hz, 1C, CH}^\text{quat}\).

\(^{31}\text{P}{^1\text{H}}\)-NMR (121.49 MHz, CDCl\(_3\), 298 K) \(\delta = 26.4 \text{ (s).}\)

ATR IR (\(\nu \text{ in cm}^{-1}\)): 2956 (w), 2845 (w), 2116 (w), 1471 (w), 1455 (w), 1393 (w), 1365 (w), 1293 (w), 1255 (m), 1215 (w), 1162 (w), 1100 (s), 1051 (m), 1016 (s), 993 (m), 960 (s), 847 (w), 789 (s), 758 (m), 703 (w), 662 (w), 639 (w).
2-(diphenylphosphino)benzaldehyde

(12)

MF = C_{19}H_{15}OP

MW = 290.30 g/mol

MP = 114-115 °C

Air stable

BuLi (1.6 M in hexane, 7.88 mL, 12.6 mmol, 0.99 eq.) was added to a solution of 2-(2-bromophenyl)-1,3-dioxolane (2.90 g, 1.80 mL, 12.7 mmol, 1 eq.) in THF (20 mL) at -78 °C. The resulting yellow mixture was stirred for one hour then chlorodiphenylphosphane (2.80 g, 2.28 mL, 12.7 mmol, 1 eq.) was added. The mixture was warmed to room temperature then hydrolysed with degassed water. After phase separation the solvent of the organic phase was removed in vacuum, the residue was dissolved in acetone (70 mL) and p-TsOH (0.10 g, 0.52 mmol, 0.09 eq.) was added. The resulting solution was degassed for 30 minutes then refluxed for 3 hours. After the yellow solution was cooled to room temperature, water (20 mL) was added and the acetone was removed under reduced pressure. The yellow precipitate was filtrated and carefully dried under high vacuum. Yield: 3.71 g, 90%.

$^{1}$H-NMR (300.13 MHz, CDCl$_3$, 298 K): $\delta$ = 6.98-7.02 (m, 1H, $CH^p$), 7.28-7.55 (m, 12H, $CH^p$), 7.99-8.01 (m, 1H, $CH^p$), 10.53 (d, $^1J_{PH} = 5.5$ Hz, 1H, CHO).

$^{13}$C{$^{1}$H}-NMR (75.48 MHz, CDCl$_3$, 298 K): $\delta$ = 128.7 (d, $^3J_{PC} = 7.5$ Hz, 4C, $CH^a$), 128.9 (s, 1C, $CH^a$), 129.1 (s, 2C, $CH^a$), 130.6 (d, $J = 3.8$ Hz, 1C, $CH^a$), 133.6 (s, 1C, $CH^a$), 133.9 (s, 1C, $CH^a$), 134.1 (d, $^2J_{PC} = 20.4$ Hz, 4C, $CH^a$), 136.1 (d, $^1J_{PC} = 9.7$ Hz, 2C, $C^{quat}$), 138.5 (d, $^2J_{PC} = 14.6$ Hz, 1C, $C^{quat}$), 141.2 (d, $^1J_{PC} = 26.3$ Hz, 1C, $C^{quat}$), 191.7 (d, $^2J_{PC} = 19.3$ Hz, 1C, CHO).

$^{31}$P{$^{1}$H}-NMR (121.49 MHz, CDCl$_3$, 298 K) $\delta$ = -11.6 (s).

ATR IR (v in cm$^{-1}$): 3050 (w), 2976 (w), 2890 (w), 2759 (w), 1967 (w), 1696 (m), 1673 (m), 1583 (w), 1559 (w), 1506 (w), 1477 (w), 1462 (w), 1433 (m), 1399 (w), 1327 (w), 1307 (w), 1296 (w), 1199 (m), 1162 (w), 1153 (w), 1126 (w), 1093 (m), 1068 (m), 1024 (w), 999 (w), 979 (w), 953 (w), 916 (w), 877 (w), 844 (m), 759 (s), 751 (s), 744 (s), 720 (w), 695 (s), 670 (s), 654 (m), 614 (w).
(E)-(2-(2-(5,5-dimethyl-1,3-dioxan-2-yl)
styryl)phenyl)diphenylphosphane (28)
MF = C₃₂H₃₁O₂P

MW = 478.56 g/mol

MP = 124-125 °C

Air stable

BuLi (1.6 M in hexane, 0.913 mL, 1.46 mmol, 1 eq.) was added to a solution of diethyl 2-(5,5-dimethyl-1,3-dioxan-2-yl) benzylphosphonate 27 (0.377 mL, 0.500 g, 1.46 mmol, 1 eq.) in THF (5 mL) at -78 °C. The resulting mixture was stirred for 20 minutes then a solution of 2-(diphenylphosphino)benzaldehyde 12 (0.424 g, 1.46 mmol, 1 eq.) in THF (2 mL) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 2 hours then diluted with DCM and saturated NH₄Cl. The aqueous phase was extracted twice with DCM then the combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated. The resulting crude product was purified by column chromatography (Eluent: PET:EtOAc 10:1) to give the title compound as a white solid. Yield: 0.512 g, 73%.

¹H-NMR (300 MHz, CDCl₃, 298 K): δ = 0.83 (s, 3H, CH₃), 1.29 (s, 3H, CH₃), 3.66 (d, 2 JHH = 10.5 Hz, CH₂CMe₂), 3.79 (d, 2 JHH = 10.5 Hz, CH₂CMe₂), 5.56 (s, 1H, CHmethine), 6.85-6.95 (m, 1H, CHolefin), 7.21-7.24 (m, 1H, CHar), 7.24-7.74 (m, 16H, CHar), 7.62-7.74 (m, 3H, CHolefin; CHar).

¹³C{¹H}-NMR (75 MHz, CDCl₃, 298 K): δ = 21.9 (s, 1C, CCH₃), 23.2 (s, 1C, CCH₃), 30.2 (s, 1C, CMe₂), 77.8 (s, 2C, CH₂CMe₂), 99.5 (s, 1C, CHmethine), 125.9 (d, 3 JPC = 4.5 Hz, CHolefin), 126.1 (s, 1C, CH²), 126.5 (s, 1C, CH³), 127.6 (s, 1C, CH⁴), 127.6 (d, 4 JPC = 0.8 Hz, CHolefin), 128.0 (d, 3 JPC = 2.3 Hz, 1C, C²), 128.6 (d, 3 JPC = 2.3 Hz, 4C, C⁴), 128.8 (s, 2C, C⁴), 128.9 (s, 1C, CH⁵), 129.0 (s, 1C, CH⁶), 130.0 (d, 2 JPC = 23.3 Hz, 1C, CH⁶), 133.5 (s, 1C, CH⁷), 134.1 (d, 2 JPC = 19.5 Hz, 4C, CH⁸), 135.3 (s, 1C, Cquat), 135.9 (d, 2 JPC = 14.3 Hz, 1C, Cquat), 135.9 (s, 1C, Cquat), 136.5 (d, 1 JPC = 10.5 Hz, 2C, Cquat), 142.4 (d, 1 JPC = 21.8 Hz, 1C, Cquat).

³¹P{¹H}-NMR (121 MHz, CDCl₃, 298 K): δ = -13.6 (s).

ATR IR (v in cm⁻¹): 3053 (w), 2960 (w), 2822 (w), 2116 (w), 1583 (w), 1468 (w), 1434 (w), 1387 (w), 1362 (w), 1323 (w), 1292 (w), 1261 (w), 1231 (w), 1213 (w), 1185 (w), 1160 (w), 1111 (s), 1087 (s), 1027 (m), 1016 (s), 998 (m), 969 (s), 933 (w), 925 (w), 901 (w), 801 (m), 763 (s), 745 (s), 693 (s), 666 (w), 645 (m).

EA found% (calc%) for C₃₂H₃₁O₂P: C: 80.23 (80.31), H: 6.53 (6.53).
(E)-2-(2-(diphenylphosphino)styryl) benzaldehyde (17)  
MF = C_{27}H_{21}OP  
MW = 392.43 g/mol  
MP = 133-134 °C

Air stable

To a solution of (E)-(2-(2-(5,5-dimethyl-1,3-dioxan-2-yl)styryl)phenyl)diphenyl-phosphane 28 (1.00 g, 2.09 mmol) in THF (80 mL) was added aqueous HCl (10%, 40 mL). The resulting solution was degassed and stirred for 1 day then NaOH was added as solid until the pH of the aqueous phase was above 13. The aqueous phase was extracted three times with Et2O then the combined organic phases were washed with brine, dried with Na2SO4 and concentrated. The title compound was obtained as yellow solid. Yield: 0.82 g, 100%.

Old method: BuLi (1.6 M in Hexane, 2.2 mL, 3.50 mmol, 1.05 eq.) was added to a solution of diethyl-2-(1,3-doxolane-2-yl) benzylphosphonate 16 (1.00 g, 3.50 mmol, 1.05 eq.) in THF (10 ml) at -78 °C. The resulting mixture was stirred for 20 minutes then a solution of 2-(diphenylphosphino)benzaldehyde 12 (0.97 g, 3.33 mmol, 1 eq.) in THF (4 mL) was added dropwise. The reaction was warmed to room temperature and stirred for 5 hours then diluted with DCM and saturated NH4Cl. The aqueous phase was extracted twice with DCM then the combined organic phases were washed with brine, dried over Na2SO4, filtered and concentrated. The resulting crude product was purified by column chromatography (PET:EtOAc 10:1). The obtained solid was dissolved in acetone (40 mL) and p-TsOH (0.10 g, 0.52 mmol, 0.15 eq.) was added. The resulting solution was degassed for 30 minutes then refluxed for 3 hours. After the yellowish solution was cooled to room temperature, water was added and the acetone was removed under reduced pressure. The yellowish precipitate was filtrated and dried under high vacuum Yield: 0.520 g, 40%.

1H-NMR (500.23 MHz, CDCl3, 298 K): δ = 6.91-6.93 (m, 1H, CHar), 7.25 (dd, J = 7.5 Hz, J = 7.5 Hz, 1H, CHp), 7.32-7.41 (m, 10H, CHar), 7.44 (dd, J = 7.5 Hz, J = 7.5 Hz, 3H, CHp), 7.75 (dd, 3JHH = 16.0 Hz, J = 4.5 Hz, 1H, CHolefin), 7.81-7.85 (m, 2H, CHar), 7.62-7.74 (d, 1H, 3JHH = 16.0 Hz, CHolefin; CHar), 10.23 (s, 1H, CHO).

13C{1H}-NMR (125.78 MHz, CDCl3, 298 K): δ = 126.6 (d, 3JPC = 4.0 Hz, 1C, CCholefin), 127.2 (d, JPC = 2.4 Hz, 1C, CCholefin), 127.9 (s, 1C, CHar), 128.0 (s, 1C, CHar), 128.6 (s, 1C, CHar), 129.0 (d, 3JPC = 7.3 Hz, 4C, CHar), 129.3 (s, 2C, CHar), 129.6 (s, 1C, CHar), 132.4 (s, 1C, CHp), 133.1 (d, 1JPC = 24.5 Hz, 2C, Cquat) 133.3 (s, 1C, Cquat), 133.8 (s, 1C, CHar), 134.1 (s, 1C, CHar), 134.5 (d, 2JPC = 19.6 Hz, 2C, Cquat), 136.6 (d, 2JPC = 10.6 Hz, 1C, Cquat), 140.5 (s, 1C, Cquat), 142.0 (d, 1JPC = 21.6 Hz, 2C, Cquat), 192.9 (s, 1C, CHO).

31P{1H}-NMR (202.50 MHz, CDCl3, 298 K): δ = -12.4 (s).

\[ \text{(E)-2-(2-(diphenylphosphino)styryl) benzaldehyde (17)} \]
ATR IR (ν in cm⁻¹): 3049 (w), 2721 (w), 1686 (m), 1592 (w), 1564 (w), 1477 (w), 1452 (w), 1434 (m), 1406 (w), 1294 (w), 1180 (w), 1091 (w), 1071 (w), 1026 (w), 999 (w), 959 (m), 870 (w), 840 (w), 809 (w), 762 (s), 742 (s), 694 (s), 659 (w), 618 (w).

EA found% (calc%) for C₂₇H₂₁OP: C: 82.39 (82.64), H: 5.40 (5.39).
(E)-1-(2-(2-(diphenylphosphino)styryl)phenyl)-N-methyl-5H-dibenzo[a,d]cycloheptene-5-amine (3)

MF = C_{42}H_{34}NP  

MW = 583.70 g/mol  

MP = 80-81 °C  

Slightly air sensitive

To a solution of (E)-2-(2-(diphenylphosphino)styryl)benzaldehyde 17 (550 mg, 1.40 mmol, 1 eq.) in DCM (10 mL) was added tropNH₂ (290 mg, 1.40 mmol, 1 eq.) and Na₂SO₄ (2.0 g). The resulting suspension was stirred for 2 days, then filtered and concentrated to give crude N-(2-(2-(diphenylphosphino)styryl)benzylidene)-5H-dibenzo[a,d]cycloheptene-5-amine. Due to its high moisture sensitivity purification attempts failed and it was directly used in the reduction step. The crude product was dissolved in DCM/methanol 3:2 (23 mL) and NaBH₄ (106 mg, 2.8 mmol, 2 eq.) was added. The resulting solution was stirred for 1 hour then water was added carefully and the reaction mixture was extracted 4 times with small portions of DCM. The combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated. The resulting crude product was purified by column chromatography (Eluent: PET:EtOAc 5:1) to give the title compound as a white solid. Yield: 600 mg, 73%.

**endo conformer (65%)**:

^{1}H-NMR (500.23 MHz, CD₂Cl₂, 203 K): δ = 2.00 (br, 1H, NH), 3.43 (br, 2H, CH₂benzyl), 4.95 (d, J_{HH} = 10.0 Hz, 1H, CH₂benzyl), 6.65 (s, 2H, CH₂ar), 6.79 (s, 1H, CH₂ar), 7.14-7.76 (m, 27H, CH₂ar, CH₂olefin).

^{13}C{^{1}H}-NMR (125.78 MHz, CD₂Cl₂, 203 K): δ = 49.7 (s, 1C, CH₂benzyl), 69.8 (s, 1C, CH₂benzyl), 122.6 (s, 1C, CH₂ar), 125.9 (s, 1C, CH₂ar), 126.4 (d, J = 4.1 Hz, 1C, CH₂olefin, stilb), 127.2 (s, 2C, CH₂ar), 127.8 (d, J = 2.1 Hz, 1C, CH₂olefin, stilb), 127.9 (s, 1C, CH₂ar), 128.2 (s, 1C, CH₂ar), 129.0 (d, J = 7.1 Hz, 4C, CH₂ar), 129.3 (s, 4C, CH₂ar), 129.5 (s, 1C, CH₂olefin, trop), 130.0 (s, 2C, CH₂ar), 130.4 (s, 2C, CH₂ar), 130.5 (s, 1C, CH₂olefin, trop), 130.8 (s, 2C, CH₂ar), 133.7 (d, J = 22.6 Hz, 2C, C^quat), 133.7 (s, 2C, C^quat), 134.4 (s, 3C, CH₂ar), 134.5 (s, 3C, CH₂ar), 136.0 (d, J = 13.3 Hz, 1C, C^quat), 136.6 (s, 1C, CH₂ar), 136.6 (s, 1C, C^quat), 136.7 (s, 1C, C^quat), 138.0 (s, 1C, C^quat), 140.2 (s, 1C, C^quat), 142.3 (d, J = 21.8 Hz, 1C, C^quat).

^{31}P{^{1}H}NMR (202.50 MHz, CD₂Cl₂) δ = -13.9 (s).

**exo conformer (35%)**: 

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$^1$H-NMR (500.23 MHz, CD$_2$Cl$_2$, 203 K): δ = 2.12 (t, $^3$$J_{HH}$ = 7.4 Hz, 1H, NH), 3.85 (d, $^3$$J_{HH}$ = 7.4 Hz, 2H, CH$_2$$_{benzyl}$), 4.19 (s, 1H, CH$_{benzyl}$), 6.75 (s, 1H, CH$_{ar}$), 6.89 (d, $J$ = 4.4 Hz, 2H, CH$_{ar}$), 7.14-7.76 (m, 27H, CH$_{ar}$, CH$_{olefin}$).

$^{13}$C{$^1$H}NMR (125.78 MHz, CD$_2$Cl$_2$, 203 K): δ = 50.5 (s, 1C, CH$_2$$_{benzyl}$), 61.4 (s, 1C, CH$_{benzyl}$), 122.6 (s, 1C, CH$_{ar}$), 126.1 (s, 2C, CH$_{ar}$), 126.2 (s, 1C, CH$_{ar}$), 126.2 (s, 2C, CH$_{ar}$), 128.0 (s, 1C, CH$_{olefin}$, stilb), 128.2 (s, 1C, CH$_{ar}$), 128.3 (s, 1C, CH$_{ar}$), 128.4 (d, $J$ = 2.6 Hz, 1C, CH$_{olefin}$, stilb), 128.9 (s, 2C, CH$_{ar}$), 129.0 (d, $J$ = 7.0 Hz, 4C, CH$_{ar}$), 129.1 (br, 6C, CH$_{ar}$), 129.5 (s, 1C, CH$_{olefin}$, trop), 130.0 (s, 1C, CH$_{olefin}$, trop), 130.5 (s, 2C, CH$_{ar}$), 133.7 (d, $J$ = 22.6 Hz, 2C, C$_{quat}$), 134.1 (s, 2C, C$_{quat}$), 134.4 (s, 2C, CH$_{ar}$), 134.5 (s, 2C, CH$_{ar}$), 136.0 (d, $J$ = 13.6 Hz, 1C, C$_{quat}$), 136.6 (s, 1C, C$_{quat}$), 136.9 (s, 1C, C$_{quat}$), 138.4 (s, 1C, C$_{quat}$), 140.4 (s, 1C, C$_{quat}$), 142.3 (d, $J$ = 21.5 Hz, 1C, C$_{quat}$).

$^{31}$P{$^1$H}NMR (202.50 MHz, CD$_2$Cl$_2$) δ = -13.5 (s).

ATR IR (v in cm$^{-1}$): 3045 (w), 3010 (w), 2833 (w), 2159 (w), 2034 (w), 1971 (w), 1734 (w), 1583 (w), 1481 (w), 1434 (m), 1370 (w), 1327 (w), 1304 (w), 1239 (w), 1182 (w), 1158 (w), 1088 (w), 1026 (w), 959 (m), 876 (w), 829 (w), 799 (m), 760 (s), 741 (s), 695 (s), 629 (w).

EA found% (calc%) for C$_{42}$H$_{34}$NP: C: 85.56 (86.42), H: 6.06 (5.87), N: 2.35 (2.40).
[RhCl(tropNHCH2StilbPPh2)] (29)

MF = C42H34ClNPRh

MW = 722.06 g/mol

MP = > 220 °C (decomposition)

Air stable

To a solution of [Rh(COD)Cl]2 (126 mg, 0.257 mmol, 0.5 eq.) in DCM (10 mL) was added (E)-1-(2-(2-(diphenylphosphino)styryl) phenyl)-N-methyl-5H-dibenzo[a,d] cycloheptene-5-amine 3 (300 mg, 0.513 mmol, 1 eq.). The resulting yellow solution was stirred overnight and concentrated. Addition of n-hexane precipitated the yellow product complex [Rh(tropNHCH2StilbPPh2)] which was isolated by filtration followed by drying under vacuum. Yield: 360 mg, 97%.

Major isomer (88%):

$^1$H-NMR (500.23 MHz, CDCl3, 298 K): δ = 3.26 (dd, $J = 9.0$ Hz, $J = 11.7$ Hz, 1H, CH$_2$), 3.72 (dd, $J = 13.1$ Hz, $J = 13.1$ Hz, 1H, CH$_2$), 3.79 (d, $J = 9.2$ Hz, 1H, CHolefin, trop), 4.09 (d, $J = 9.2$ Hz, 1H, CHolefin, stilbene), 4.24 (d, $J = 8.3$ Hz, 1H, NH), 4.32 (d, $J = 9.6$ Hz, 1H, CHolefin, stilbene), 4.48 (d, $J = 9.4$ Hz, 1H, CHolefin, trop), 4.64 (d, $J = 8.3$ Hz, 1H, CH$_2$benzyl), 6.99-7.72 (m, 24H, CHar), 8.34-8.37 (m, 2H, CH$^\text{ar}$).

$^{13}$C{$_1$H}-NMR (125.78 MHz, CDCl3, 298 K): δ = 54.4 (s, 1C, CH$_2$), 68.9 (d, $J = 10.1$ Hz, 1C, CHolefin, trop), 69.4 (d, $J = 15.4$ Hz, 1C, CHolefin, stilbene), 73.3 (s, 1C, CH$_2$benzyl), 73.7 (d, $J = 7.4$ Hz, 1C, CHolefin, trop), 75.9 (d, $J = 6.0$ Hz, 1C, CHolefin, trop), 125.2 (s, 1C, CH$^\text{ar}$), 126.0 (s, 1C, CH$^\text{ar}$), 126.3 (d, $J = 6.5$ Hz, 1C, CH$^\text{ar}$), 126.4 (s, 1C, CH$^\text{ar}$), 127.6 (d, $J = 16.1$ Hz, 1C, CH$^\text{ar}$), 128.1 (s, 1C, CH$^\text{ar}$), 128.6 (m, 5C, CH$^\text{ar}$), 128.8 (s, 1C, CH$^\text{ar}$), 128.9 (s, 1C, CH$^\text{ar}$), 129.4 (s, 2C, C$^\text{quat}$), 129.4 (s, 1C, CH$^\text{ar}$), 129.6 (s, 1C, CH$^\text{ar}$), 130.0 (s, 1C, CH$^\text{ar}$), 130.3 (s, 1C, CH$^\text{ar}$), 130.7 (s, 2C, C$^\text{quat}$), 130.9 (s, 1C, CH$^\text{ar}$), 131.0 (s, 1C, CH$^\text{ar}$), 131.1 (s, 2C, CH$^\text{ar}$), 132.9 (d, $J = 9.4$ Hz, 2C, CH$^\text{ar}$), 133.0 (s, 1C, CH$^\text{ar}$), 133.5 (s, 1C, C$^\text{quat}$), 135.2 (s, 2C, C$^\text{quat}$), 135.4 (d, $J = 9.8$ Hz, 2C, C$^\text{quat}$), 139.5 (s, 1C, C$^\text{quat}$), 140.9 (s, 1C, C$^\text{quat}$).

$^{31}$P{$_1$H}-NMR (202.50 MHz, CDCl3, 298 K) δ = 53.1 (d, $^1$J$_{RhP} = 132.0$ Hz).

$^1$H, $^{103}$Rh-NMR (15.81 MHz, CDCl3, 298 K): δ = -7306 (d, $^1$J$_{PRh} = 132.0$ Hz).
Minor isomer (12%):

$^1$H-NMR (500.23 MHz, CDCl$_3$, 298 K): $\delta = 3.58$ (dd, $J = 14.0$, $J = 7.6$ Hz, 1H, C$^\text{olefin}$), 4.15 (d, $J = 12.4$ Hz, 1H, NH), 4.68-4.70 (m, 1H, C$^\text{benzyl}$), 4.81 (d, $J = 9.6$ Hz, 2H, C$H_2$), 4.98 (d, $J = 8.3$ Hz, 1H, C$^\text{olefin}$), 5.18 (d, $J = 8.9$ Hz, 1H, C$^\text{olefin}$), 5.43 (d, $J = 10.3$ Hz, 1H, C$^\text{olefin}$), 6.40 (d, $J = 7.6$ Hz, 1H, C$^\text{ar}$), 6.56 (d, $J = 7.3$ Hz, 1H, C$^\text{ar}$), 6.64-6.66 (m, 1H, C$^\text{ar}$), 6.72-6.78 (m, 5H, C$^\text{ar}$), 6.99-7.72 (m, 18H, C$^\text{ar}$).

$^{13}$C$\{^1$H$\}$-NMR (125.78 MHz, CDCl$_3$, 298 K): $\delta = 56.0$ (s, 1C, C$_2$), 68.9-69.0 (m, 1C, C$^\text{olefin}$), 69.3-69.4 (m, 1C, C$^\text{olefin}$), 73.5 (s, 1C, C$^\text{benzyl}$), 73.7-73.8 (m, 1C, C$^\text{olefin}$), 75.9-76.0 (m, 1C, C$^\text{olefin}$) 125.0-136.6 (m, 36C, C$^\text{ar}$, C$^\text{quat}$).

$^{31}$P$\{^1$H$\}$-NMR (202.50 MHz, CDCl$_3$, 298 K) $\delta = 45.9$ (d, $^1$J$_{RHp} = 129.6$ Hz).

$^1$H, $^{103}$Rh-NMR (15.81 MHz, CDCl$_3$, 298 K): $\delta = -7266$ (d, $^1$J$_{PRh} = 129.6$ Hz).

ATR IR (v in cm$^{-1}$): 3176 (w), 3050 (w), 2998 (w), 2859 (w), 2183 (w), 1584 (w), 1584 (w), 1482 (w), 1463 (w), 1434 (m), 1310 (w), 1270 (w), 1232 (w), 1188 (w), 1156 (w), 1094 (m), 1069 (w), 1000 (w), 936 (w), 908 (w), 865 (w), 837 (w), 747 (s), 694 (s), 639 (m), 618 (w).
[Rh(tropNHCH2StilbPPh2)]OTf (5)

MF = C43H34F3NO3PRhS

MW = 835.68 g/mol

MP = 195-197 °C (decomposition)

Air stable

To a solution of [Rh(tropNHCH2StilbPPh2)]Cl (29) (225 mg, 0.312 mmol, 1 eq.) in DCM (7 mL) was added AgOTf (88 mg, 0.343 mmol, 1.1 eq.). The resulting mixture was stirred overnight and filtered through a plug of celite. DCM was removed under reduced pressure and the residue recrystallised from THF/n-hexane and dried under vacuum. Yield: 160 mg, 61%.

Crystals suitable for X-ray analysis were obtained by slow evaporation of a concentrated solution of 5 in CDCl3.

Major isomer (73%):

$^1$H-NMR (500.23 MHz, CDCl3, 298 K): $\delta$ 3.41 (dd, $J = 12.4$ Hz, $J = 8.2$ Hz, 1H, CH$_2$), 3.74-3.79 (m, 1H, CH$_2$), 4.33 (d, $J = 9.4$ Hz, 1H, CH$_{\text{olefin, trop}}$), 4.36-4.41 (m, 2H, CH$_{\text{olefin, stilb}}$), 4.81 (d, $J = 8.0$ Hz, 1H, CH$_{\text{benzyl}}$), 5.05 (dt, $J = 9.4$ Hz, $J = 2.6$ Hz, 1H, CH$_{\text{olefin, trop}}$), 5.48 (d, br, $J = 8.9$ Hz, 1H, NH), 7.02 (d, $J = 7.3$ Hz, 1H, CH$_{\text{ar}}$), 7.06-7.13 (m, 4H, CH$_{\text{ar}}$), 7.20-7.28 (m, 4H, CH$_{\text{ar}}$), 7.31-7.37 (m, 3H, CH$_{\text{ar}}$), 7.37-7.42 (m, 2H, CH$_{\text{ar}}$), 7.43-7.47 (m, 2H, CH$_{\text{ar}}$), 7.48-7.58 (m, 5H, CH$_{\text{ar}}$), 7.62-7.69 (m, 2H, CH$_{\text{ar}}$), 7.74 (t, $J = 7.7$ Hz, 1H, CH$_{\text{ar}}$), 8.06 (dd, $J = 11.2$ Hz, $J = 7.4$ Hz, 2H, CH$_{\text{ar}}$).

$^{13}$C$\{^1$H$\}$-NMR (125.78 MHz, CDCl3, 298 K): $\delta$ 54.6 (d, $J = 1.4$ Hz, 1C, CH$_2$), 72.0-72.1 (m, 1C, CH$_{\text{olefin, trop}}$), 73.5 (s, 1C, CH$_{\text{benzyl}}$), 75.6 (d, $J = 11.5$ Hz, 1C, CH$_{\text{olefin, stilb}}$), 76.6 (dd, $J = 8.6$ Hz, $J = 2.4$ Hz, 1C, CH$_{\text{olefin, stilb}}$), 78.8 (d, $J = 5.3$ Hz, 1C, CH$_{\text{olefin, trop}}$), 120.3 (q, $J = 32.0$ Hz, 1C, CF$_3$), 126.1 (s, 1C, CH$_{\text{ar}}$), 127.1 (d, $J = 6.7$ Hz, 1C, CH$_{\text{ar}}$), 127.4 (d, $J = 1.9$ Hz, 2C, CH$_{\text{ar}}$), 128.4 (s, 1C, CH$_{\text{ar}}$), 128.5 (s, 1C, CH$_{\text{ar}}$), 129.0 (d, $J = 10.8$ Hz, 4C, CH$_{\text{ar}}$), 129.1 (s, 1C, CH$_{\text{ar}}$), 129.2 (s, 1C, CH$_{\text{ar}}$), 129.5 (s, 1C, CH$_{\text{ar}}$), 130.0 (s, 1C, CH$_{\text{ar}}$), 130.1 (s, 1C, CH$_{\text{ar}}$), 131.1 (d, $^1$J$_{PC} = 48.7$ Hz, 1C, C$_{\text{quat}}$), 131.5 (s, 1C, CH$_{\text{ar}}$), 131.5 (d, $J = 2.4$ Hz, 1C, CH$_{\text{ar}}$), 131.7 (d, $J = 2.6$ Hz, 1C, CH$_{\text{ar}}$), 132.5 (d, $^1$J$_{PC} = 58.1$ Hz, 2C, C$_{\text{quat}}$), 133.1 (s, 1C, CH$_{\text{ar}}$), 133.2 (s, 1C, CH$_{\text{ar}}$), 133.3 (s, 1C, CH$_{\text{ar}}$), 134.0 (s, 1C, C$_{\text{quat}}$), 134.8 (d, $J = 10.6$ Hz, 4C, CH$_{\text{ar}}$), 135.3 (s, 1C, C$_{\text{quat}}$), 135.6 (s, 1C, C$_{\text{quat}}$), 137.4 (s, 1C, C$_{\text{quat}}$), 137.6 (d, $J = 2.2$ Hz, 1C, C$_{\text{quat}}$), 138.9 (s, 1C, C$_{\text{quat}}$), 157.3 (d, $J = 20.6$ Hz, 1C, C$_{\text{quat}}$).

$^{19}$F-NMR (188.31 MHz, CDCl3, 298 K): $\delta = -77.7$ (s).

$^{31}$P$\{^1$H$\}$-NMR (202.50 MHz, CDCl3, 298 K) $\delta = 53.0$ (d, $^1$J$_{RHP}$ = 131.2 Hz).

$^1$H, $^{103}$Rh-NMR (15.81 MHz, CDCl3, 298 K): $\delta = -6934$ (d, $^1$J$_{PRh}$ = 131.2 Hz).
Minor isomer (27%):

$^1$H-NMR (500.23 MHz, CDCl$_3$, 298 K): $\delta = 3.67$ (dd, $J = 14.7$ Hz, $J = 6.9$ Hz, 1H, CH$_2$), 4.86 (dd, $J = 14.7$ Hz, $J = 9.4$ Hz, 1H, CH$_2$), 4.90 (d, $J = 8.5$ Hz, CH$_\text{benzyl}$), 5.20 (dt, $J = 10.5$ Hz, $J = 2.7$ Hz, 1H, CH$_\text{olefin, stilb}$), 5.37 (br, 1H, NH), 5.42 (d, $J = 9.2$ Hz, 1H, CH$_\text{olefin, trop}$), 5.89 (dd, $J = 9.2$ Hz, $J = 2.3$ Hz, 1H, CH$_\text{olefin, trop}$), 5.93 (d, $J = 10.8$ Hz, 1H, CH$_\text{olefin, stilb}$), 6.64 (t, $J = 7.6$ Hz, 1H, CH$_\text{ar}$), 6.67 (t, $J = 7.1$ Hz, 1H, CH$_\text{ar}$), 6.73-6.80 (m, 2H, CH$_\text{ar}$), 6.92 (t, $J = 7.3$ Hz, 1H, CH$_\text{ar}$), 6.95 (t, $J = 6.5$ Hz, 1H, CH$_\text{ar}$), 7.02-7.69 (m, 13H, CH$_\text{ar}$), 7.81 (dd, $J = 11.2$ Hz, $J = 7.6$ Hz, 1H, CH$_\text{ar}$).

$^{13}$C$\{^1$H$\}$-NMR (125.78 MHz, CDCl$_3$, 298 K): $\delta = 56.2$ (s, 1C, CH$_2$), 73.3 (d, $J = 6.7$ Hz, 1C, CH$_\text{olefin, trop}$), 74.5 (s, 1C, CH$_\text{benzyl}$), 75.4 (d, $J = 10.1$ Hz, 1C, CH$_\text{olefin, stilb}$), 76.9 (m, 1C, CH$_\text{olefin, trop}$), 79.1 (d, $J = 14.4$ Hz, 1C, CH$_\text{olefin, stilb}$), 120.3 (q, $J = 320.3$ Hz, 1C, CF$_3$), 125.7-157.4 (m, 36C, CH$_\text{ar}$, C$_\text{quart}$).

$^{19}$F-NMR (188.31 MHz, CDCl$_3$, 298 K): $\delta = -77.7$ (s).

$^{31}$P$\{^1$H$\}$-NMR (202.50 MHz, CDCl$_3$, 298 K): $\delta = 44.9$ (d, $^1$J$_{RhP} = 131.2$ Hz).

$^1$H, $^{103}$Rh-NMR (15.81 MHz, CDCl$_3$, 298 K): $\delta = -6977$ (d, $^1$J$_{PRh} = 131.2$ Hz).

ATR IR (ν in cm$^{-1}$): 3159 (w), 3050 (w), 3010 (w), 1598 (w), 1585 (w), 1492 (w), 1481 (w), 1461 (w), 1436 (w), 1293 (m), 1277 (m), 1225 (s), 1155 (m), 1096 (w), 1070 (w), 1024 (s), 999 (w), 939 (w), 912 (w), 819 (w), 749 (s), 723 (w), 696 (s), 632 (s).
10-(2-(methoxymethoxy)phenyl)5H-dibenzo[a,d]cyclohepten-5-one (20)

$ MF = C_{23}H_{18}O_3 $ 

$ MW = 342.39 \text{ g/mol} $ 

$ MP = 104-105 ^\circ C $ 

Air stable

BuLi (1.55 M in hexane, 102.7 mL, 159 mmol, 1.1 eq.) was added dropwise to an ice cooled solution of (methoxymethoxy)benzene (20.0 mL, 22.0 g, 159 mmol, 1.1 eq.) in THF (300 mL). The solution was stirred at 0 °C for 2 h. B(OEt)$_3$ (27.1 mL, 24.8 g, 239 mmol, 1.65 eq.) was added and the solution stirred for 1 hour. Then aq. NH$_4$Cl was added and the product was hydrolysed for 1 hour. The aqueous phase was extracted three times with ethyl acetate. The organic phases were washed with brine, dried over MgSO$_4$ and the solvent removed under reduced pressure. The crude product was dissolved in DME (500 mL) then H$_2$O (95 mL), tropO$_{18}$ 18 (41.31 g, 144.9 mmol, 1 eq.) and K$_2$CO$_3$ (24.03 g, 174 mmol, 1.2 eq.) were added. The resulting biphasic system was degassed for 20 minutes with argon then Pd(PPh$_3$)$_4$ (1.07 g, 0.927 mmol, 0.0064 eq.) was added under a stream of argon. The reaction mixture was refluxed for 12 hours. After cooling to room temperature ethyl acetate was added and the organic phase separated. The aqueous phase was extracted twice with ethyl acetate and the combined organic phases were washed with brine dried over MgSO$_4$ and the solvents were removed under reduced pressure. The crude product was purified by column chromatography (Eluent DCM) to give the title compound as a yellowish solid. Yield: 41.5 g, 84%.

$ ^1 $H-NMR (300.13 MHz, CDCl$_3$, 298 K): $ \delta = 3.15 $ (s, 3H, CH$_3$), 4.94 (s, 2H, CH$_2$), 7.18 (m, 4H, CH$_{ar}$), 7.51 (m, 7H, CH$_{ar}$), 8.07 (m, 2H, CH$_{ar}$).

$ ^13 $C-$ ^1 $H-NMR (75.48 MHz, CDCl$_3$, 298 K): $ \delta = 56.0 $ (s, 1C, CH$_3$), 94.2 (s, 1C, CH$_2$), 114.9 (s, 1C, CH$_{ar}$), 122.1 (s, 1C, CH$_{ar}$), 128.5 (s, 2C, CH$_{ar}$), 128.7 (s, 1C, CH$_{ar}$), 129.0 (s, 2C, CH$_{ar}$), 129.4 (s, 1C, CH$_{ar}$), 130.5 (s, 1C, CH$_{ar}$), 130.9 (s, 1C, CH$_{ar}$), 131.2 (s, 1C, CH$_{ar}$) 131.6 (s, 1C, CH$_{ar}$), 132.0 (s, 1C, CH$_{ar}$), 133.7 (s, 1C, C$^{quat}$), 134.5 (s, 1C, C$^{quat}$), 136.1 (s, 1C, C$^{quat}$), 139.2 (s, 1C, C$^{quat}$), 139.9 (s, 1C, C$^{quat}$), 140.0 (s, 1C, C$^{quat}$), 154.7 (s, 1C, C$^{quat}$), 195.5 (s, 1C, CO).

ATR IR (v in cm$^{-1}$): 3723 (w), 3627 (w), 2987 (w), 2930 (w), 2816 (w), 1645 (m), 1592 (m), 1486 (m), 1447 (m), 1402 (w), 1312 (m), 1298 (m), 1260 (w), 1239 (m), 1198 (m), 1153 (s), 1116 (w), 1097 (w), 1076 (s), 1046 (m), 1010 (s), 953 (w), 921 (s), 897 (m), 879 (w), 863 (w), 805 (w), 794 (w), 784 (m), 765 (s), 758 (s), 748 (s), 737 (s), 702 (s), 657 (w), 644 (m), 604 (m).

EA found% (calc%) for C$_{23}$H$_{18}$O$_3$: C: 80.39 (80.68), H: 5.45 (5.30).
10-(2-(hydroxy)phenyl)5H-dibenzo[a,d]cyclohepten-5-one (100)

MF = C$_{21}$H$_{14}$O$_2$

MW = 298.33 g/mol

MP = 220 °C

Air stable

10-(2-(methoxymethoxy)phenyl)5H-dibenzo[a,d]cyclohepten-5-one 20 (25.0 g, 73.0 mmol) was dissolved in THF (330 mL) and aq. HCl (3 M, 170 mL) was added. The mixture was refluxed for 3 hours. After cooling to room temperature the mixture was neutralised by careful addition of solid Na$_2$CO$_3$ then extracted 3 times with ethyl acetate. The organic phases were washed with brine, dried over MgSO$_4$ and the solvent was removed under reduced pressure to give the title compound as yellowish product. Yield: 21.4 g, 98%.

$^1$H-NMR (400.13 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 6.91$ (d, $J = 7.8$ Hz, 1H, CH$_{ar}$), 6.97 (t, $J = 7.1$ Hz, 1H, CH$_{ar}$), 7.15 (dd, $J = 4.4$; $J = 2.7$ Hz, 1H, CH$_{ar}$), 7.23 (s, 1H, CHolefin), 7.28 (t, $J = 7.1$ Hz, 1H, CH$_{ar}$), 7.38 (d, $J = 7.4$ Hz, 1H, CH$_{ar}$), 7.54-7.56 (m, 2H, CH$_{ar}$), 7.60 (t, $J = 8.0$ Hz, 1H, CH$_{ar}$), 7.69-7.75 (m, 2H, CH$_{ar}$), 7.90-7.94 (m, 2H, CH$_{ar}$) 9.32 (s, 1H, OH).

$^{13}$C{1H}-NMR (100.61 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 116.6$ (s, 1C, CH$_{ar}$), 120.2 (s, 1C, CH$_{ar}$), 128.9 (s, 1C, CH$_{ar}$), 129.4 (s, 1C, CH$_{ar}$), 129.6 (s, 1C, CH$_{ar}$), 130.2 (s, 1C, CHolefin), 131.1 (s, 1C, C$^{quat}$), 131.7 (s, 1C, CH$_{ar}$), 131.8 (s, 1C, CH$_{ar}$), 132.2 (s, 1C, CH$_{ar}$), 132.3 (s, 1C, CH$_{ar}$), 132.9 (s, 1C, CH$_{ar}$), 134.8 (s, 1C, C$^{quat}$), 136.2 (s, 1C, C$^{quat}$), 139.2 (s, 1C, C$^{quat}$), 140.2 (s, 1C, C$^{quat}$), 140.8 (s, 1C, C$^{quat}$), 155.6 (s, 1C, C$^{quat}$), 195.4 (s, 1C, CO).

ATR IR (v in cm$^{-1}$): 3676 (w), 3296 (br), 2988 (w), 2965 (w), 2896 (w), 1624 (w), 1616 (m), 1582 (m), 1499 (w), 1478 (w), 1444 (m), 1376 (w), 1353 (m), 1327 (m), 1273 (m), 1240 (w), 1160 (w), 1084 (m), 1066 (m), 948 (w), 927 (m), 898 (m), 865 (w), 854 (w), 817 (m), 777 (m), 766 (m), 750 (s), 738 (s), 700 (s), 668 (s), 640 (s), 633 (s), 611 (m).

EA found% (calc%) for C$_{21}$H$_{14}$O$_2$: C: 84.32 (84.54), H: 4.89 (4.73).
10-(2-(Trifluoromethylsulfonyl-oxy)phenyl)5H-dibenzo[a,d]cyclohepten-5-one (21)
MF = C_{22}H_{13}F_{3}O_{4}S
MW = 430.40 g/mol
MP = 88–89 °C
Air stable

10-(2-(Hydroxy)phenyl)5H-dibenzo[a,d]cyclohepten-5-one 100 (21.40 g, 71.73 mmol, 1 eq.) was suspended in dry DCM (200 mL) and pyridine (58.0 mL, 56.7 g, 717 mmol, 10 eq.) added. The mixture was cooled by an ice-salt mixture then Tf₂O (12.67 mL, 21.25 g, 75.32 mmol, 1.05 eq.) was added dropwise and the mixture was stirred overnight, warming slowly to room temperature. The reaction was quenched by the addition of aqueous Na₂CO₃. The organic phase was separated and the aqueous phase extracted twice with DCM. The volatiles were removed under reduced pressure. The crude product was purified by column chromatography (Eluent: DCM) to give the title compound as yellowish oil. When almost all DCM was removed hexane was added, and the mixture was put in the ultrasonic bath. The product precipitated as white solid which was dried under high vacuum. Yield: 30.20 g, 98%.

¹H-NMR (500.23 MHz, CDCl₃, 298 K): δ = 7.35 (d, J = 14.7 Hz, 1H, CHolefin), 7.52 (s, 1H, CHar), 7.72–8.01 (m, 9H, CHar), 8.45 (d, J = 15.4 Hz, 2H, CHar).

¹³C{¹H}-NMR (125.78 MHz, CDCl₃, 298 K): δ = 118.7 (q, J_{FC} = 320.3 Hz, 1C, CF₃), 122.5 (s, 1C, CHar) 129.0 (s, 1C, CHolefin), 129.2 (s, 1C, CHar), 129.4 (s, 1C, CHar), 129.6 (s, 1C, CHar), 129.7 (s, 2C, CHar), 130.2 (s, 1C, CHar), 131.0 (s, 1C, CHar), 131.5 (s, 1C, CHar), 132.1 (s, 1C, CHar), 133.2 (s, 1C, CHar), 133.9 (s, 1C, Cquart), 134.6 (s, 1C, CHar), 135.0 (s, 1C, Cquart), 136.3 (s, 1C, Cquart), 137.6 (s, 1C, Cquart), 140.0 (s, 1C, Cquart), 141.2 (s, 1C, Cquart), 144.6 (s, 1C, Cquart), 195.1 (s, 1C, CO).

¹⁹F-NMR (188.31 MHz, CDCl₃, 298 K): δ = -74.1 (s).

ATR IR (ν in cm⁻¹): 3667 (w), 2988 (w), 2896 (w), 1637 (m), 1590 (w), 1483 (w), 1440 (w), 1412 (m), 1320 (w), 1302 (w), 1247 (m), 1203 (s), 1161 (w), 1137 (s), 1076 (s), 1036 (w), 958 (w), 947 (w), 926 (w), 912 (w), 893 (s), 867 (s), 850 (m), 806 (w), 783 (w), 761 (s), 740 (m), 730 (m), 694 (m), 630 (s).

EA found% (calc%) for C_{22}H_{13}F_{3}O_{4}S: C: 61.38 (61.39), H: 3.19 (3.04).
OH

\[
\begin{align*}
\text{MF} & = C_{22}H_{15}F_{3}O_{4}S \\
\text{MW} & = 432.41 \text{ g/mol} \\
\text{MP} & = 131-132 \degree \text{C} \\
\end{align*}
\]

Air stable

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[Rh(trop_2NH)(P(OPh)_3)]OTf (20 mg, 21 \mu mol) \text{ was suspended in dry THF (exactly 2 mL) and LiHMDS (3.5 mg, 23 \mu mol) was added. The mixture was stirred until a homogenous green solution was obtained. Then 10-}\{(2-(\text{trifluoromethylsulfonyl-}
\text{oxy})\text{phenyl})5\text{H-dibenzo[a,d]cyclohepten-5-one 21 (1.79 g, 4.16 mmol, 1 eq.) was dissolved in dry THF (2 mL) and EtOH (2 mL, 1.53 g, 33.27 mmol, 8 eq.) was added. Then 0.8 mL of the [Rh(trop_2N)(P(OPh)_3)] solution (0.2 mol\%) was added. The resulting solution was stirred overnight then the solvent was removed under reduced pressure. The crude product was purified by column chromatography (DCM) to give the title compound as white powder. Yield: 1.68 g, 93\%.}
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\begin{align*}
\text{1H-NMR (400.13 MHz, CDCl}_3, 333 K):} & \ \\ & \delta = 2.61 \ (d, 3J_{HH} = 4.0 \text{ Hz, 1H, } \text{OH}), \ 5.64 \ (br, 1H, \text{CH}^{\text{benzyl}}), \ 6.95 \ (d, J = 7.8 \text{ Hz, 1H, CH}^{\text{ar}}), \ 7.16 \ (t, J = 7.4 \text{ Hz, 1H, CH}^{\text{ar}}), \ 7.31 \ (t, J = 7.4 \text{ Hz, 1H, CH}^{\text{ar}}), \ 7.40-7.52 \ (m, 7H, CH^{\text{ar}}, \text{CH}^{\text{olefin}}), \ 7.63 \ (dd, J = 5.7 \text{ Hz, J = 3.6 Hz, 1H, CH}^{\text{ar}}), \ 7.82 \ (dd, J = 15.6 \text{ Hz, J = 7.2 Hz, 2H, CH}^{\text{ar}}).
\end{align*}
\]

\[
\begin{align*}
\text{13C{\{^{1}H\}}-NMR (100.61 MHz, CDCl}_3, 333 K):} & \ \\ & \delta = 71.9 \ (br, 1C, \text{CH}^{\text{benzyl}}), \ 119.0 \ (d, \text{J}_{FC} = 320.3 \text{ Hz, 1C, CF}_3), \ 122.1 \ (s, 1C, \text{CH}^{\text{ar}}), \ 122.4 \ (br, 2C, \text{CH}^{\text{ar}}), \ 126.7 \ (br, 2C, \text{CH}^{\text{ar}}), \ 128.1 \ (s, 1C, \text{CH}^{\text{ar}}), \ 128.8 \ (s, 1C, \text{CH}^{\text{ar}}), \ 128.9 \ (s, 1C, \text{CH}^{\text{ar}}), \ 129.6 \ (s, 1C, \text{CH}^{\text{ar}}), \ 129.9 \ (s, 1C, \text{CH}^{\text{ar}}), \ 132.2 \ (s, 1C, \text{C}^{\text{quat}}), \ 133.3 \ (s, 1C, \text{C}^{\text{quat}}), \ 133.4 \ (s, 1C, \text{CH}^{\text{ar}}), \ 133.7 \ (s, 1C, \text{CH}^{\text{ar}}), \ 137.3 \ (s, 1C, \text{C}^{\text{quat}}), \ 137.8 \ (s, 1C, \text{C}^{\text{quat}}), \ 142.2 \ (s, 1C, \text{C}^{\text{quat}}), \ 142.8 \ (s, 1C, \text{C}^{\text{quat}}), \ 148.0 \ (s, 1C, \text{C}^{\text{quat}}).
\end{align*}
\]

\[
\begin{align*}
\text{19F-NMR (188.31 MHz, CDCl}_3, 333 K):} & \ \\ & \delta = -84.8 \ (s).
\end{align*}
\]

ATR IR (v in cm\textsuperscript{-1}): 3568 (w), 3438 (w), 2988 (w), 2895 (w), 2154 (w), 1482 (w), 1443 (w) 1421 (m), 1410 (s), 1382 (w), 1247 (w), 1228 (m), 1199 (s), 1144 (s), 1133 (s), 1121 (m), 1079 (m), 1042 (s), 950 (w), 899 (s), 890 (s), 864 (w), 849 (m), 833 (w), 819 (w), 782 (m), 765 (s), 752 (s), 718 (m), 654 (w), 645 (w), 620 (s).

EA found\% (calc\%) for C\textsubscript{22}H\textsubscript{15}F\textsubscript{3}O\textsubscript{4}S: C: 60.95 (61.11), H: 3.63 (3.50).
2-(5-((5H-dibenzo[a,d]cyclohepten-5-yl)amino)-5H-dibenzo[a,d]cyclohepten-10-yl)phenyl trifluoromethanesulfonate (22)

MF = C_{37}H_{26}F_{3}NO_{3}S

MW = 621.67 g/mol

MP = 88-90 °C

Air stable

To a solution of 10-(2-(trifluoromethylsulfonyloxy)phenyl)5H-dibenzo[a,d]cyclohepten-5-ol 30 (400 mg, 0.925 mmol, 1 eq.) in THF (20 mL) was added N-ethyl-N,N-diisopropyl-amine (1.60 mL, 1.20 g, 9.25 mmol, 10 eq.) then the solution was stirred for 10 minutes. 2,2,2-trifluoroacetic anhydride (0.135 mL, 204 mg, 0.971 mmol, 1.05 eq.) was added. After stirring the reaction mixture for 3 hours the N-ethyl-N,N-diisopropyl-ammonium 2,2,2-trifluoroacetate was observed as a white precipitate. N-(5H-dibenzo[a,d]cyclohepten-5-yl)-amine (201 mg, 0.71 mmol, 1.05 eq.) was added to the mixture which was then stirred overnight. Water was added and the aqueous phase was extracted 3 times with Et_{2}O. The combined organic phases were washed with brine, dried over Na_{2}SO_{4}, filtered and all volatiles were removed under reduced pressure. The residue was purified by column chromatography (eluent: DCM). Yield: 560 mg, 97%.

Old method: To an ice cooled solution of 10-(2-(trifluoromethylsulfonyloxy)phenyl)5H-dibenzo[a,d] cyclohepten-5-ol 30 (4.41 g, 10.2 mmol, 1 eq.) in dry DCM (80 mL) fresh (distilled from 10% w/w P(OPh)_{3}) SOCl_{2} (2.4 mL, 30.6 mmol, 3 eq.) was added dropwise. The solution was warmed to room temperature and stirred for 4 hours. The volatiles were carefully removed under reduced pressure. The residue was dissolved in DCM again and the solvent was removed under reduced pressure. This was repeated twice to remove residual SOCl_{2}. Due to its high moisture sensitivity purification attempts failed and it was directly used in the reduction step. The crude product was dissolved in DCM (20 mL) and added dropwise to a solution of tropNH_{2} (2.32 g, 11.2 mmol, 1.1 eq.), N-ethyl-N,N-diisopropyl-amine (8.7 mL, 51 mmol, 5 eq) in DCM (40 mL) at 0 °C. The reaction was left to stir overnight warming slowly to room temperature. Then the solution was washed with aqueous Na_{2}CO_{3} and brine. The organic phase was dried over Na_{2}SO_{4}, filtered and all volatiles were removed under reduced pressure. The residue was purified by column chromatography (eluent: DCM). Yield: 5.96 g, 94%.

exo-endo conformer (69%):

^{1}H-NMR (700.13 MHz, CDCl_{3}, 298 K): δ = 3.13 (d, ^{3}J_{HH} = 8.3 Hz, 1H, NH), 4.00 (s, 1H, CH^{benzyl}), 5.17 (br, 1H, CH^{benzyl}), 6.96 (d, J = 7.8 Hz, 1H, CH^{ar}), 7.04-7.48 (m, 20H, CH^{ar}, CH^{defra}), 7.63 (d, J = 7.9 Hz, 1H, CH^{ar}), 7.76 (d, J = 7.9 Hz, 1H, CH^{ar}).

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$^{13}$C-$^{1}$H-NMR (176.05 MHz, CDCl₃, 298 K): $\delta = 57.2$ (s, 1C, CH$_{benzyl}$), 65.8 (s, 1C, CH$_{benzyl}$), 118.5 (q, $J_{FC} = 320.2$ Hz, 1C, CF₃), 121.8 (s, 1C, CH$_{ar}$), 122.1 (br, 1C, CH$_{ar}$), 122.5 (s, 1C, CH$_{ar}$), 125.5 (s, 1C, CH$_{ar}$), 126.6 (s, 1C, CH$_{ar}$), 127.0 (s, 1C, CH$_{ar}$), 127.0 (s, 1C, CH$_{ar}$), 128.0 (s, 1C, C$_{olefin}$), 128.0 (s, 1C, CH$_{ar}$), 128.2 (s, 1C, CH$_{ar}$), 128.3 (s, 1C, CH$_{ar}$), 128.6 (s, 1C, CH$_{ar}$), 128.9 (s, 1C, CH$_{ar}$), 129.1 (s, 1C, CH$_{ar}$), 129.3 (s, 1C, CH$_{olefin}$, 129.5 (s, 2C, CH$_{olefin}$), 130.1 (s, 1C, CH$_{ar}$), 130.2 (s, 1C, CH$_{ar}$), 130.5 (s, 1C, CH$_{ar}$), 131.0 (s, 1C, CH$_{ar}$), 132.9 (s, 1C, CH$_{ar}$), 133.2 (s, 1C, C$_{quat}$), 133.3 (s, 1C, CH$_{ar}$), 133.5 (s, 1C, CH$_{ar}$), 133.9 (br, 1C, C$_{quat}$), 134.3 (s, 1C, C$_{quat}$), 136.3 (br, 1C, C$_{quat}$), 137.1 (s, 1C, C$_{quat}$), 139.9 (s, 1C, C$_{quat}$), 140.0 (s, 1C, C$_{quat}$), 141.1 (s, 1C, C$_{quat}$), 141.6 (s, 1C, C$_{quat}$), 147.5 (br, 1C, C$_{quat}$).

$^{19}$F-NMR (188.31 MHz, CDCl₃, 298 K): $\delta = -84.8$ (s).

**endo-exo conformer (14%)**:

$^{1}$H-NMR (700.13 MHz, CDCl₃, 298 K): $\delta = 3.26$ (d, $J = 9.5$ Hz, 1H, NH), 3.93 (s, 1H, CH$_{benzyl}$), 5.10 (d, $J = 8.9$ Hz, 1H, CH$_{benzyl}$), 6.81-7.88 (m, 23H, CH$_{ar}$, CH$_{olefin}$).

$^{13}$C-$^{1}$H-NMR (176.05 MHz, CDCl₃, 298 K): $\delta = 57.6$ (s, 1C, CH$_{benzyl}$), 66.2 (s, 1C, CH$_{benzyl}$), 118.5 (q, $J_{FC} = 320.0$ Hz, 1C, CF₃), 121.7-143.6 (m, 33C, CH$_{ar}$, CH$_{olefin}$, CO$_{olefin}$, C$_{quat}$), 147.3 (s, 1C, C$_{quat}$).

$^{19}$F-NMR (188.31 MHz, CDCl₃, 298 K): $\delta = -84.8$ (s).

**exo-exo conformer (11.5%)**:

$^{1}$H-NMR (700.13 MHz, CDCl₃, 298 K): $\delta = 3.56$ (s, 1H, NH), 4.70 (s, 1H, CH$_{benzyl}$), 4.74 (s, 1H, CH$_{benzyl}$), 6.81-7.88 (m, 23H, CH$_{ar}$, CH$_{olefin}$).

$^{13}$C-$^{1}$H-NMR (176.05 MHz, CDCl₃, 298 K): $\delta = 57.4$ (s, 1C, CH$_{benzyl}$), 66.2 (s, 1C, CH$_{benzyl}$), 118.5 (q, $J_{FC} = 320.0$ Hz, 1C, CF₃), 121.7-143.6 (m, 33C, CH$_{ar}$, CH$_{olefin}$, CO$_{olefin}$, C$_{quat}$), 147.6 (br, 1C, C$_{quat}$).

$^{19}$F-NMR (188.31 MHz, CDCl₃, 298 K): $\delta = -84.8$ (s).

**endo-endo conformer (5.5%)**:

$^{1}$H-NMR (700.13 MHz, CDCl₃, 298 K): $\delta = 3.47$ (t, $J = 6.8$ Hz, 1H, NH), 4.50 (d, $J = 7.4$ Hz, 1H, CH$_{benzyl}$), 4.64 (d, $J = 5.7$ Hz, 1H, CH$_{benzyl}$), 6.81-7.88 (m, 23H, CH$_{ar}$, CH$_{olefin}$).

$^{13}$C-$^{1}$H-NMR (176.05 MHz, CDCl₃, 298 K): $\delta = 67.3$ (s, 1C, CH$_{benzyl}$), 67.5 (s, 1C, CH$_{benzyl}$), 118.4 (q, $J_{FC} = 320.5$ Hz, 1C, CF₃), 121.7-143.6 (m, 33C, CH$_{ar}$, CH$_{olefin}$, CO$_{olefin}$, C$_{quat}$), 147.2 (s, 1C, C$_{quat}$).
$^{19}$F-NMR (188.31 MHz, CDCl$_3$, 298 K): $\delta = -84.8$ (s).

ATR IR ($\nu$ in cm$^{-1}$): 3062 (w), 3016 (w), 2120 (w), 2086 (w), 1718 (w), 1701 (w), 1649 (w), 1587 (w), 1561 (w), 1483 (w), 1438 (w), 1420 (m), 1316 (w), 1246 (w), 1206 (s), 1138 (s), 1108 (w), 1080 (m), 1042 (w), 979 (w), 943 (w), 887 (s), 845 (w), 820 (w), 801 (m), 763 (s), 742 (s), 722 (m), 697 (w), 643 (w), 624 (m).
10-(2-(diphenylphosphane)phenyl)5H-dibenzo[a,d]cyclohepten-5-one (31)

\[
MF = C_{33}H_{23}OP
\]

\[
MW = 466.51 \text{ g/mol}
\]

\[
MP = 161-164 ^\circ \text{C}
\]

Air stable

[Pd(OAc)\textsubscript{2}] (52 mg, 0.23 mmol, 0.025 eq.) was added to a suspension of 1,3-bis(diphenylphosphino)propane (95 mg, 0.23 mmol, 0.025 eq.) in DMSO (1 mL) and stirred for 30 minutes. Then 10-(2-(trifluoromethylsulfonyloxy)phenyl)5H-dibenzo[a,d]cyclohepten-5-one 21 (4.00 g, 9.29 mmol, 1 eq.), diphenylphosphane (2.43 mL, 2.60 g, 13.9 mmol, 1.5 eq.) and \(N\)-ethyl-\(N\)-,\(N\)-diisopropyl-amine (3.21 mL, 2.40 g, 18.6 mmol, 2 eq.) were added all at once. The reaction mixture was stirred at 100°C overnight then the Schlenkflask was fitted with a micro-distillation apparatus and all volatiles were distilled off. After cooling to RT the residual oil was dissolved in DCM (50 mL) and washed 5 times with small portions of 0.5 M HCl. The organic phase was dried over Na\textsubscript{2}SO\textsubscript{4}, filtered then all volatiles were removed under reduced pressure and the residue purified by column chromatography (Eluent: DCM). The oily product was solidified by addition of hexane (10 mL) then the flask was put in the ultrasonic bath. The solvent was decanted and the solid dried under high vacuum. Yield: 3.90 g, 89%.

\(^1\)H-NMR (700.13 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 298 K): \(\delta = 6.67-6.68 \text{(m, 1H, } CH\text{ar}), 6.68 \text{(s, 1H, } CH\text{ar}), 7.15 \text{(dd, } J = 8.0 \text{ Hz, } J = 0.8 \text{ Hz, 1H, } CH\text{ar}), 7.18 \text{(t, } J = 6.6 \text{ Hz, 2H, } CH\text{ar}), 7.22 \text{(ddd, } J = 7.8 \text{ Hz, } J = 3.5 \text{ Hz, } J = 1.0 \text{ Hz, 1H, } CH\text{ar}), 7.29 \text{(s, 1H, } CH\text{olefin}), 7.30-2.35 \text{(m, 5H, } CH\text{ar}), 7.38-7.51 \text{(m, 9H, } CH\text{ar}), 8.03 \text{(dd, } J = 7.7 \text{ Hz, } J = 1.5 \text{ Hz, 1H, } CH\text{ar}), 8.08 \text{(dd, } J = 7.9 \text{ Hz, } J = 1.1 \text{ Hz, 1H, } CH\text{ar}).

\(^{13}\)C\{\(^1\)H\}\text{-NMR (176.05 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 298 K): } \delta = 127.9 \text{(s, 1C, } CH\text{ar}), 128.4-128.5 \text{(m, 4C, } CH\text{ar}), 128.5 \text{(s, 2C, } CH\text{ar}), 128.6 \text{(s, 1C, } CH\text{olefin}), 128.7 \text{(s, 1C, } CH\text{ar}), 128.8 \text{(s, 1C, } CH\text{ar}), 129.1 \text{(s, 1C, } CH\text{ar}), 129.2 \text{(s, 1C, } CH\text{ar}), 130.1 \text{(d, } J = 1.1 \text{ Hz, 1C, } CH\text{ar}), 130.3 \text{(s, 1C, } CH\text{ar}), 130.4 \text{(d, } J = 5.4 \text{ Hz, 1C, } CH\text{ar}), 131.0 \text{(s, 1C, } CH\text{ar}), 131.4 \text{(s, 1C, } CH\text{ar}), 133.7 \text{(s, 1C, } CH\text{ar}), 133.8 \text{(m, 2C, } CH\text{ar}), 134.1 \text{(d, } J = 19.9 \text{ Hz, 2C, } CH\text{ar}), 134.6 \text{(d, } J = 1.3 \text{ Hz, 1C, } CH\text{ar}), 135.7 \text{(d, } J = 1.3 \text{ Hz, 1C, } C\text{quat}), 137.2 \text{(d, } J = 13.2 \text{ Hz, 2C, } C\text{quat}), 137.5 \text{(d, } J = 11.8 \text{ Hz, 1C, } C\text{quat}), 139.1 \text{(s, 1C, } C\text{quat}), 140.5 \text{(s, 1C, } C\text{quat}), 141.2 \text{(d, } J = 6.7 \text{ Hz, 1C, } C\text{quat}), 149.4 \text{(s, 1C, } C\text{quat}), 149.5 \text{(s, 1C, } C\text{quat}), 195.2 \text{(s, 1C, } CO).}

\(^{31}\)P\{\(^1\)H\}\text{-NMR (283.24 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 298 K) } \delta = -13.7 \text{(s).}
ATR IR (v in cm\(^{-1}\)): 3049 (w), 2952 (w), 1643 (m), 1592 (w), 1476 (w), 1459 (w), 1433 (m), 1390 (w), 1348 (w), 1316 (m), 1301 (m), 1262 (w), 1222 (w), 1161 (w), 1128 (w), 1091 (w), 1069 (w), 1025 (w), 997 (w), 963 (w), 944 (w), 925 (w), 905 (m), 873 (m), 804 (w), 772 (w), 747 (s), 694 (s), 643 (m), 632 (m), 609 (m).

EA found\% (calc\%) for C\(_{33}\)H\(_{23}\)OP: C: 84.18 (94.96), H: 5.20 (4.97).
10-(2-(diphenylphosphane)phenyl)5H-dibenzo[a,d] cyclohepten-5-ol (32)

MF = C\textsubscript{33}H\textsubscript{25}OP

MW = 468.52 g/mol

MP = 175-176 °C

Air stable

To a solution of 10-(2-(diphenylphosphane)phenyl)5H-dibenzo[a,d] cyclohepten-5-one 31 (2.00 g, 4.29 mmol, 1 eq.) in THF (10 mL) was added NaBH\textsubscript{4} (243 mg, 6.43mmol, 1.5 eq.) and methanol (1 mL). The resulting suspension was stirred overnight then all volatiles were removed under reduced pressure. The residue was dissolved in DCM and washed with water and brine then the organic phase was dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated. The resulting crude product was purified by column chromatography (Eluent: DCM) to give the title compound as yellowish oil. When almost all DCM was removed hexane was added, and the mixture was put in the ultrasonic bath. The product precipitated as white solid which was collected by decantation and dried under high vacuum. Yield: 1.87 g, 93%.

**endo conformer (72%):**

\[^{1}\text{H}-\text{NMR} (400.13 \text{ MHz, CDCl}_3, 233 \text{ K})\]: 2.87 (br, 1H, OH), 5.35-5.41 (m, 1H, CH\textsuperscript{ar}), 5.91 (d, \textit{J}\textsubscript{HH} = 6.8 Hz, 1H, CH\textsuperscript{benzyl}), 6.56-6.64 (m, 2H, CH\textsuperscript{ar}), 6.99 (t, \textit{J} = 7.8 Hz, 2H, CH\textsuperscript{ar}), 7.04-7.56 (m, 16H, CH\textsuperscript{ar}, CH\textsuperscript{olefin}), 7.60 (t, \textit{J} = 7.4 Hz, 1H, CH\textsuperscript{ar}), 7.67-7.72 (m, 1H, CH\textsuperscript{ar}), 7.76 (d, \textit{J} = 7.3 Hz, 1H, CH\textsuperscript{ar}).

\[^{13}\text{C}\{^{1}\text{H}\}\text{-NMR} (100.61 \text{ MHz, CDCl}_3, 233 \text{ K})\]: 80.3 (s, 1C, CH\textsuperscript{benzyl}), 121.4 (m, 1C, CH\textsuperscript{ar}), 127.5 (s, 1C, CH\textsuperscript{ar}), 128.1 (s, 1C, CH\textsuperscript{ar}), 128.4 (d, \textit{J} = 4.6 Hz, 1C, CH\textsuperscript{ar}), 128.6-129.1 (m, 7C, CH\textsuperscript{ar}, CH\textsuperscript{olefin}), 129.3 (s, 2C, CH\textsuperscript{ar}), 129.6 (m, 1C, CH\textsuperscript{ar}), 130.5 (s, 1C, CH\textsuperscript{ar}), 131.0 (d, \textit{J} = 12.1 Hz, 1C, CH\textsuperscript{ar}), 131.8 (s, 1C, CH\textsuperscript{ar}), 132.0 (s, 1C, C\textsuperscript{quat}), 133.3 (d, \textit{J} = 17.1 Hz, 2C, CH\textsuperscript{ar}), 134.0 (d, \textit{J} = 19.4 Hz, 2C, CH\textsuperscript{ar}), 135.0 (d, \textit{J} = 5.9 Hz, 1C, C\textsuperscript{quat}), 135.3 (s, 1C, C\textsuperscript{quat}), 135.9 (s, 1C, CH\textsuperscript{ar}), 136.9 (d, \textit{J} = 3.0 Hz, 1C, C\textsuperscript{quat}), 138.7 (s, 1C, C\textsuperscript{quat}), 141.2 (s, 1C, C\textsuperscript{quat}), 143.5 (d, \textit{J} = 9.8 Hz, 1C, C\textsuperscript{quat}), 150.6 (d, \textit{J} = 31.3 Hz, 1C, C\textsuperscript{quat}).

\[^{31}\text{P}\{^{1}\text{H}\}\text{-NMR} (161.98 \text{ MHz, CDCl}_3, 233 \text{ K})\] \(\delta = -16.6 \text{ (s).}

**exo-conformer (28%):**

\[^{1}\text{H}-\text{NMR} (400.13 \text{ MHz, CDCl}_3, 233 \text{ K})\]: 2.76 (br, 1H, OH), 5.35-5.41 (m, 1H, CH\textsuperscript{ar}), 5.52 (br, 1H, CH\textsuperscript{benzyl}), 6.42 (d, \textit{J} = 7.5 Hz, 1H, CH\textsuperscript{ar}), 6.74 (d, \textit{J} = 7.8 Hz, 1H, CH\textsuperscript{ar}), 6.86 (t, \textit{J} = 7.5 Hz, 1H, CH\textsuperscript{ar}), 6.93 (t, \textit{J} = 7.4 Hz, 2H, CH\textsuperscript{ar}), 7.04-7.56 (m, 15H, CH\textsuperscript{ar}, CH\textsuperscript{olefin}), 7.67-7.72 (m, 1H, CH\textsuperscript{ar}), 7.81 (d, \textit{J} = 7.8 Hz, 1H, CH\textsuperscript{ar}).
$^{13}$C$\{^1$H$\}$-NMR (100.61 MHz, CDCl$_3$, 233 K): $\delta = 71.2$ (s, 1C, $CH^\text{benzyi}$), 121.4 (m, 1C, $CH^\text{ar}$), 126.3 (d, $J = 24.0$ Hz, 1C, $CH^\text{ar}$), 126.8 (m, 1C, $CH^\text{ar}$), 128.1 (d, $J = 4.6$ Hz, 1C, $CH^\text{ar}$), 128.6-129.1 (m, 7C, $CH^\text{ar}$, $CH^\text{olefin}$), 129.3 (m, 1C, $CH^\text{ar}$), 129.6 (m, 1C, $CH^\text{ar}$), 129.8 (s, 1C, $CH^\text{ar}$), 130.7 (d, $J = 7.3$ Hz, 1C, $CH^\text{ar}$), 132.5 (s, 1C, $C^\text{quat}$), 132.7 (d, $J = 11.0$ Hz, 1C, $C^\text{quat}$), 133.3 (s, 1C, $CH^\text{ar}$), 133.8 (s, 1C, $CH^\text{ar}$), 134.2 (d, $J = 8.0$ Hz, 1C, $CH^\text{ar}$), 134.4-134.5 (m, 2C, $CH^\text{ar}$), 135.3 (s, 1C, $CH^\text{ar}$), 135.8 (m, 1C, $C^\text{quat}$), 136.8 (d, $J = 8.2$ Hz, 2C, $C^\text{quat}$), 138.0 (d, $J = 11.4$ Hz, 1C, $C^\text{quat}$), 141.8 (s, 1C, $C^\text{quat}$), 144.0 (d, $J = 7.5$ Hz, 1C, $C^\text{quat}$), 150.0 (d, $J = 30.4$ Hz, 1C, $C^\text{quat}$).

$^{31}$P$\{^1$H$\}$-NMR (161.98 MHz, CDCl$_3$, 233 K) $\delta = -13.7$ (s).

ATR IR ($\nu$ in cm$^{-1}$): 3560 (w), 3049 (w), 2832 (w), 1583 (w), 1476 (m), 1460 (w), 1431 (w), 1377 (w), 1357 (w), 1320 (w), 1241 (w), 1197 (m), 1124 (w), 1088 (w), 1065 (w), 1047 (m), 1025 (w), 983 (w), 949 (w), 894 (w), 861 (w) 851 (w), 817 (w), 782 (m), 772 (m), 760 (m), 741 (s), 724 (m), 694 (s), 654 (w), 643 (m), 622 (w), 607 (m).
$N$-(5H-dibenzo[a,d]cyclohepten-5-yl)-$N$-(10-(2-(diphenylphosphane)phenyl)5H-dibenzo[a,d]cyclohepten-5-yl)amine (4)

MF = C$_{48}$H$_{36}$NP

MW = 657.78 g/mol

MP = 159-160 °C

Slightly air sensitive

To a solution of 10-(2-(diphenylphosphane)phenyl)5H-dibenzo[a,d]cyclohepten-5-ol 32 (500 mg, 1.07 mmol, 1 eq.) in THF (20 mL) was added $N$-ethyl-$N,N$-disopropyl-amine (1.85 mL, 1.38 g, 10.7 mmol, 10 eq.) then the solution was stirred for 10 minutes. 2,2,2-trifluoroacetic anhydride (0.156 mL, 235 mg, 1.12 mmol, 1.05 eq.) was added. After stirring the reaction mixture overnight the $N$-ethyl-$N,N$-disopropyl-ammonium 2,2,2-trifluoroacetate was observed as a white precipitate. $N$-(5H-dibenzo[a,d]cyclohepten-5-yl)-amine (232 mg, 1.12 mmol, 1.05 eq.) was added to the mixture which was stirred for another 20 hours. Then water was added and the aqueous phase was extracted 3 times with Et$_2$O. The combined organic phases were washed with brine, dried over Na$_2$SO$_4$, filtered and all volatiles were removed under reduced pressure. The residue was purified by column chromatography (stationary phase: neutral alumina, eluent: PET:DCM 1:1). When almost all solvent was removed hexane was added, and the mixture was put in the ultrasonic bath. The product precipitated as white solid which was dried under high vacuum. Yield: 650 mg, 93%.

Old method: [Pd(OAc)$_2$] (21.7 mg, 0.1 mmol, 0.06 eq.) was added to a suspension of 1,3-bis(diphenyl-phosphino)propane (43 mg, 0.1 mmol, 0.06 eq.) in DMSO (2 mL). This mixture was stirred for 30 minutes upon which a pale yellow solution formed. Then the 2-(5-((5H-dibenzo[a,d]cyclohepten-5-yl)amino)-5H-dibenzo[a,d]cyclohepten-10-yl)phenyl trifluoromethanesulfonate 22 (1.08 g, 1.74 mmol, 1 eq.), diphenylphosphane (0.45 mL, 485 mg, 2.6 mmol, 1.5 eq.) and $N$-ethyl-$N,N$-diisopropyl-amine (0.60 mL, 449 mg, 3.5 mmol, 2 eq.) were added all at once. The reaction mixture was stirred at 90°C overnight then all volatiles were distilled off and the residue dissolved in DCM (20 mL). The organic phase was washed three times with water (20 mL) and dried over MgSO$_4$. The DCM was removed under reduced pressure and the residue purified by column chromatography (stationary phase: neutral alumina, eluent: DCM:PET 1:1). When almost all solvent was removed hexane was added, and the mixture was put in the ultrasonic bath. The product precipitated as white solid which was dried under high vacuum. Yield: 830 mg, 72%.

Conformer 1 (26%):

$^1$H-NMR (700.13 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = 3.01 (d, $^1J_{HH}$ = 12.4 Hz, 1H, NH), 3.76 (s, 1H, CH$_{benzyl}$), 5.16 (d, $^1J_{HH}$ = 12.4 Hz, 1H, CH$_{benzyl}$), 6.04-7.98 (m, 33H, CH$^{ar}$, CH$^{olef}$).
$^{13}$C{$_{1}^1$H}  NMR (176.05 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = 56.5 (s, 1C, $CH^{benzyl}$), 65.1 (s, 1C, $CH^{benzyl}$) 120.7-150.4 (m, 46C, CH$^{ar}$, CH$^{olef}$, C$^{quat}$).

$^{31}$P-NMR (283.42 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = -14.4 (s).

Conformer 2 (26%):

$^1$H-NMR (700.13 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = 3.24 (d, $^1J_{HH}$ = 11.5 Hz, 1H, NH), 4.49 (s, 1H, $CH^{benzyl}$), 5.08 (d, $^1J_{HH}$ = 11.5 Hz, 1H, $CH^{benzyl}$), 6.04-7.98 (m, 33H, CH$^{ar}$, CH$^{olef}$).

$^{13}$C{$_{1}^1$H}  NMR (176.05 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = 57.0 (s, 1C, $CH^{benzyl}$), 65.3 (s, 1C, $CH^{benzyl}$) 120.7-150.4 (m, 46C, CH$^{ar}$, CH$^{olef}$, C$^{quat}$).

$^{31}$P-NMR (283.42 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = -15.7 (s).

Conformer 3 (14%):

$^1$H-NMR (700.13 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = 3.56 (dd, $^1J_{HH}$ = 6.6 Hz, 1H, NH), 4.53 (d, $^1J_{HH}$ = 7.1 Hz, 1H, $CH^{benzyl}$), 4.94 (d, $^1J_{HH}$ = 5.8 Hz, 1H, $CH^{benzyl}$), 6.04-7.98 (m, 33H, CH$^{ar}$, CH$^{olef}$).

$^{13}$C{$_{1}^1$H}  NMR (176.05 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = 57.5 (s, 1C, $CH^{benzyl}$), 57.5 (s, 1C, $CH^{benzyl}$) 120.7-150.4 (m, 46C, CH$^{ar}$, CH$^{olef}$, C$^{quat}$).

$^{31}$P-NMR (283.42 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = -16.7 (s).

Conformer 4 (11%):

$^1$H-NMR (700.13 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = 3.39 (d, $^1J_{HH}$ = 11.9 Hz, 1H, NH), 3.74 (s, 1H, $CH^{benzyl}$), 5.04 (d, $^1J_{HH}$ = 12.4 Hz, 1H, $CH^{benzyl}$), 6.04-7.98 (m, 33H, CH$^{ar}$, CH$^{olef}$).

$^{13}$C{$_{1}^1$H}  NMR (176.05 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = 57.0 (s, 1C, $CH^{benzyl}$), 65.4 (s, 1C, $CH^{benzyl}$) 120.7-150.4 (m, 46C, CH$^{ar}$, CH$^{olef}$, C$^{quat}$).

$^{31}$P-NMR (283.42 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = -14.5 (s).

Conformer 5 (10%):

$^1$H-NMR (700.13 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ = 2.49 (dd, $^1J_{HH}$ = 4.0 Hz, $^1J_{HH}$ = 2.7 Hz 1H, NH), 4.57 (d, $^1J_{HH}$ = 4.0 Hz, 1H, $CH^{benzyl}$), 4.68 (d, $^1J_{HH}$ = 2.7 Hz, 1H, $CH^{benzyl}$), 6.04-7.98 (m, 33H, CH$^{ar}$, CH$^{olef}$).
$^{13}$C-$^{1}$H-NMR (176.05 MHz, CD$_2$Cl$_2$, 233 K): $\delta = 66.4$ (s, 1C, CH$_{\text{benzyl}}$), 66.6 (s, 1C, CH$_{\text{benzyl}}$) 120.7-150.4 (m, 46C, CH$_{\text{ar}}$, CH$_{\text{olef}}$, C$_{\text{olef}}$, C$_{\text{quat}}$).

$^{31}$P-NMR (283.42 MHz, CD$_2$Cl$_2$, 233 K): $\delta = -14.7$ (s).

Conformer 6 (9%):

$^1$H-NMR (700.13 MHz, CD$_2$Cl$_2$, 233 K): $\delta = 4.09$ (s, 1H, CH$_{\text{benzyl}}$), 4.32 (dd, $^1J_{HH} = 11.1$ Hz, $^1J_{HH} = 4.9$ Hz 1H, NH), 5.13 (d, $^1J_{HH} = 11.5$ Hz, 1H, CH$_{\text{benzyl}}$), 6.04-7.98 (m, 33H, CH$_{\text{ar}}$, CH$_{\text{olef}}$).

$^{13}$C-$^{1}$H-NMR (176.05 MHz, CD$_2$Cl$_2$, 233 K): $\delta = 57.8$ (s, 1C, CH$_{\text{benzyl}}$), 65.9 (s, 1C, CH$_{\text{benzyl}}$) 120.7-150.4 (m, 46C, CH$_{\text{ar}}$, CH$_{\text{olef}}$, C$_{\text{olef}}$, C$_{\text{quat}}$).

$^{31}$P-NMR (283.42 MHz, CD$_2$Cl$_2$, 233 K): $\delta = -18.0$ (s).

Conformer 7 (3%):

$^1$H-NMR (700.13 MHz, CD$_2$Cl$_2$, 233 K): $\delta = 3.08$ (d, $^1J_{HH} = 12.4$ Hz, 1H, NH), 3.64 (s, 1H, CH$_{\text{benzyl}}$), 4.99 (d, $^1J_{HH} = 11.9$ Hz, 1H, CH$_{\text{benzyl}}$), 6.04-7.98 (m, 33H, CH$_{\text{ar}}$, CH$_{\text{olef}}$).

$^{13}$C-$^{1}$H-NMR (176.05 MHz, CD$_2$Cl$_2$, 233 K): $\delta = 56.6$ (s, 1C, CH$_{\text{benzyl}}$), 64.9 (s, 1C, CH$_{\text{benzyl}}$) 120.7-150.4 (m, 46C, CH$_{\text{ar}}$, CH$_{\text{olef}}$, C$_{\text{olef}}$, C$_{\text{quat}}$).

$^{31}$P-NMR (283.42 MHz, CD$_2$Cl$_2$, 233 K): $\delta = -14.3$ (s).

Conformer 8 (1%):

$^1$H-NMR (700.13 MHz, CD$_2$Cl$_2$, 233 K): $\delta = 3.52$ (dd, $^1J_{HH} = 6.6$ Hz, $^1J_{HH} = 6.6$ Hz 1H, NH), 4.29 (d, $^1J_{HH} = 6.6$ Hz, 1H, CH$_{\text{benzyl}}$), 4.49 (d, $^1J_{HH} = 6.6$ Hz, 1H, CH$_{\text{benzyl}}$), 6.04-7.98 (m, 33H, CH$_{\text{ar}}$, CH$_{\text{olef}}$).

$^{13}$C-$^{1}$H-NMR (176.05 MHz, CD$_2$Cl$_2$, 233 K): $\delta = 57.3$ (s, 1C, CH$_{\text{benzyl}}$), 66.3 (s, 1C, CH$_{\text{benzyl}}$) 120.7-150.4 (m, 46C, CH$_{\text{ar}}$, CH$_{\text{olef}}$, C$_{\text{olef}}$, C$_{\text{quat}}$).

$^{31}$P-NMR (283.42 MHz, CD$_2$Cl$_2$, 233 K): $\delta = -15.4$ (s).

ATR IR (v in cm$^{-1}$): 3044 (w), 3018 (w), 2956 (w), 2920 (w), 2853 (w), 1584 (w), 1479 (w), 1458 (w), 1433 (m), 1305 (w), 1261 (w), 1244 (w) (w), 1182 (w), 1157 (w), 1072 (w), 1036 (w), 1027 (w), 946 (w), 894 (w), 830 (w), 797 (m), 764 (s), 740 (s), 694 (s), 667 (m), 643 (w), 628 (w), 606 (m).
[RhCl(tropNHtropPhPPh2)] (33)

MF = C48H36ClNPRh

MW = 796.14 g/mol

MP = >220 °C (decomposition)

Air stable

[Rh(Cl)(COD)]2 (273 mg, 0.55 mmol, 0.5 eq.) was added to a solution of N-(5H-dibenzo[a,d]cyclohepten-5-yl)-N-(10-(2-(diphenylphosphane)phenyl)5H-dibenzo[a,d]cyclohepten-5-yl)amine 4 (730 mg, 1.11 mmol, 1 eq.) in DCM (10 mL). The reaction was left standing overnight. All volatiles were removed under reduced pressure and the residue was recrystallised from THF/hexane and a clean mixture of two isomers was obtained as orange precipitate. The solvent was decanted off and the precipitate dried under high vacuum. Yield: 810 mg, 92%.

Major isomer (55%):

$^1$H-NMR (700.13 MHz, CDCl3, 298 K): $\delta = 4.54$ (d, $J = 6.1$ Hz, 1H, NH), 4.70 (d, $J = 8.6$ Hz, 1H, $CH^{benzyl}$), 4.85 (d, $J = 8.4$ Hz, 1H, $CH^{benzyl}$), 4.91 (t, $J = 2.1$ Hz, 1H, $CH^{olefin}$), 5.00 (dt, $J_{HH} = 9.5$ Hz, $J = 2.5$ Hz, 1H, $CH^{olefin}$), 5.33 (d, $J_{HH} = 9.5$ Hz, 1H, $CH^{olefin}$), 6.56 (d, $J = 7.5$ Hz, 1H, CHar), 6.71 (d, $J = 7.3$ Hz, 1H, CHar), 6.73-6.78 (m, 2H, CHar), 6.78-6.84 (m, 2H, CHar), 6.98 (td, $J = 7.3$ Hz, $J = 0.9$ Hz, 1H, CHar), 7.03 (d, $J = 6.6$ Hz, 1H, CHar), 7.06 (td, $J = 7.5$ Hz, $J = 1.1$ Hz, 1H, CHar), 7.10 (td, $J = 7.5$ Hz, $J = 0.8$ Hz, 1H, CHar), 7.13 (d, $J = 6.6$ Hz, 1H, CHar), 7.17-7.25 (m, 2H, CHar), 7.28-7.31 (m, 2H, CHar), 7.31-7.37 (m, 3H, CHar), 7.42-7.45 (m, 1H, CHar), 7.50-7.58 (m, 7H, CHar), 7.83 (dd, $J = 7.7$ Hz, $J = 3.5$ Hz, 1H, CHar), 7.89 (d, $J = 8.1$ Hz, 1H, CHar), 8.24-8.28 (m, 2H, CHar).

$^{13}$C{1H}NMR (176.06 MHz, CDCl3, 298 K): $\delta = 66.8$ (d, $J = 7.0$ Hz, 1C, CHolefin), 70.3 (d, $J = 11.5$ Hz, 1C, CHolefin), 71.8 (d, $J = 1.2$ Hz, 1C, CHbenzyl), 73.2 (dd, $J = 12.5$ Hz, $J = 1.7$ Hz, 1C, CHolefin), 74.2 (d, $J = 1.7$ Hz, 1C, CHbenzyl), 84.5 (dd, $J = 8.0$ Hz, $J = 1.8$ Hz, 1C, Colefin), 125.2 (d, $J = 5.0$ Hz, 2C, CHar), 125.7 (d, $J = 1.9$ Hz, 2C, CHar), 126.6 (d, $J = 7.0$ Hz, 1C, CHar), 127.0 (s, 1C, CHar), 127.4 (s, 1C, CHar), 127.8 (s, 1C, CHar), 128.0 (s, 1C, CHar), 128.2 (s, 1C, CHar), 128.3 (s, 1C, CHar), 128.4 (s, 1C, CHar), 128.6 (s, 1C, CHar), 128.6 (d, $J = 1.9$ Hz, 2C, CHar), 128.7 (s, 1C, CHar), 128.8 (s, 1C, CHar), 129.0 (s, 1C, CHar), 129.4 (s, 1C, CHar), 129.5 (s, 1C, CHar), 129.8 (d, $J = 2.4$ Hz, 1C, CHar), 130.5 (d, $J = 2.4$ Hz, 1C, CHar), 130.9 (d, $J = 2.9$ Hz, 1C, CHar), 132.4 (d, $J_{PC} = 13.9$ Hz, 2C, Cquat), 132.4 (d, $J = 8.9$ Hz, 2C, CHar), 132.7 (d, $J_{PC} = 16.8$ Hz, 1C, Cquat), 132.8 (s, 1C, CHar), 133.2 (s, 1C, CHar), 133.5 (s, 1C, Cquat), 133.6 (dd, $J_{PC} = 46.8$ Hz, $J = 1.8$ Hz, 1C, Cquat), 134.4 (s, 1C, Cquat), 134.6 (s, 1C, Cquat), 135.2 (d, $J = 10.1$ Hz, 2C, CHar), 135.3 (s, 1C, Cquat), 135.9 (d, $J = 1.4$ Hz, 1C, Cquat), 139.1 (s, 1C, Cquat), 139.8 (s, 1C, Cquat), 155.1 (d, $J = 21.3$ Hz, 1C, Cquat).
$^{31}$P-$^1$H-NMR (283.42 MHz, CDCl$_3$, 298 K) $\delta = 52.6$ (d, $^1J_{RhP} = 132.0$ Hz).

$^1$H, $^{103}$Rh-NMR (15.81 MHz, CDCl$_3$, 298 K): $\delta = -7421$ (d, $^1J_{PRh} = 132.0$ Hz).

Minor isomer (45%):

$^1$H-NMR (700.13 MHz, CDCl$_3$, 298 K): $\delta = 4.51$ (d, $J = 9.2$ Hz, 1H, CH$_{olefin}$), 4.62-4.64 (m, 2H, NH, CH$_{olefin}$), 4.80 (d, $J = 8.8$ Hz, 1H, CH$_{benzyl}$), 4.82 (d, $J = 7.6$ Hz, 1H, CH$_{benzyl}$), 4.84 (s, 1H, CH$_{olefin}$), 6.54 (d, $J = 7.7$ Hz, 1H, CH$_{ar}$) 6.67-7.65 (m, 23H, CH$_{ar}$) 6.68-6.73 (m, 1H), 7.76-7.77 (m, 3H, CH$_{ar}$).

$^{13}$C-$^1$H-NMR (176.06 MHz, CDCl$_3$, 298 K): $\delta = 68.6$ (d, $J = 11.6$ Hz, 1C, CH$_{olefin}$), 72.6 (d, $J = 6.7$ Hz, 1C, CH$_{olefin}$), 72.7 (s, 1C, CH$_{benzyl}$), 74.6 (s, 1C, CH$_{benzyl}$), 75.4 (dd, $J = 7.8$ Hz, $J = 2.4$ Hz, 1C, CH$_{olefin}$), 83.0 (dd, $J = 13.7$ Hz, $J = 1.9$ Hz, 1C, C$_{olefin}$), 124.7 (s, 1C, CH$_{pek}$), 125.6 (s, 1C, CH$_{pek}$), 125.8 (s, 1C, CH$_{pek}$), 126.1 (s, 1C, CH$_{pek}$), 126.6 (d, $J = 9.1$ Hz, 2C, CH$_{pek}$), 126.8 (s, 1C, CH$_{pek}$), 127.7 (s, 1C, CH$_{pek}$), 128.1 (s, 1C, CH$_{pek}$), 128.2 (s, 1C, CH$_{pek}$), 128.2 (s, 1C, CH$_{pek}$), 128.3 (s, 1C, CH$_{pek}$), 128.4 (s, 1C, CH$_{pek}$), 128.6 (s, 1C, CH$_{pek}$), 128.7 (s, 1C, CH$_{pek}$), 130.1 (d, $J = 3.8$ Hz, 2C, CH$_{pek}$), 130.8 (d, $J = 2.4$ Hz, 1C, CH$_{pek}$), 130.8 (m, 1C, CH$_{pek}$), 131.2 (d, $J = 48.0$ Hz, 2C, CH$_{pek}$), 131.4 (d, $J = 14.8$ Hz, 2C, CH$_{pek}$), 131.6 (s, 1C, CH$_{pek}$), 132.8 (d, $^1J_{PC} = 50.8$ Hz, 1C, C$_{quat}$), 133.0 (s, 1C, C$_{quat}$), 133.0 (s, 1C, C$_{quat}$), 133.4 (s, 1C, CH$_{pek}$), 133.5 (s, 1C, CH$_{pek}$), 134.7 (s, 1C, C$_{quat}$), 134.7 (s, 1C, C$_{quat}$), 135.1 (d, $^1J_{PC} = 15.3$ Hz, 2C, C$_{quat}$), 135.2-135.3 (m, 2C, C$_{quat}$), 135.0 (d, $J = 1.6$ Hz, 1C, C$_{quat}$), 138.7 (s, 1C, C$_{quat}$), 139.2 (s, 1C, C$_{quat}$), 156.7 (d, $J = 21.5$ Hz, 1C, C$_{quat}$).

$^{31}$P-$^1$H-NMR (283.42 MHz, CDCl$_3$, 298 K) $\delta = 59.6$ (d, $^1J_{RhP} = 134.3$ Hz).

$^1$H, $^{103}$Rh-NMR (15.81 MHz, CDCl$_3$, 298 K): $\delta = -7426$ (d, $^1J_{PRh} = 134.3$ Hz).

ATR IR (v in cm$^{-1}$): 3164 (w), 3045 (w), 2947 (w), 2919 (w), 1595 (w), 1584 (w), 1487 (m), 1467 (m), 1433 (m), 1327 (w), 1307 (w), 1256 (w), 1224 (w), 1187 (w), 1156 (w), 1133 (w), 1118 (w), 1090 (m), 1061 (m), 977 (m), 942 (w), 910 (w), 870 (w), 859 (w), 847 (w), 808 (w), 745 (s), 719 (s), 698 (s), 671 (w), 639 (m), 617 (w), 606 (s).
[Rh(tropNHtropPhPPh2)]OTf (34)

MF = C49H36F3NO3PRhS

MW = 909.75 g/mol

MP = 206-208 (decomposition)

Air stable

To a solution of [RhCl(tropNHtropPhPPh2)] (220 mg, 0.276 mmol, 1 eq.) in DCM (5 mL) was added AgOTf (85 mg, 0.33 mmol, 1.2 eq.). The resulting suspension was stirred overnight then filtered over celite. The solvent was removed under reduced pressure and the residue was recrystallised from THF/hexane and the obtained orange powder was dried under high vacuum. Yield: 231 mg, 92%.

Major isomer (70%):

$^1$H-NMR (500.23 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 5.18$ (d, $J = 7.9$ Hz, 1H, $CH$\textsubscript{benzyl}), 5.40 (d, $J = 4.8$ Hz, 1H, NH), 5.48-5.51 (m, 3H, $CH$\textsubscript{benzyl}, $CH$\textsubscript{olefin}), 5.96 (dt, $J = 9.4$ Hz, $J = 2.8$ Hz, 1H, $CH$\textsubscript{olefin}), 6.75 (d, $J = 7.4$ Hz, 1H, $CH$\textsubscript{ar}), 6.82-6.83 (m, 2H, $CH$\textsubscript{ar}), 6.87-6.90 (m, 2H, $CH$\textsubscript{ar}), 7.16 (t, $J = 7.4$ Hz, 1H, $CH$\textsubscript{ar}), 7.19-7.75 (m, 21H, $CH$\textsubscript{ar}), 7.81-7.84 (m, 2H, $CH$\textsubscript{ar}).

$^{13}$C\{$^1$H\}-NMR (125.78 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 71.1$ (s, 1C, $CH$\textsubscript{benzyl}), 73.5 (s, 1C, $CH$\textsubscript{benzyl}), 80.9 (d, $J = 12.0$ Hz, 1C, $CH$\textsubscript{olefin}), 81.7 (d, $J = 13.0$ Hz, 1C, $CH$\textsubscript{olefin}), 90.0 (d, $J = 6.2$ Hz, 1C, $CH$\textsubscript{olefin}), 120.3 (q, $J = 320.3$ Hz, 1C, $CF$), 126.3 (s, 1C, $CH$\textsubscript{ar}), 126.4 (s, 1C, $CH$\textsubscript{ar}), 126.9 (s, 1C, $CH$\textsubscript{ar}), 127.2 (s, 1C, $CH$\textsubscript{ar}), 127.6 (s, 1C, $CH$\textsubscript{ar}), 127.8 (s, 1C, $CH$\textsubscript{ar}), 127.9 (s, 1C, $CH$\textsubscript{ar}), 128.0 (s, 1C, $CH$\textsubscript{ar}), 128.4 (s, 1C, $CH$\textsubscript{ar}), 128.7 (s, 1C, $CH$\textsubscript{ar}), 128.8 (s, 1C, $CH$\textsubscript{ar}), 129.4 (s, 1C, $CH$\textsubscript{ar}), 129.4 (d, $J = 10.5$ Hz, 2C, $CH$\textsubscript{ar}), 129.8 (s, 1C, $CH$\textsubscript{ar}), 129.8 (d, $J = 10.0$ Hz, 2C, $CH$\textsubscript{ar}), 129.9 (s, 1C, $CH$\textsubscript{ar}), 130.2 (s, 1C, $CH$\textsubscript{ar}), 131.0 (s, 1C, $CH$\textsubscript{ar}), 131.1 (d, $J = 2.4$ Hz, 1C, $CH$\textsubscript{ar}), 131.8 (d, $J = 2.6$ Hz, 1C, $CH$\textsubscript{ar}), 131.9 (d, $J = 2.2$ Hz, 1C, $CH$\textsubscript{ar}), 131.9 (d, $J = 9.6$ Hz, 2C, $CH$\textsubscript{ar}), 133.0 (s, 1C, $CH$\textsubscript{ar}), 133.6 (m, 2C, $CH$\textsubscript{ar}, $C$\textsubscript{quat}), 134.4 (d, $J = 10.3$ Hz, 2C, $CH$\textsubscript{ar}), 134.5 (s, 1C, $C$\textsubscript{quat}), 134.8-135.0 (m, 1C, $CH$\textsubscript{ar}), 135.3 (s, 2C, $C$\textsubscript{quat}), 135.7 (d, $J = 2.2$ Hz, 1C, $C$\textsubscript{quat}), 136.2 (s, 1C, $C$\textsubscript{quat}), 137.2 (s, 1C, $C$\textsubscript{quat}), 137.6 (s, 1C, $C$\textsubscript{quat}), 154.3 (d, $J_{PC} = 21.8$ Hz, 1C, $C$\textsubscript{quat}).

$^{19}$F-NMR (188.31 MHz, CD$_2$Cl$_2$, 298 K): $\delta = -77.9$ (s).

$^{31}$P\{$^1$H\}-NMR (202.50 MHz, CD$_2$Cl$_2$, 298 K) $\delta = 52.8$ (d, $J_{RHP} = 133.5$ Hz).

$^1$H, $^{103}$Rh-NMR (15.81 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 7103$ (d, $J_{PPrh} = 133.5$ Hz).
Minor isomer (30%):

$^1$H-NMR (500.23 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 4.91$ (s, 1H, CH$^{\text{olefin}}$), 5.01 (d, $J = 9.2$ Hz, 1H, CH$^{\text{olefin}}$), 5.28 (d, $J = 7.0$ Hz, 1H, CH$^{\text{benzyl}}$), 5.32-5.36 (m, 1H, NH), 5.48-5.51 (m, 2H, CH$^{\text{olefin}}$, CH$^{\text{benzyl}}$), 6.57 (d, $J = 7.7$ Hz, 1H, CH$^{\text{ar}}$), 6.75 (d, $J = 7.2$ Hz, 1H, CH$^{\text{ar}}$), 6.81-6.85 (m, 3H, CH$^{\text{ar}}$), 6.95 (d, $J = 7.3$ Hz, 1H, CH$^{\text{ar}}$), 7.06 (t, $J = 7.4$ Hz, 1H, CH$^{\text{ar}}$), 7.19-7.75 (m, 21H, CH$^{\text{ar}}$), 7.81-7.84 (m, 2H, CH$^{\text{ar}}$).

$^{13}$C($^1$H)-NMR (125.78 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 72.3$ (s, 1C, CH$^{\text{benzyl}}$), 73.9 (s, 1C, CH$^{\text{benzyl}}$), 78.8 (d, $J = 6.7$ Hz, 1C, CH$^{\text{olefin}}$), 81.3 (d, $J = 7.4$ Hz, 1C, CH$^{\text{olefin}}$), 81.7 (d, $J = 13.0$ Hz, 1C, CH$^{\text{olefin}}$), 93.8 (m, 1C, CH$^{\text{olefin}}$), 120.3 (q, $J = 320.3$ Hz, 1C, CH$_3$), 126.6 (s, 1C, CH$^{\text{ar}}$), 126.8 (s, 1C, CH$^{\text{ar}}$), 126.9 (s, 1C, CH$^{\text{ar}}$), 127.1 (s, 1C, CH$^{\text{ar}}$), 127.6 (s, 1C, CH$^{\text{ar}}$), 127.8 (s, 1C, CH$^{\text{ar}}$), 127.9 (s, 1C, CH$^{\text{ar}}$), 128.0 (s, 1C, CH$^{\text{ar}}$), 128.1 (s, 1C, CH$^{\text{ar}}$), 128.1 (s, 1C, CH$^{\text{ar}}$), 128.2 (s, 1C, CH$^{\text{ar}}$), 128.2 (s, 1C, CH$^{\text{ar}}$), 128.3 (s, 1C, CH$^{\text{ar}}$), 128.4 (s, 1C, CH$^{\text{ar}}$), 128.6 (s, 1C, CH$^{\text{ar}}$), 128.7 (s, 1C, CH$^{\text{ar}}$), 128.9 (s, 1C, CH$^{\text{ar}}$), 129.2 (s, 1C, CH$^{\text{ar}}$), 129.3 (s, 1C, CH$^{\text{ar}}$), 129.3 (s, 1C, CH$^{\text{ar}}$), 130.3 (s, 1C, CH$^{\text{ar}}$), 130.5 (s, 1C, CH$^{\text{ar}}$), 130.8 (d, $J = 2.2$ Hz, 1C, CH$^{\text{ar}}$), 131.3-131.5 (m, 1C, CH$^{\text{quat}}$), 131.9 (d, $J = 2.2$ Hz, 1C, CH$^{\text{ar}}$), 132.0 (d, $J = 2.4$ Hz, 1C, CH$^{\text{ar}}$), 133.1 (d, $J = 9.6$ Hz, 2C, CH$^{\text{ar}}$), 133.6 (m, 2C, CH$^{\text{ar}}$, CH$^{\text{quat}}$), 134.0 (d, $^1$J$^{\text{PC}}$ = 9.1 Hz, 2C, CH$^{\text{quat}}$), 134.2 (d, $J = 10.3$ Hz, 2C, CH$^{\text{ar}}$), 134.2 (m, 1C, CH$^{\text{quat}}$), 134.8-135.0 (m, 3C, CH$^{\text{ar}}$, CH$^{\text{quat}}$), 136.3 (s, 1C, CH$^{\text{quat}}$), 136.5 (d, $J = 2.9$ Hz, 1C, CH$^{\text{quat}}$), 136.7 (s, 1C, CH$^{\text{quat}}$), 137.2 (s, 1C, CH$^{\text{quat}}$), 155.9 (d, $^2$J$^{\text{PC}}$ = 21.6 Hz, 1C, CH$^{\text{quat}}$).

$^{19}$F-NMR (188.31 MHz, CD$_2$Cl$_2$, 298 K): $\delta = -77.9$ (s).

$^{31}$P($^1$H)-NMR (202.50 MHz, CD$_2$Cl$_2$, 298 K) $\delta = 59.8$ (d, $^1$J$_{^1\text{H}^\text{Rh}}$ = 137.3 Hz).

$^1$H, $^{103}$Rh-NMR (15.81 MHz, CD$_2$Cl$_2$, 298 K): $\delta = -7146$ (d, $^1$J$_{^1\text{H}^\text{Rh}}$ = 137.3 Hz).

ATR IR (ν in cm$^{-1}$): 3050 (w), 2959 (w), 1598 (w), 1584 (w), 1481 (w), 1467 (w), 1435 (w), 1333 (w), 1276 (m), 1253 (m), 1224 (m), 1158 (m), 1097 (w), 1028 (s), 996 (w), 945 (w), 877 (w), 845 (w), 808 (w), 753 (s), 719 (w), 696 (m), 636 (s).
[Rh(tropNHtropPhPPh2)] (35)

MF = C_{48}H_{35}NPRh

MW = 759.68 g/mol

MP = >220 °C

Air sensitive

To a suspension of [RhCl(tropNHtropPhPPh2)] 33 (137 mg, 0.172 mmol, 1 eq) in THF (2 mL) t-BuOK (19.5 mg, 0.174 mmol, 1.01 eq.) was added and the resulting deep green solution stirred for 20 minutes. Toluene (1 mL) was added and all volatiles were removed under reduced pressure. Again toluene (1 mL) was added and all volatiles were removed under reduced pressure. The residue was dissolved in THF and filtered over celite. The resulting solution was concentrated to 1 mL under reduced pressure, layered with hexane and stored in the fridge of the glove box. A green precipitate was obtained. The mother liquor was decanted off and the precipitate dried under high vacuum. Yield: 103 mg, 79%.

$^{1}$H-NMR (500.23 MHz, [D8]THF, 298 K): $\delta = 4.96$ (d, $J = 12.7$ Hz, 1H, $CH^{benzyl}$), 5.14 (d, $J = 14.1$ Hz, 1H, $CH^{benzyl}$), 5.24 (dt, $J = 9.3$ Hz, $J = 3.5$ Hz, 1H, $CH^{olefin}$), 5.33 (ddd, $J = 9.3$ Hz, $J = 4.0$ Hz, $J = 1.2$ Hz, 1H, $CH^{olefin}$), 5.37 (t, $J = 2.7$ Hz, 1H, $CH^{olefin}$), 6.50-6.52 (m, 1H, $CH^{ar}$), 6.53 (td, $J = 7.4$ Hz, $J = 1.1$ Hz, C$^{H ar}$) 6.59 (td, $J = 7.2$ Hz, 1H, C$^{H ar}$), 6.75 (d, $J = 7.2$ Hz, 1H, C$^{H ar}$), 6.79 (d, $J = 7.0$ Hz, 1H, C$^{H ar}$), 6.89 (td, $J = 7.3$ Hz, $J = 1.1$ Hz, 1H, C$^{H ar}$), 7.16-7.21 (m, 3H, C$^{H ar}$), 7.37-7.48 (m, 9H, C$^{H ar}$), 7.56-7.58 (m, 3H, C$^{H ar}$), 7.67 (dd, $J = 7.3$ Hz, $J = 3.3$ Hz, 1H, C$^{H ar}$), 7.71 (td, $J = 7.8$ Hz, $J = 0.9$ Hz, 1H, C$^{H ar}$), 7.83-7.87 (m, 2H, C$^{H ar}$).

$^{13}$C$^{[1]}$H-NMR (125.78 MHz, [D8]THF, 298 K): $\delta = 73.9$ (d, $J = 7.2$ Hz, 1C, C$^{olefin}$), 81.3 (s, 1C, C$^{benzyl}$), 84.6 (s, 1C, C$^{benzyl}$), 87.7 (d, $J = 13.9$ Hz, 1C, C$^{olefin}$), 89.2 (d, $J = 16.1$ Hz, 1C, C$^{olefin}$), 92.8 (d, $J = 8.9$ Hz, 1C, C$^{olefin}$), 125.3 (s, 1C, C$^{ar}$), 125.5 (s, 1C, C$^{ar}$), 125.7 (s, 2C, C$^{ar}$), 125.7 (s, 1C, C$^{ar}$), 125.8 (s, 1C, C$^{ar}$), 125.8 (s, 1C, C$^{ar}$), 126.0 (s, 2C, C$^{P}$), 126.5 (s, 1C, C$^{ar}$), 126.8 (d, $J = 1.4$ Hz, 1C, C$^{ar}$), 127.2 (d, $J = 12.7$ Hz, 2C, C$^{P}$), 127.4 (m, 2C, C$^{ar}$), 128.3 (s, 1C, C$^{ar}$), 128.5 (s, 1C, C$^{ar}$), 129.0 (d, $J = 8.9$ Hz, 2C, C$^{ar}$), 129.1 (s, 2C, C$^{P}$), 129.2 (s, 1C, C$^{ar}$), 129.8 (d, $J = 1.9$ Hz, 1C, C$^{P}$), 129.9 (d, $J = 1.9$ Hz, 1C, C$^{P}$), 130.8 (d, $J = 2.4$ Hz, 1C, C$^{P}$), 131.9 (d, $J = 10.1$ Hz, 2C, C$^{P}$), 132.4 (d, $J = 15.6$ Hz, 1C, C$^{ar}$), 133.2 (s, 1C, C$^{ar}$), 133.4 (d, $J_{PC} = 37.4$ Hz, 1C, C$^{quat}$), 133.9 (d, $J_{PC} = 38.9$ Hz, 1C, C$^{quat}$), 134.9 (d, $J = 13.2$ Hz, 2C, C$^{P}$), 135.4 (d, $J = 2.4$ Hz, 1C, C$^{quat}$), 135.6 (d, $J_{PC} = 41.8$ Hz, 1C, C$^{quat}$), 136.2 (d, $J = 2.6$ Hz, 1C, C$^{quat}$), 136.7 (s, 1C, C$^{quat}$), 137.3 (s, 1C, C$^{quat}$), 143.6 (s, 1C, C$^{quat}$), 143.8 (d, $J = 1.4$ Hz, 1C, C$^{quat}$), 144.3 (s, 1C, C$^{quat}$), 148.4 (s, 1C, C$^{quat}$).

$^{31}$P$^{[1]}$H-NMR (202.50 MHz, [D8]THF, 298 K) $\delta = 62.1$ (d, $J_{RhP} = 125.1$ Hz).
\(^{1}\text{H}, ^{103}\text{Rh-NMR}\) (15.81 MHz, [D8]THF, 298 K): \(\delta = -7585\) (d, \(^{1}J_{\text{PRh}} = 125.1\) Hz).

ATR IR (\(\nu\) in \(\text{cm}^{-1}\)): 3062 (w), 3022 (w), 2959 (w), 2942 (w), 2868 (w), 2850 (w), 1584 (w), 1558 (w), 1493 (m), 1466 (m), 1433 (m), 1393 (w), 1324 (w), 1304 (w), 1250 (w), 1187 (w), 1156 (w), 1094 (m), 1065 (w), 1031 (w), 991 (m), 971 (w), 934 (w), 879 (w), 848 (w), 805 (w), 745 (s), 718 (m), 694 (s), 640 (w), 611 (w).
[RhH(tropNHtropPhPPh₂)] (36)

MF = C₄₈H₃₇NPRh

MW = 761.69 g/mol

Air sensitive

A solution of [Rh(tropNHtropPhPPh₂)] 35 (20 mg, 26 μmol, 1 eq.) in [D₈]THF (0.5 mL) was put in a Young-NMR tube and degassed by 3 pump freeze thaw cycles. Hydrogen was filled in the evacuated Young-NMR tube and the formed hydride complex was analysed in-situ by NMR.

$^1$H-NMR (500.23 MHz, [D₈]THF, 298 K): $\delta = -7.40$ (dd, $^1J_{RH} = 28.0$ Hz, 1H, Rh-H), 2.97 (d, $J = 9.2$ Hz, 1H, CHolefin), 3.84 (s, 1H, CHolefin), 4.36 (d, $J = 9.2$ Hz, 1H, CHolefin), 4.57 (d, $J = 5.3$ Hz, 1H, CHbenzyl), 4.69 (d, $J = 5.3$ Hz, 1H, CHbenzyl), 5.02 (br, 1H, NH), 6.12 (d, $J = 7.6$ Hz, 1H, CH₂), 6.43 (d, $J = 7.6$ Hz, 1H, CH₂), 6.59 (d, $J = 3.7$ Hz, 2H, CH₂), 6.62 (t, $J = 8.4$ Hz, 1H, CH₂), 6.78 (t, $J = 7.5$ Hz, 1H, CH₂), 6.84 (d, $J = 7.4$ Hz, 1H, CH₂), 6.87 (t, $J = 7.5$ Hz, 1H, CH₂), 6.92 (td, $J = 7.4$ Hz, $J = 0.9$ Hz, 1H, CH₂), 6.95-7.00 (m, 3H, CH₂), 7.05 (d, $J = 7.3$ Hz, 1H, CH₂), 7.05 (d, $J = 7.3$ Hz, 1H, CH₂), 7.14 (dd, $J = 7.5$ Hz, $J = 1.1$ Hz, 1H, CH₂), 7.30-7.35 (m, 2H, CH₂), 7.39 (t, $J = 7.2$ Hz, 2H, CH₂), 7.44 (t, $J = 8.0$ Hz, 2H, CH₂), 7.49-7.54 (m, 3H, CH₂), 7.57 (d, $J = 7.8$ Hz, 1H, CH₂), 7.64 (t, $J = 7.1$ Hz, 1H, CH₂), 7.91 (d, $J = 7.9$ Hz, 1H, CH₂), 8.54 (t, $J = 7.9$ Hz, 2H, CH₂).

$^{13}$C{¹H}-NMR (125.78 MHz, [D₈]THF, 298 K): $\delta = 54.4$ (d, $J = 8.6$ Hz, 1C, CHolefin), 57.7 (d, $J = 8.2$ Hz, 1C, CHolefin), 65.0 (d, $J = 8.2$Hz, 1C, CHolefin), 71.9 (s, 1C, CHbenzyl), 74.0 (s, 1C, CHbenzyl), 76.6 (d, $J = 10.1$ Hz, 1C, Colefin), 121.2 (s, 1C, CH₂), 122.1 (s, 1C, CH₂), 123.4 (s, 1C, CH₂), 123.8 (s, 1C, CH₂), 125.6 (s, 1C, CH₂), 126.4 (d, $J = 6.2$ Hz, 1C, CH₂), 127.0 (s, 1C, CH₂), 127.4 (s, 1C, CH₂), 127.4 (s, 1C, CH₂), 127.6 (s, 1C, CH₂), 127.9 (s, 2C, CH₂), 128.1 (d, $J = 10.6$ Hz, 2C, CH₂), 128.3 (s, 1C, CH₂), 128.4 (s, 1C, CH₂), 128.4 (s, 1C, CH₂), 128.8 (d, $J = 10.6$ Hz, 2C, CH₂), 129.0 (s, 1C, CH₂), 129.2 (s, 1C, CH₂), 129.4 (s, 1C, CH₂), 129.8 (s, 1C, CH₂), 129.8 (s, 1C, CH₂), 130.6 (s, 1C, CH₂), 131.1 (d, $J = 9.1$ Hz, 2C, CH₂), 131.9 (s, 1C, Cquat), 132.2 (s, 1C, CH₂), 132.2 (d, $J = 15.8$ Hz, 1C, CH₂), 132.4 (s, 1C, Cquat), 134.6 (d, $^1J_{PC} = 57.8$ Hz, 1C, Cquat), 135.8 (d, $J = 12.0$ Hz, 2C, CH₂), 136.3 (s, 1C, Cquat), 136.5 (d, $^1J_{PC} = 47.5$ Hz, 1C, Cquat), 136.7 (s, 1C, Cquat), 137.5 (s, 1C, Cquat), 137.7 (s, 1C, Cquat), 143.7 (s, 1C, Cquat), 145.0 (s, 1C, Cquat), 158.8 (d, $J = 25.0$ Hz, 1C, Cquat).

$^{31}$P{¹H}-NMR (202.50 MHz, [D₈]THF, 298 K) $\delta = 68.2$ (d, $^1J_{RHP} = 141.1$ Hz).

$^1$H, $^{103}$Rh-NMR (15.81 MHz, [D₈]THF, 298 K): $\delta = -8596$ (dd, $^1J_{PRh} = 141.1$ Hz, $^1J_{HRh} = 28.0$ Hz).
[RhCl(tropNHtropPhPPh2)] (single isomer) (37)

MF = C₄₈H₃₆ClNPRh

MW = 796.14 g/mol

MP = >220 °C (decomposition)

Air stable

A Schlenk was charged with a suspension of [RhCl(tropNHtropPhPPh2)] (110 mg, 0.138 mmol, 1 eq.) in a mixture of THF (5 mL) and ethanol (5 mL). Another Schlenk was charged with degassed aqueous HCl (2 M, 5 mL). Then the suspension of [RhCl(tropNHtropPhPPh2)] was treated with t-BuOK (62 mg, 0.55 mmol, 4 eq.) and stirred for 30 min. A brown solution of [RhH(tropNHtropPhPPh2)] was obtained. The HCl was added quickly to this solution. The obtained suspension was extracted with DCM then the combined organic phases were dried over Na₂SO₄, filtered and concentrated. The residue was recrystallised from DCM/ hexane and dried under vacuum. Yield: 96 mg, 87%.

¹H-NMR (500.23 MHz, CDCl₃, 298 K): δ = 4.54 (d, J = 6.1 Hz, 1H, NH), 4.70 (d, J = 8.6 Hz, 1H, CHbenzyl), 4.85 (d, J = 8.4 Hz, 1H, CHbenzyl), 4.91 (t, J = 2.1 Hz, 1H, CHolefin), 5.00 (dt, JHH = 9.5 Hz, JHH = 2.5 Hz, 1H, CHolefin), 5.33 (d, JHH = 9.5 Hz, 1H, CHolefin), 6.56 (d, J = 7.5 Hz, 1H, CHar), 6.71 (d, J = 7.3 Hz, 1H, CHar), 6.73-6.78 (m, 2H, CHar), 6.78-6.84 (m, 2H, CHar), 6.98 (td, JHH = 7.3 Hz, JHH = 0.9 Hz, 1H, CHar), 7.03 (d, J = 6.6 Hz, 1H, CHar), 7.06 (td, J = 7.5 Hz, J = 1.1 Hz, 1H, CHar), 7.10 (td, J = 7.5 Hz, J = 0.8 Hz, 1H, CHar), 7.13 (d, J = 6.6 Hz, 1H, CHar), 7.17-7.25 (m, 2H, CHar), 7.28-7.31 (m, 2H, CHar), 7.31-7.37 (m, 3H, CHar), 7.42-7.45 (m, 1H, CHar), 7.50-7.58 (m, 7H, CHar), 7.83 (dd, J = 7.7 Hz, J = 3.5 Hz, 1H, CHar), 7.89 (d, J = 8.1 Hz, 1H, CHar), 8.24-8.28 (m, 2H, CHar).

¹³C{¹H}-NMR (125.78 MHz, CDCl₃, 298 K): δ = 67.2 (d, J = 7.0 Hz, 1C, CHolefin), 70.7 (d, J = 11.5 Hz, 1C, CHolefin), 72.2 (d, J = 1.2 Hz, 1C, CHbenzyl), 73.6 (dd, J = 12.5 Hz, J = 1.7 Hz, 1C, CHolefin), 74.6 (d, J = 1.7 Hz, 1C, CHbenzyl), 84.9 (dd, J = 8.0 Hz, J = 1.8 Hz, 1C, Colefin), 125.7 (d, J = 5.0 Hz, 2C, CHar), 126.1 (s, 2C, CHar), 127.0 (d, J = 7.0 Hz, 1C, CHar), 127.4 (s, 1C, CHar), 127.8 (s, 1C, CHar), 128.2 (s, 1C, CHar), 128.4 (s, 1C, CHar), 128.6 (s, 1C, CHar), 128.7 (s, 1C, CHar), 128.7 (s, 1C, CHar), 128.8 (s, 1C, CHar), 129.0 (s, 1C, CHar), 129.1 (d, J = 1.9 Hz, 2C, CHar), 129.1 (s, 1C, CHar), 129.2 (s, 1C, CHar), 129.4 (s, 1C, CHar), 129.8 (s, 1C, CHar), 130.0 (s, 1C, CHar), 130.2 (d, J = 2.4 Hz, 1C, CHar), 131.0 (d, J = 2.4 Hz, 1C, CHar), 131.3 (d, J = 2.9 Hz, 1C, CHar), 132.8 (d, J = 13.9 Hz, 2C, Cquat), 132.8 (d, J = 8.9 Hz, 2C, CHar), 133.1 (d, JPC = 16.8 Hz, 1C, Cquat), 133.2 (s, 1C, CHar), 133.4 (s, 1C, CHar), 133.8 (s, 1C, Cquat), 133.9 (dd, JPC = 46.8 Hz, J = 1.8 Hz, 1C, Cquat), 134.8 (s, 1C, Cquat), 135.0 (s, 1C, Cquat), 135.6 (d, J = 10.1 Hz, 2C, CHar), 135.7 (s, 1C, Cquat), 136.3 (d, J = 1.4 Hz, 1C, Cquat), 139.6 (s, 1C, Cquat), 140.2 (s, 1C, Cquat), 155.5 (d, J = 21.3 Hz, 1C, Cquat).
$^{31}$P-$^1$H-NMR (202.50 MHz, CDCl$_3$, 298 K) $\delta = 52.6$ (d, $^1J_{RhP} = 132.0$ Hz).

$^1$H, $^{103}$Rh-NMR (15.81 MHz, CDCl$_3$, 298 K): $\delta = -7421$ (d, $^1J_{PPh}$ = 132.0 Hz).

ATR IR (\textit{v} in cm$^{-1}$): 3193 (w), 1987 (w), 2902 (w), 1597 (w), 1583 (w), 1558 (w), 1535 (w), 1486 (m), 1467 (m), 1431 (m), 1308 (w), 1252 (w), 1224 (w), 1186 (w), 1132 (w), 1102 (m), 1090 (m), 1060 (m), 989 (w), 971 (m), 940 (w), 899 (w), 860 (w), 846 (w), 811 (w), 772 (m), 754 (s), 745 (s), 719 (s), 692 (s), 673 (m), 643 (w), 617 (w), 607 (m).
[Rh(tropNHtropPhPPh₂)]OTf (single isomer) (6)
MF = C₄₉H₃₆F₃NO₃PRhS
MW = 909.75 g/mol
MP = 180-182 °C (decomposition)
Air stable
To a solution of [RhCl(tropNHtropPhPPh₂)] (single isomer) (37) (92 mg, 0.116 mmol, 1 eq.) in DCM (5 mL) was added AgOTf (33 mg, 0.127 mmol, 1.1 eq.). The resulting suspension was stirred overnight then filtered over celite. The solvent was removed under reduced pressure and the residue was recrystallised from THF/hexane and the obtained orange powder was dried under high vacuum. Yield: 103 mg, 98%.

H-NMR (500.23 MHz, CD₂Cl₂, 298 K): δ = 5.18 (d, J = 7.9 Hz, 1H, CH₇₇), 5.40 (d, J = 4.8 Hz, 1H, NH), 5.48-5.51 (m, 3H, CH₇₇, CH₇₈), 5.96 (dt, J = 9.4 Hz, J = 2.8 Hz, 1H, CH₇₉), 6.75 (d, J = 7.4 Hz, 1H, CH₈₀), 6.82-6.83 (m, 2H, CH₈₁), 6.87-6.90 (m, 2H, CH₈₂), 7.16 (t, J = 7.4 Hz, 1H, CH₈₃), 7.19-7.75 (m, 21H, CH₈₄), 7.81-7.84 (m, 2H, CH₈₅).

C{H}NMR (125.78 MHz, CD₂Cl₂, 298 K): δ = 71.1 (s, 1C, CH₇₇), 73.5 (s, 1C, CH₇₈), 73.9 (d, J = 6.4 Hz, CH₇₉), 80.9 (d, J = 12.0 Hz, 1C, CH₈₀), 126.3 (s, 1C, CH₈₁), 126.4 (s, 1C, CH₈₂), 126.9 (s, 1C, CH₈₃), 127.2 (s, 1C, CH₈₄), 127.6 (s, 1C, CH₈₅), 127.8 (s, 1C, CH₈₆), 127.9 (s, 1C, CH₈₇), 128.0 (s, 1C, CH₈₈), 128.4 (s, 1C, CH₈₉), 128.7 (s, 1C, CH₉₀), 128.8 (s, 1C, CH₉₁), 129.4 (d, J = 10.5 Hz, 2C, CH₉₂), 129.8 (s, 1C, CH₉₃), 129.9 (s, 1C, CH₉₄), 130.2 (s, 1C, CH₉₅), 131.0 (s, 1C, CH₉₆), 131.1 (d, J = 2.4 Hz, 1C, CH₉₇), 131.8 (d, J = 2.6 Hz, 1C, CH₉₈), 131.9 (d, J = 2.2 Hz, 1C, CH₉₉), 131.9 (d, J = 2.2 Hz, 1C, CH₁₀₀), 131.9 (d, J = 2.2 Hz, 1C, CH₁₀₁), 132.5 (d, J = 14.6 Hz, 2C, Cₙ₉₂), 133.1 (d, J = 9.6 Hz, 2C, Cₙ₉₃), 133.0 (s, 1C, CH₉₄), 133.6 (m, 2C, CH₉₅, Cₙ₉₆), 134.2 (d, J = 10.3 Hz, 2C, CH₉₇), 134.5 (s, 1C, Cₙ₉₈), 134.8-135-0 (m, 1C, CH₉₉), 135.3 (s, 2C, Cₙ₉₁₀), 135.7 (d, J = 2.2 Hz, 1C, Cₙ₉₁₁), 136.2 (s, 1C, Cₙ₉₁₂), 137.2 (s, 1C, Cₙ₉₁₃), 137.6 (s, 1C, Cₙ₉₁₄), 154.3 (d, J = 21.8 Hz, 1C, Cₙ₉₁₅).

F-NMR (188.31 MHz, CD₂Cl₂, 298 K): δ = -77.9 (s).

P{H}-NMR (202.50 MHz, CD₂Cl₂, 298 K) δ = 52.8 (d, J = 133.5 Hz).

H, Rh-NMR (15.81 MHz, CD₂Cl₂, 298 K): δ = -7103 (d, J = 133.5 Hz).
ATR IR (ν in cm$^{-1}$): 3164 (w), 2970 (w), 2901 (w), 2159 (br), 2023 (w), 1969 (w), 1484 (w), 1467 (w), 1436 (w), 1293 (m), 1205 (s), 1152 (s), 1095 (m), 1019 (s), 791 (w), 756 (m), 720 (m), 695 (m), 631 (s).
BuLi (1.6 M in Hexane, 2.50 mL, 4.32 mmol, 1.1 eq.) was added to a solution of diethyl 2-(5,5-dimethyl-1,3-dioxan-2-yl) benzylphosphonate 27 (1.01 mL, 0.500 g, 3.92 mmol, 1 eq.) in THF (15 mL) at -78 °C. The resulting mixture was stirred for 20 minutes then a solution of 2-bromobenzaldehyde (0.46 mL, 0.725 g, 3.92 mmol, 1 eq.) in THF (5 mL) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 2 hours then diluted with Et₂O and saturated NH₄Cl. The aqueous phase was extracted twice with Et₂O then the combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated. The resulting crude product was purified by column chromatography (Eluent: PET:EtoAc 15:1) to give the title compound as a white solid. Yield: 0.935 g, 63%.

**1H-NMR (500 MHz, CDCl₃, 298 K):** δ = 0.85 (s, 3H, CCH₃), 1.37 (s, 3H, CCH₃), 3.73 (d, 2JHH = 11.0 Hz, 2H, CH₂CMe₂), 3.73 (d, 2JHH = 11.0 Hz, 2H, CH₂CMe₂), 5.67 (s, 1H, CH₃methine), 7.17, (ddd, 3JHH = 7.5 Hz, 3JHH = 7.5 Hz, 4JHH = 1.5 Hz, 1H, CH₃), 7.34-7.43 (m, 4H, 3CH₃, 1 CH₂olefin), 7.48-7.51 (m, 1H, CH₃), 7.63 (dd, 3JHH = 8.0 Hz, 4JHH = 1.0 Hz, 1H, CH₃), 7.67-7.74 (m, 4H, 3CH₃, 1 CH₂olefin).

**13C{1H}-NMR (125 MHz, CDCl₃, 298 K):** δ = 22.3 (s, 1C, CCH₃), 23.7 (s, 1C, CCH₃), 30.6 (s, 1C, CMe₂), 78.3 (s, 2C, CH₂CMe₂), 100.7 (s, 1C, CH₃methine), 124.6 (s, 1C, CBr), 127.0 (s, 1C, CH₃), 127.0 (s, 1C, CH₃), 127.4 (s, 1C, CH₂olefin), 127.9 (s, 1C, CH₃), 128.4 (s, 1C, CH₂olefin), 129.2 (s, 2C, CH₃), 129.5 (s, 1C, CH₃), 130.3 (s, 1C, CH₃), 135.9 (s, 1C, Cquat), 136.0 (s, 1C, Cquat), 137.9 (s, 1C, Cquat).

**ATR IR (ν in cm⁻¹):** 3062 (w), 2955 (w), 2862 (w), 2161 (w), 1580 (w), 1558 (w), 1461 (m), 1435 (w), 1393 (m), 1367 (w), 1343 (w), 1328 (w), 1313 (w), 1294 (w), 1277 (w), 1253 (w), 1234 (w), 1216 (m), 1106 (s), 1085 (s), 1016 (s), 995 (s), 977 (s), 959 (s), 928 (m), 904 (w), 878 (w), 841 (w), 787 (w), 769 (s), 756 (s), 739 (s), 704 (w), 683 (w), 659 (s), 641 (m).

EA found% (calc%) for C₂₀H₂₁BrO₂: C: 64.35 (64.35), H: 5.67 (5.68)
bis(2-((E)-2-(5,5-dimethyl-1,3-dioxan-2-yl)styryl)phenyl)(phenyl)phosphane (39)

MF = C_{46}H_{47}O_{4}P

MW = 694.84 g/mol

MP = 80-82 °C

Slightly air sensitive

BuLi (1.6 M in Hexane, 1.76 mL, 2.81 mmol, 2.1 eq.) was added to a solution of (E)-2-(2-(2-bromostyryl)phenyl)-5,5-dimethyl-1,3-dioxane 38 (1.00 g, 2.68 mmol, 2 eq.) in THF (20 mL) at -78 °C. The resulting mixture was stirred for 30 minutes then dichloro(phenyl)phosphane (0.182 mL, 0.240 g, 1.34 mmol, 1 eq.) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 1.5 hours. The solvent was removed and the resulting mixture was purified by column chromatography (Eluent: DCM) to give the title compound as a white solid. Yield: 0.55 g, 59%.

$^1$H NMR (500 MHz, CD$_2$Cl$_2$, 298 K) $\delta = 0.82$ (s, 6H, CCH$_3$), 1.33 (s, 6H, CCH$_3$), 3.67 (d, $J_{HH} = 11.1$ Hz, 4H, CH$_2$CMe$_2$), 3.73-3.79 (m, 4H, CH$_2$CMe$_2$), 5.56 (s, 2H, CH$_{\text{methine}}$), 6.93-6.98 (m, 2H, CH$_{\text{ar}}$), 7.22-7.28 (m, 6H, CH$_{\text{ar}}$, CH$_{\text{olefin}}$), 7.35-7.45 (m, 10H, CH$_{\text{ar}}$), 7.58-7.78 (m, 7H, CH$_{\text{ar}}$, CH$_{\text{olefin}}$).

$^{13}$C{$^1$H}-NMR (125.78 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 22.0$ (s, 2C, CCH$_3$), 23.3 (s, 2C, CCH$_3$), 30.4 (s, 2C, CCH$_3$), 78.1 (s, 4C, CH$_2$CMe$_2$), 100.3 (s, 2C, CH$_{\text{methine}}$), 126.3 (d, $J = 4.3$ Hz, 2C, CH$_{\text{ar}}$), 126.6 (s, 2C, CH$_{\text{olefin}}$), 126.7 (s, 2C, CH$_{\text{ar}}$), 127.8 (s, 2C, CH$_{\text{ar}}$), 128.1 (s, 2C, CH$_{\text{olefin}}$), 128.3 (d, $J = 2.6$ Hz, 2C, CH$_{\text{ar}}$), 129.0 (s, 2C, CH$_{\text{ar}}$), 129.0 (s, 1C, CH$_{\text{ar}}$), 129.2 (s, 2C, CH$_{\text{ar}}$), 129.3 (s, 2C, C$_{\text{quat}}$), 129.5 (s, 2C, CH$_{\text{ar}}$), 130.0 (d, $J = 24.7$ Hz, 2C, CH$_{\text{ar}}$) 134.3 (s, 2C, CH$_{\text{ar}}$), 134.7 (s, 2C, C$_{\text{quat}}$) 134.8 (s, 2C, CH$_{\text{ar}}$) 135.7 (d, $J = 12.7$ Hz, 1C, C$_{\text{quat}}$) 136.1 (s, 2C, C$_{\text{quat}}$), 136.2 (s, 2C, C$_{\text{quat}}$).

$^{31}$P{$^1$H}-NMR (202.50 MHz, CD$_2$Cl$_2$, 298 K): $\delta = -21.1$ (s).

ATR IR (v in cm$^{-1}$): 3062 (w), 2953 (w), 2850 (w), 1692 (w), 1597 (w), 1584 (w), 1560 (w), 1544 (w), 1481 (w), 1459 (m), 1434 (m), 1391 (m), 1361 (w), 1330 (w), 1294 (w), 1259 (w), 1230 (w), 1214 (w), 1189 (w), 1159 (w), 1108 (s), 1087 (s), 1031 (w), 1015 (m), 997 (m), 972 (s), 929 (m), 877 (w), 808 (w), 744 (s), 717 (w), 695 (s), 668 (w), 642 (m), 614 (w).
2,2'-(1E,1'E)-(phenylphosphanediyl)bis(2,1-phenylene)bis(ethene-2,1-diyl)dibenzaldehyde (24)

\[
\text{MF} = \text{C}_{36}\text{H}_{27}\text{O}_2\text{P}
\]

\[
\text{MW} = \text{g/mol}
\]

\[
\text{MP} = 83-85 \degree \text{C}
\]

Slightly air sensitive

To a solution of bis(2-((E)-2-(5,5-dimethyl-1,3-dioxan-2-yl)styryl)phenyl)(phenyl) phosphane 39 (0.50 g, 0.72 mmol) in THF (80 mL) was added aqueous HCl (10%, 40 mL). The resulting solution was degassed and stirred for 1 day then NaOH was added as solid until the pH of the aqueous phase was above 13. The aqueous phase was extracted three times with Et₂O then the combined organic phases were washed with brine, dried with Na₂SO₄ and concentrated. The title compound was obtained as yellow solid. Yield: 0.347 g, 92%.

\(^1\text{H} \text{NMR} (500 \text{ MHz, CD}_2\text{Cl}_2, 298 \text{ K}) \delta = 6.97-6.99 \text{ (m, } 2\text{H, CH}^{\text{ar}}\text{)}, 7.27 \text{ (t, } J = 7.5 \text{ Hz, } 2\text{H, CH}^{\text{ar}}\text{)}, 7.37-7.51 \text{ (m, } 13\text{H, CH}^{\text{ar}}\text{; CH}^{\text{olefin}}\text{)}, 7.77-7.92 \text{ (m, } 8\text{H, CH}^{\text{ar}}\text{; CH}^{\text{olefin}}\text{)}, 10.24 \text{ (s, } 2\text{H, CHO}).

\(^{13}\text{C} \{^1\text{H}\} - \text{NMR (125.78 MHz, CD}_2\text{Cl}_2, 298 \text{ K}): \delta = 126.5 \text{ (d, } J = 4.1 \text{ Hz, } 2\text{C, CH}^{\text{ar}}\text{)}, 127.3 \text{ (d, } J = 2.6 \text{ Hz, } 2\text{C, CH}^{\text{olefin}}\text{)}, 127.7 \text{ (s, } 2\text{C, CH}^{\text{ar}}\text{)}, 128.1 \text{ (s, } 2\text{C, CH}^{\text{ar}}\text{)}, 128.6 \text{ (s, } 2\text{C, CH}^{\text{olefin}}\text{)}, 129.1 \text{ (d, } J = 7.2 \text{ Hz, } 2\text{C, CH}^{\text{ar}}\text{)}, 129.4 \text{ (s, } 1\text{C, CH}^{\text{ar}}\text{)}, 129.7 \text{ (s, } 2\text{C, CH}^{\text{ar}}\text{)}, 132.3 \text{ (s, } 2\text{C, CH}^{\text{ar}}\text{)}, 132.7 \text{ (d, } J = 25.2 \text{ Hz, } 2\text{C, CH}^{\text{ar}}\text{)}, 133.4 \text{ (s, } 2\text{C, C}^{\text{quat}}\text{)}, 134.0 \text{ (s, } 2\text{C, CH}^{\text{ar}}\text{)}, 134.3 \text{ (s, } 2\text{C, CH}^{\text{ar}}\text{)}, 134.8 \text{ (d, } J = 20.4 \text{ Hz, } 2\text{C, CH}^{\text{ar}}\text{)}, 135.7 \text{ (d, } J = 23.4 \text{ Hz, } 1\text{C, C}^{\text{quat}}\text{)}, 137.7 \text{ (s, } 2\text{C, C}^{\text{quat}}\text{)}, 140.2 \text{ (s, } 2\text{C, C}^{\text{quat}}\text{)}, 142.0 \text{ (s, } 2\text{C, C}^{\text{quat}}\text{)}, 192.7 \text{ (s, } 2\text{C, CHO}).

\(^{31}\text{P} \{^1\text{H}\} - \text{NMR (202.50 MHz, CD}_2\text{Cl}_2, 298 \text{ K): } \delta = -21.8 \text{ (s).}

\text{ATR IR (ν in cm}^{-1}): 3056 \text{ (w), 2959 (w), 2856 (w), 1687 (m), 1652 (w), 1593 (w), 1561 (w), 1481 (m), 1459 (m), 1435 (m), 1394 (m), 1364 (w), 1327 (w), 1294 (w), 1256 (w), 1213 (w), 1185 (m), 1159 (w), 1109 (m), 1090 (m), 1033 (w), 1016 (w), 988 (w), 962 (m), 928 (w), 870 (w), 811 (w), 759 (s), 717 (m), 695 (s), 657 (w), 634 (w).
bis(2-((E)-2-(5,5-dimethyl-1,3-dioxan-2-yl)styryl)phenyl)(phenyl)phosphate sulfide (40)

MF = C₄₆H₄₇O₄PS

MW = 726.90 g/mol

MP = 128-130 °C

Air stable

BuLi (1.6 M in Hexane, 5.02 mL, 8.04 mmol, 2 eq.) was added to a solution of (E)-2-(2-(2-bromostyryl)phenyl)-5,5-dimethyl-1,3-dioxane 38 (3.00 g, 8.04 mmol, 2 eq.) in THF (40 mL) at -78 °C. The resulting mixture was stirred for 30 minutes then dichloro(phenyl)phosphane (0.545 mL, 0.719 g, 4.02 mmol, 1 eq.) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 1.5 hours then elemental sulphur (134 mg, 0.522 mmol, 0.125 eq.) was added. The resulting suspension was stirred overnight then it was diluted with Et₂O and saturated NH₄Cl. The aqueous phase was extracted twice with Et₂O then the combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated. The resulting crude product was purified by column chromatography (Eluent: PET:DCM 1:1) to give the title compound as a white solid. Yield: 2.70 g, 92%.

1H-NMR (400.13 MHz, CDCl₃, 298 K): δ = 0.82 (s, 6H, C₆H₃), 1.31 (s, 6H, C₆H₃), 3.67 (d, 2JHH = 10.4 Hz, 4H, C₆H₂CMe₂), 3.79 (d, 2JHH = 10.4 Hz, 4H, C₆H₂CMe₂), 5.55 (s, 2H, CHmethine), 6.90 (d, J = 7.6 Hz, 2H, CHar), 7.16 (t, J = 7.0 Hz, 2H, CH₃), 7.22-7.33 (m, 6H, CHar, CHolefin), 7.42-7.52 (m, 5H, CHar), 7.57-7.61 (m, 4H, CHar, CHolefin), 7.66-7.74 (m, 4H, CHar), 7.89-7.95 (m, 2H, CHar).

13C{¹H}-NMR (100.61 MHz, CDCl₃, 298 K): δ = 22.3 (s, 2C, C₆H₃), 23.6 (s, 2C, C₆H₃), 30.6 (s, 2C, C₆H₃), 78.2 (s, 2C, CH₂CMe₂), 78.2 (s, 2C, CH₂CMe₂), 100.4 (s, 2C, CHmethine), 126.4 (s, 2C, CH₃), 126.8 (s, 2C, CH₃), 128.0 (d, J = 5.3 Hz, 2C, CHolefin), 128.1 (s, 4C, CH₃), 128.5 (s, 2C, CHolefin), 129.0 (d, J = 12.6 Hz, 2C, CHar), 129.2 (s, 2C, CHar), 130.1 (d, J = 6.6 Hz, 2C, CHar), 131.5 (d, 1JPC = 22.2 Hz, 1C, Cquat), 132.1 (d, 4JPC = 2.3 Hz, 1C, CH₃), 132.3 (d, J = 2.7 Hz, 2C, CHar), 133.0 (d, 1JPC = 14.4 Hz, 2C, Cquat), 133.4 (s, 2C, CHar), 133.5 (s, 2C, CH₃), 135.7 (s, 2C, Cquat), 141.9 (d, 2JPC = 7.5 Hz, 2C, Cquat).

31P{¹H}-NMR (161.98 MHz, CDCl₃, 298 K) δ = 43.2 (s).

ATR IR (ν in cm⁻¹): 3050 (w), 2953 (w), 2839 (w), 1692 (w), 1629 (w), 1584 (w), 1572 (w), 1558 (w), 1459 (w), 1435 (w), 1392 (w), 1361 (w), 1338 (w), 1307 (w), 1293 (w), 1250 (w), 1230 (w), 1214 (w), 1185 (w), 1165 (w), 1108 (s), 1087 (s), 1031 (m), 1015 (m), 996 (m), 972 (m), 928 (w), 899 (w), 822 (w), 782 (w), 759 (s), 723 (w), 706 (s), 670 (w), 636 (s), 615 (w).
2,2'-(1E,1'E)-((phenylphosphorothioyl)bis(2,1-phenylene))bis(ethene-2,1-diyldibenzaldehyde (41)

MF = C\textsubscript{36}H\textsubscript{27}O\textsubscript{2}PS

MW = 554.64 g/mol

MP = 172-174 °C (decomposition)

Air stable

To a solution of bis(2-((E)-2-(5,5-dimethyl-1,3-dioxan-2-yl)styryl)phenyl)(phenyl) phosphane sulfide 40 (1.60 g, 2.20 mmol) in THF (80 mL) was added aqueous HCl (10\%, 40 mL). The resulting solution was degassed and stirred for 1 day then NaOH was added as solid until the pH of the aqueous phase was above 13. The aqueous phase was extracted three times with Et\textsubscript{2}O then the combined organic phases were washed with brine, dried with Na\textsubscript{2}SO\textsubscript{4} and concentrated. The title compound was obtained as yellowish solid. Yield: 1.21 g, 99%.

\textsuperscript{1}H-NMR (500.23 MHz, CDCl\textsubscript{3}, 298 K): \(\delta = 7.23 \text{ (d, } J = 7.6 \text{ Hz, } 2\text{H, } CH^{ar})\), 7.26-7.28 (m, 2H, \(CH^{ar}\)), 7.39-7.54 (m, 11H, \(CH^{ar}, CH^{olefin}\)), 7.73-7.77 (m, 2H, \(CH^{ar}\)), 7.85-7.93 (m, 8H, \(CH^{ar}, CH^{olefin}\)), 10.22 (s, 2H, CHO).

\textsuperscript{13}C\{\textsuperscript{1}H\}-NMR (125.78 MHz, CDCl\textsubscript{3}, 298 K): \(\delta = 127.9 \text{ (s, } 2\text{C, } CH^{ar})\), 128.0 (s, 2C, \(CH^{olefin}\)), 128.1 (d, \(J = 12.7 \text{ Hz, } 2\text{C, } CH^{ar}\)), 128.1 (s, 2C, \(CH^{ar}\)), 128.7 (d, \(J = 9.6 \text{ Hz, } 2\text{C, } CH^{olefin}\)), 129.1 (d, \(J = 12.7 \text{ Hz, } 2\text{C, } CH^{ar}\)), 131.2-131.6 (m, 2C, \(C^{quat}\)), 131.8-132.2 (m, 1C, \(C^{quat}\)), 132.2 (d, \(J = 2.2 \text{ Hz, } 1\text{C, } CH^{ar}\)), 132.5 (d, \(J = 2.4 \text{ Hz, } 2\text{C, } CH^{ar}\)), 132.7 (d, \(J = 6.5 \text{ Hz, } 2\text{C, } CH^{ar}\)), 133.2 (s, 2C, \(C^{quat}\)), 133.3 (d, \(J = 11.5 \text{ Hz, } 2\text{C, } CH^{ar}\)), 133.3 (s, 2C, \(CH^{ar}\)), 133.4 (d, \(J = 10.6 \text{ Hz, } 2\text{C, } CH^{ar}\)), 134.2 (s, 2C, \(CH^{ar}\)), 139.7 (s, 2C, \(C^{quat}\)), 141.8 (d, \(J = 7.2 \text{ Hz, } 2\text{C, } C^{quat}\)), 193.2 (s, 2C, CHO).

\textsuperscript{31}P\{\textsuperscript{1}H\}-NMR (202.50 MHz, CDCl\textsubscript{3}, 298 K) \(\delta = 43.1 \text{ (s)}\).

ATR IR (\(\nu \text{ in cm}^{-1}\)): 3057 (w), 2946 (w), 2848 (w), 1682 (m), 1620 (w), 1594 (w), 1566 (w), 1478 (w), 1455 (w), 1438 (m), 1406 (w), 1290 (w), 1260 (w), 1220 (w), 1201 (w), 1186 (w), 1158 (w), 1098 (m), 1024 (w), 995 (w), 956 (m), 839 (w), 800 (br), 761 (s), 746 (m), 703 (s), 691 (m), 657 (m), 630 (s), 614 (m).
(E)-1-(2-(2-(diphenylphosphino)styryl)phenyl)-N-methyl-5H-dibenzo[a,d]cycloheptene-5-amine (44)

MF = C_{27}H_{20}NP

MW = 389.43 g/mol

MP = 171-172 °C

Air stable

BuLi (1.6 M in hexane, 12.0 mL, 19.0 mmol, 1.1 eq.) was added to a solution of (i-Pr)_2NH (2.9 mL, 20.7 mmol, 1.2 eq.) in THF (80 mL) at -78 °C. The resulting solution was stirred for 10 minutes then a solution of diethyl 2-cyanobenzylphosphonate (4.37 g, 17.3 mmol, 1 eq.) in THF (10 mL) was added dropwise. After stirring for another 20 minutes a solution of 2-(diphenylphosphino)benzaldehyde 12 (5.00 g, 17.3 mmol, 1 eq.) in THF (10 mL) was added dropwise. The reaction mixture was warmed to room temperature for 1 hour then hydrolysed with saturated NH_4Cl, and the aqueous phase was extracted three times with Et_2O. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated. The resulting crude product was purified by column chromatography (Eluent: PET:DCM 1:1) to give the title compound as a yellowish solid. Yield: 5.26 g, 78%.

^1H-NMR (300.13 MHz, CDCl_3, 298 K): δ = 6.93 (dd, J = 6.6 Hz, J = 4.8 Hz, 1H, CH^ar), 7.23-7.38 (m, 13H, CH^ar, CH^olefin), 7.43 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H, CH^ar), 7.51 (dd, J = 7.5 Hz, J = 7.5 Hz, 1H, CH^olefin), 7.60 (dd, J = 7.5 Hz, J = 7.5 Hz, 2H, CH^ar) 7.81 (dd, J = 7.0 Hz, J = 4.3 Hz, 1H, CH^ar) 7.99 (dd, J = 15.9 Hz, J = 4.4 Hz, 1H, CH^ar).

^13C{^1H}-NMR (75.48 MHz, CDCl_3, 298 K): δ = 111.3 (s, 1C, C^quat), 117.9 (s, 1C, CN), 125.4 (s, 1C, CH^olefin), 125.7 (d, J = 2.4 Hz, 1C, CH^ar) 126.1 (d, J = 4.1 Hz, 1C, CH^ar), 127.5 (s, 1C, CH^olefin), 128.6 (d, J = 7.1 Hz, 4C, CH^ar), 128.6 (d, J = 1.0 Hz, 1C, CH^ar), 128.9 (s, 2C, CH^ar), 129.3 (s, 1C, CH^ar), 132.0 (d, J_{PC} = 25.6 Hz, 1C), 132.7 (s, 1C, CH^ar), 132.9 (s, 1C, CH^ar), 133.5 (s, 1C, CH^ar), 134.0 (d, J = 19.8 Hz, 4C, CH^ar), 136.0 (d, J_{PC} = 9.4 Hz, 2C, C^quat), 136.4 (d, J = 14.2 Hz, 1C, C^quat), 140.7 (s, 1C, C^quat), 140.7 (d, J = 21.3 Hz, 1C, C^quat).

^31P{^1H}-NMR (121.49 MHz, CDCl_3, 298 K): δ = -13.8(s).

ATR IR (v in cm^{-1}): 3061 (w), 3040 (w), 2999 (w), 2219 (w), 1592 (w), 1564 (w), 1480 (m), 1448 (w), 1434 (m), 1340 (w), 1289 (w), 1260 (w), 1225 (w), 1183 (w), 1155 (w), 1091 (w), 1071 (w), 1027 (w) 1000 (w), 956 (m), 920 (w), 871 (w), 850 (w), 764 (s), 742 (s), 693 (s).
tert-butyl 1-o-tolylcyclopropylcarbamate (47)

MF = C\textsubscript{15}H\textsubscript{21}NO\textsubscript{2}

MW = 247.33 g/mol

MP = 94-95 °C

air stable

To a solution of o-tolunitrile (9.0 mL, 8.91 g, 76.1 mmol, 1 eq.) and Ti(O\textsubscript{iPr})\textsubscript{4} (27.3 mL, 25.9 g, 91.3 mmol, 1.2 eq.) in Et\textsubscript{2}O (450 mL) EtMgBr (3.0 M in Et\textsubscript{2}O, 55.8 mL, 167.3 mmol, 2.2 eq.) was added dropwise at -78°C. The resulting yellow mixture was stirred 10 minutes then warmed to room temperature for 1.5 hours. BF\textsubscript{3} (3.8 M in Et\textsubscript{2}O, 40.0 mL, 152.1 mmol, 2.0 eq.) was added dropwise and the mixture was stirred for 1 hour. Subsequently it was hydrolysed with 1 M HCl then the aqueous phase was neutralised with Na\textsubscript{2}CO\textsubscript{3} and made basic by the addition of a 10% NaOH solution. This mixture was extracted 3 times with Et\textsubscript{2}O then the combined organic phases were washed with brine, dried with Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated under reduced pressure. The free amine was distilled under vacuum (9.15 g, 62.2 mmol) and subsequently treated with Boc\textsubscript{2}O (13.3 mL, 13.8 g, 62.2 mmol, 1 eq.). After the resulting solution was cooled down, iodine (1.58 g, 6.22 mmol, 0.1 eq.) was added and the mixture was stirred vigorously overnight. Afterwards it was diluted with Et\textsubscript{2}O, washed with diluted Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} and brine, dried with Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated under reduced pressure. The crude product was recrystallised from hot hexane. Yield: 10.7 g, 57%.

\textsuperscript{1}H-NMR (300.13 MHz, CDCl\textsubscript{3}, 298 K): \( \delta = 1.11-1.21 \) (m, 4H, CH\textsubscript{2}\textsuperscript{cyPr}), 1.40 (s, 9H, C(CH\textsubscript{3})\textsubscript{3}), 2.48 (s, 3H, ArCH\textsubscript{3}), 5.18 (br, 1H, NH), 7.14-7.20 (m, 3H, CH\textsubscript{ar}), 7.37-7.66 (br, 1H, CH\textsubscript{ar}).

\textsuperscript{13}C{\textsuperscript{1}H}-NMR (75.48 MHz, CDCl\textsubscript{3}): \( \delta = 15.1 \) (br, 2C, CH\textsubscript{2}\textsuperscript{cyPr}), 19.4 (s, 1C, ArCH\textsubscript{3}), 28.4 (s, 3C, C(CH\textsubscript{3})\textsubscript{3}), 35.2 (br, 1C, C\textsubscript{quat}, cyPr), 79.3 (s, 1C, C(CH\textsubscript{3})\textsubscript{3}), 125.4 (br, 1C, CH\textsubscript{ar}), 127.3 (s, 1C, CH\textsubscript{ar}), 130.1 (s, 1C, CH\textsubscript{ar}), 130.5 (s, 1C, CH\textsubscript{ar}), 137.5 (s, 1C, C\textsubscript{quat}), 139.7 (s, 1C, C\textsubscript{quat}), 154.9 (br, 1C, C=O).

ATR IR (\( \nu \) in cm\textsuperscript{-1}): 3240 (br), 3113 (w), 2982 (w), 2925 (w), 1690 (s), 1477 (m), 1454 (m), 1420 (w), 1365 (s), 1326 (w), 1282 (w), 1257 (w), 1161 (s), 1095 (w), 1063 (s), 1044 (w), 1026 (s), 1004 (m), 947 (w), 936 (w), 922 (w), 899 (m), 851 (m), 805 (w), 787 (w), 777 (m), 756 (s), 726 (s), 659 (m), 608 (s).

EA found% (calc%) for C\textsubscript{15}H\textsubscript{21}NO\textsubscript{2}: C: 72.80 (72.84), H: 8.54 (8.56), N: 5.62 (5.66).
**tert-butyl 1-(2-(bromomethyl)phenyl)cyclopropylcarbamate (101)**

\[
MF = C_{15}H_{20}BrNO_{2}
\]

\[
MW = 326.23 \text{ g/mol}
\]

\[
MP = 114-115 ^\circ \text{C}
\]

Air stable

To a solution of tert-butyl 1-o-tolylcyclopropylcarbamate 47 (7.50 g, 30.3 mmol, 1 eq.) in CCl₄ (60 mL) NBS (6.98 g, 39.4 mmol, 1.3 eq.) and AIBN (498 mg, 3.03 mmol, 0.1 eq.) was added. The resulting solution was refluxed for two hours, filtered and concentrated. The residue was dissolved in Et₂O, washed with Na₂S₂O₃ and brine, dried with Na₂SO₄, filtered and concentrated under reduced pressure. The crude product was filtered over silica gel (Eluent: PET:EE 4:1) then recrystallised from hot hexane. Yield: 6.00 g, 61%.

\[
^1H-NMR \text{ (500.23 MHz, CDCl}_3, 298 K): \ \delta = 1.22-1.32 \text{ (m, 4H, } CH_2\text{cyPr), 1.40 \text{ (s, 9H, } C(CH_3)_{3}\text{), 4.89 \text{ (br, 2H, } CH_2Br)\text{, 5.41 \text{ (br, 1H, } NH)\text{, 7.29-7.31 \text{ (m, 2H, } CH_{ar}\text{), 7.41-7.33 \text{ (m, 1H, } CH_{ar}\text{), 7.60-7.67 \text{ (br, 1H, } CH_{ar}\text{).}}}
\]

\[
^{13}C\{^1H\}-NMR \text{ (125.78 MHz, CDCl}_3, 298 K): \ \delta = 15.6 \text{ (br, 2C, } CH_2\text{cyPr), 28.8 \text{ (s, 3C, } C(CH_3)_{3}\text{), 31.6 \text{ (br, 1C, } CH_2Br)\text{, 34.9 \text{ (s, 1C, } C_{quat, cyPr}\text{), 79.8 \text{ (s, 1C, } C(CH_3)_{3}\text{), 128.6 \text{ (s, 1C, } CH_{ar}\text{), 129.0 \text{ (br, 1C, } CH_{ar}\text{), 131.6 \text{ (s, 1C, } CH_{ar}\text{), 132.0 \text{ (br, 1C, } CH_{ar}\text{), 137.4 \text{ (s, 1C, } C_{quat}\text{), 140.6 \text{ (s, 1C, } C_{quat}\text{), 155.4 \text{ (br, 1C, } C=O).}}}
\]

ATR IR (v in cm⁻¹): 3233 (w), 3113 (w), 3090 (w), 2977 (w), 2160 (w), 1690 (s), 1477 (m), 1452 (m), 1421 (w), 1381 (s), 1367 (s), 1327 (m), 1287 (w), 1269 (w), 1221 (m), 1158 (s), 1068 (s), 1028 (s), 1005 (m), 940 (w), 925 (w), 903 (m), 865 (w), 849 (w), 817 (w), 777 (s), 755 (w), 710 (m), 658 (m), 609 (s).
tert-butyl 1-(2-((diethoxyphosphoryl) methyl)phenyl)cyclopropylcarbamate

(46)

MF = C_{19}H_{30}NO_{5}P

MW = 383.42 g/mol

Air stable

A solution of tert-butyl 1-(2-(bromomethyl)phenyl) cyclopropylcarbamate 101 (9.64 g, 29.6 mmol, 1 eq.) and P(OEt)₃ (8.69 mL, 8.59 g, 51.7 mmol, 1.75 eq.) was refluxed for 3 hours then all volatiles were removed. The residue was purified by column chromatography (Eluent: PET:EE 10:1, then 3:1, then DCM:EtOH 10:1). Yield: 8.20 g, 72%.

¹H-NMR (300.13 MHz, CDCl₃, 298 K): δ = 1.07-1.10 (m, 2H, CH₂cyPr), 1.17-1.23 (m, 2H, CH₂cyPr), 1.23 (t, J_HH = 7.07 Hz, 6H, CH₂CH₃), 1.38 (s, 9H, C(CH₃)₃), 3.50 (d, J_PH = 22.78 Hz, 2H, CH₂P), 3.95-4.12 (m, 4H, CH₂CH₃), 6.67 (br, 1H, NH), 7.16-7.31 (m, 3H, CHar), 7.75 (s, 1H, CHar).

¹³C{¹H}-NMR (75.48 MHz, CDCl₃, 298 K): δ = 15.2 (br, 2C, CH₂cyPr), 16.3 (d, J_pc = 5.8 Hz, 2C, CH₂CH₃), 28.4 (s, 3C, C(CH₃)₃), 30.8 (d, J_pc = 138.3 Hz, 1C, CH₂P), 34.5 (s, 1C, Cquat, cyPr), 62.3 (d, J_pc = 6.7 Hz, 2C, CH₂CH₃), 78.8 (br, 1C, C(CH₃)₃), 127.0 (br, 1C, CHar), 127.5 (d, J = 3.5 Hz, 1C, CHar), 130.8 (d, J = 8.8 Hz, 1C, Cquat), 131.2 (d, J = 5.5 Hz, 1C, CHar), 132.0 (s, 1C, CHar), 140.8 (d, J = 7.0 Hz, 1C, Cquat), 155.8 (s, 1C, C=O).

³¹P{¹H}-NMR (121.49 MHz, CDCl₃, 298 K): δ = 27.2 (s).

ATR IR (ν in cm⁻¹): 3266 (br), 2976 (w), 2925 (w), 1715 (m), 1507 (m), 1491 (m), 1452 (w), 1390 (w), 1365 (m), 1322 (w), 1245 (s), 1165 (s), 1093 (w), 1051 (s), 1022 (s), 959 (s), 894 (w), 866 (w), 843 (m), 828 (m), 759 (s), 706 (w).
tert-butyl (2-((diethoxyphosphoryl)methyl)phenyl)carbamate (50)

\[
\text{MF} = \text{C}_{16}\text{H}_{26}\text{NO}_{5}\text{P}
\]

MW = 343.36 g/mol

MP = 56-57 °C

Air stable

A solution of tert-butyl (2-(bromomethyl)phenyl)carbamate 49 (6.50 g, 22.7 mmol, 1 eq.) and P(OEt)₃ (5.84 mL, 5.66 g, 34.1 mmol, 1.5 eq.) was refluxed for 3 hours then all volatiles were removed. The residue was purified by column chromatography (Eluent: PET:EE 3:1, then DCM:EtOH 10:1). Yield: 7.58 g, 97%.

\(^1\)H-NMR (500.23 MHz, CDCl₃, 298 K): \(\delta = 1.28\) (t, \(^3\)J\text{HH} = 7.1 Hz, 6H, CH₂CH₃), 1.55 (s, 9H, C(CH₃)), 3.18 (d, \(^2\)J\text{HH} = 21.1 Hz, 2H, CH₂P), 4.01-4.09 (m, 4H, CH₂CH₃), 7.07 (t, J = 7.5 Hz, 1H, CH₉), 7.16 (d, J = 7.8 Hz, 1H, CH₉), 7.27-7.30 (m, 1H, CH₉), 7.76 (d, br, J = 7.6 Hz, 1H, CH₉), 8.20 (s, br, 1H, NH).

\(^13\)C\{\(^1\)H\}NMR (125.78 MHz, CDCl₃, 298 K): \(\delta = 16.7\) (d, \(^3\)J\text{PC} = 6.0 Hz, 2C, CH₂CH₃), 28.8 (s, 3C, C(CH₃)), 31.4 (d, \(^1\)J\text{PC} = 138.2 Hz, 1C, CH₂P), 63.1 (d, \(^2\)J\text{PC} = 6.7 Hz, 2C, CH₂CH₃), 80.4 (s, 1C, C(CH₃)), 123.4 (m, 1C, C\text{quat}), 124.7 (d, J = 3.1 Hz, 1C, CH₉), 124.8 (d, br, J = 3.1 Hz, 1C, CH₉), 128.3 (d, J = 3.8 Hz, 1C, CH₉), 131.5 (d, J = 6.7 Hz, 1C, CH₉), 137.8 (d, J = 5.3 Hz, 1C, C\text{quat}), 154.3 (s, 1C, CO).

\(^3\)P\{\(^1\)H\}NMR (202.50 MHz, CDCl₃, 298 K) \(\delta = 28.7\) (s).

ATR IR (ν in cm\(^{-1}\)): 3341 (w), 2982 (w), 2925 (w), 1724 (m), 1586 (w), 1509 (m), 1478 (m), 1449 (m), 1387 (w), 1364 (m), 1301 (m), 1236 (s), 1222 (s), 1159 (s), 1095 (m), 1040 (s), 1018 (s), 969 (s), 934 (s), 876 (w), 858 (m), 837 (m), 823 (m), 805 (m), 777 (s), 769 (s), 737 (s), 700 (w), 616 (m).
(E)-methyl 2-(2-(diphenylphosphino) styryl)benzoate (102)

\[ \text{MF} = \text{C}_{28}\text{H}_{23}\text{O}_2\text{P} \]

\[ \text{MW} = 422.45 \text{ g/mol} \]

\[ \text{MP} = 113-115 \, ^\circ\text{C} \]

Air stable

BuLi (1.6 M in Hexane, 2.37 mL, 3.79 mmol, 1.1 eq.) was added to a solution of \((i-\text{Pr})_2\text{NH}\) (0.63 mL, 450 mg, 4.5 mmol, 1.3 eq.) in THF (15 mL) at -78 \, ^\circ\text{C}. The resulting solution was stirred for 20 minutes, then methyl 2-((diethoxyphosphoryl)methyl)benzoate (1.04 g, 3.62 mmol, 1.05 eq.) was added dropwise. After stirring for another 20 minutes a solution of 2-(diphenylphosphino)benzaldehyde \(12\) (1.00 g, 3.44 mmol, 1 eq.) in THF (5 mL) was added dropwise. The resulting solution was stirred for 10 minutes then warmed to room temperature for 1 hour then hydrolysed with saturated \text{NH}_4\text{Cl}. The aqueous phase was extracted 3 times with \text{Et}_2\text{O} then the combined organic phases were washed with brine, dried over \text{Na}_2\text{SO}_4, filtered and concentrated. The resulting crude product was purified by column chromatography (Eluent: PET:DCM 1:1) to give the title compound as a yellowish solid.

Yield: 570 mg, 39%.

\[^1\text{H}-\text{NMR}\] (500.23 MHz, CDCl\textsubscript{3}, 298 K): \(\delta = 3.94 \, (s, \, 3\text{H, COOCH}_3), \, 6.89 \, (dd, \, J = 6.8 \, Hz, J = 4.7 \, Hz, \, 1\text{H, CH}^\text{ar}), \, 7.21 \, (t, \, J = 7.33 \, Hz, \, 1\text{H, CH}^\text{ar}), \, 7.28-7.45 \, (m, \, 14\text{H, CH}^\text{ar, CH}^\text{olefin}), \, 7.66 \, (dd, \, 3J_{\text{HH}} = 15.9 \, Hz, \, 4J_{\text{PH}} = 4.0 \, Hz, \, 1\text{H, CH}^\text{olefin}), \, 7.82-7.88 \, (m, \, 2\text{H, CH}^\text{olefin}), \, 7.91 \, (d, \, J = 7.8 \, Hz, \, 1\text{H, CH}^\text{ar}).

\[^{13}\text{C}\{^1\text{H}\}-\text{NMR}\] (125.78 MHz, CDCl\textsubscript{3}, 298 K): \(\delta = 52.4 \, (s, \, 1\text{C, COOCH}_3), \, 126.5 \, (d, \, 3J_{\text{PC}} = 4.1 \, Hz, \, 1\text{C, CH}^\text{olefin}, \, 127.5 \, (s, \, 1\text{C, CH}^\text{ar}), \, 127.8 \, (s, \, 1\text{C, C}^\text{quat}), \, 128.2 \, (d, \, 4J_{\text{PC}} = 1.0 \, Hz, \, 1\text{C, CH}^\text{olefin}), \, 128.8 \, (s, \, 1\text{C, CH}^\text{ar}), \, 128.9 \, (d, \, J = 7.2 \, Hz, \, 4\text{C, CH}^\text{ar}), \, 129.2 \, (s, \, 2\text{C, CH}^\text{ar}), \, 129.5 \, (s, \, 1\text{C, CH}^\text{ar}), \, 129.7 \, (d, \, J = 2.6 \, Hz, \, 1\text{C, CH}^\text{ar}), \, 130.5 \, (d, \, J = 24.7 \, Hz, \, 1\text{C, CH}^\text{ar}), \, 130.9 \, (s, \, 1\text{C, CH}^\text{ar}), \, 132.5 \, (s, \, 1\text{C, CH}^\text{ar}), \, 133.6 \, (s, \, 1\text{C, CH}^\text{ar}), \, 134.5 \, (d, \, J = 19.9 \, Hz, \, 4\text{C, CH}^\text{ar}), \, 136.1 \, (d, \, J = 14.2 \, Hz, \, 1\text{C, C}^\text{quat}), \, 136.8 \, (d, \, J = 9.8 \, Hz, \, 1\text{C, C}^\text{quat}), \, 139.9 \, (s, \, 1\text{C, C}^\text{quat}), \, 142.4 \, (d, \, J = 21.6 \, Hz, 2\text{C, C}^\text{quat}), 168.2 \, (s, \, 1\text{C, COOCH}_3).

\[^{31}\text{P}\{^1\text{H}\}-\text{NMR}\] (202.50 MHz, CDCl\textsubscript{3}, 298 K) \(\delta = -12.1 \, (s)\).

ATR IR (\(\nu\) in cm\(^{-1}\)): 3062 (w), 3050 (w), 2947 (w), 1803 (w), 1720 (m), 1584 (w), 1567 (w), 1482 (w), 1453 (w), 1433 (m), 1298 (w), 1265 (m), 1248 (m), 1216 (w), 1193 (w), 1163 (w), 1132 (m), 1078 (m), 1025 (w), 996 (w), 964 (m), 838 (w), 797 (w), 763 (s), 741 (s), 730 (m), 695 (s), 666 (w).

EA found\% (calc\%) for \text{C}_{28}\text{H}_{23}\text{O}_2\text{P}: \text{C: 79.61 (78.68), H: 5.49 (5.69).}
(E)-2-(2-(2-(diphenylphosphino)styryl)phenyl)propan-2-ol (51)

\[
\text{MF} = C_{29}H_{27}OP
\]

\[
\text{MW} = 422.50 \text{ g/mol}
\]

\[
\text{MP} = 123-124 \ ^\circ \text{C}
\]

Air stable

To a solution of (E)-methyl 2-(2-(diphenylphosphino)styryl)benzoate 102 (2.00 g, 4.73 mmol, 1 eq.) in THF (20 mL) MeMgBr (3.0 M in \( \text{Et}_2\text{O} \), 4.73 mL, 14.20 mmol, 3 eq.) was added. The resulting solution was refluxed overnight then saturated \( \text{NH}_4\text{Cl} \) was added and the mixture was extracted 3 times with \( \text{Et}_2\text{O} \). The combined organic phases were washed with brine, dried over \( \text{Na}_2\text{SO}_4 \), filtered and concentrated. The resulting crude product was purified by column chromatography (Eluent: DCM:PET 3:1) to give the title compound as a white solid. Yield: 1.76 g, 88%.

\( ^1\text{H}-\text{NMR} \) (500.23 MHz, CDCl\(_3\), 298 K): \( \delta = 1.62 \) (s, 6H, \( \text{CH}_3 \)), 1.73 (br, 1H, \text{OH}), 6.88 (dd, \( J = 7.0 \text{ Hz} \), \( J = 4.7 \text{ Hz} \), 1H, \( \text{CH}^\text{ar} \)), 7.18-7.47 (m, 17H, \( \text{CH}^\text{ar} \), \( \text{CH}^\text{olefin} \)), 7.74 (dd, \( J = 7.5 \text{ Hz} \), \( J = 4.24 \text{ Hz} \), 1H, \( \text{CH}^\text{ar} \)).

\( ^{13}\text{C}\{^1\text{H}\}-\text{NMR} \) (125.78 MHz, CDCl\(_3\), 298 K): \( \delta = 31.8 \) (s, 2C, \( \text{CH}_3 \)), 74.1 (s, 1C, \( \text{C(CH}_3)_2\text{OH} \)), 125.4 (s, 1C, \( \text{CH}^\text{olefin} \)), 126.4 (d, \( J = 4.1 \text{ Hz} \), 1C, \( \text{CH}^\text{ar} \)), 127.7 (s, 1C, \( \text{CH}^\text{olefin} \)), 127.8 (s, 2C, \( \text{CH}^\text{ar} \)), 128.9 (d, \( J = 7.0 \text{ Hz} \), 4C, \( \text{CH}^\text{ar} \)), 129.1 (d, \( J = 23.8 \text{ Hz} \), 1C, \( \text{CH}^\text{ar} \)), 129.2 (s, 2C, \( \text{CH}^\text{ar} \)) 129.4 (s, 1C, \( \text{CH}^\text{ar} \)), 129.4 (s, 1C, \( \text{CH}^\text{ar} \)), 132.5 (d, \( J = 2.4 \text{ Hz} \), 1C, \( \text{CH}^\text{ar} \)), 133.5 (s, 1C, \( \text{CH}^\text{ar} \)), 134.5 (d, \( J = 19.9 \text{ Hz} \), 4C, \( \text{CH}^\text{ar} \)), 135.9 (d, \( J = 13.4 \text{ Hz} \), 1C, \( \text{C}^\text{quat} \)), 136.8 (d, \( J = 10.1 \text{ Hz} \), 2C, \( \text{C}^\text{quat} \)), 137.4 (s, 1C, \( \text{C}^\text{quat} \)), 142.9 (d, \( J = 21.5 \text{ Hz} \), 1C, \( \text{C}^\text{quat} \)), 145.3 (s, 1C, \( \text{C}^\text{quat} \)).

\( ^{31}\text{P}\{^1\text{H}\}-\text{NMR} \) (202.50 MHz, CDCl\(_3\), 298 K) \( \delta = -12.0 \) (s).

ATR IR (\( \nu \) in cm\(^{-1}\)): 3406 (w), 3050 (w), 2957 (w), 2160 (w), 1584 (w), 1476 (m), 1457 (w), 1434 (m), 1377 (w), 1357 (w), 1302 (w), 1252 (w), 1194 (w), 1162 (m), 1104 (m), 1093 (m), 1079 (w), 1048 (w), 1026 (w), 981 (w), 962 (m), 946 (w), 892 (w), 867 (w), 820 (w), 761 (m), 747 (s), 732 (m), 693 (s), 634 (w).

EA found\% (calc\%) for \( C_{29}H_{27}OP \): C: 81.69 (82.44), H: 6.55 (6.44).
2,5,5-trimethyl-2-(o-tolyl)-1,3-dioxane

(103)

MF = C₁₄H₂₀O₂

MW = 220.31 g/mol

Air stable

A solution of 2'-methylacetophenone (24.4 mL, 25.0 g, 186 mmol, 1 eq.), 2,2-
dimethylpropane-1,3-diol (23.3 g, 224 mmol, 1.2 eq.) and p-TsOH (642 mg, 3.73 mmol,
0.02 eq.) in benzene (300 mL) was refluxed in a Dean Stark apparatus overnight. Then the
solvent was removed under reduced pressure and the residue was dissolved in Et₂O and 5%
NaOH solution. After phase separation the aqueous phase was extracted 3 times with small
portion of Et₂O. The combined organic phases were washed with water and brine, dried with
Na₂SO₄, filtered and concentrated. The product was purified by vacuum distillation. Yield:
39.05 g, 95%.

¹H-NMR (400.13 MHz, CDCl₃, 298 K): δ = 0.61 (s, 3H, C(CH₃)₂), 1.31 (s, 3H, C(CH₃)₂),
1.58 (s, 3H, ArCCΗ₃), 2.43 (s, 3H, ArCH₃), 3.42 (s, 4H, CH₂CMe₂), 7.18-7.27 (m, 3H, CH₉),
7.48-7.50 (m, 1H, CH₉).

¹³C{¹H}-NMR (100.61 MHz, CDCl₃, 298 K): δ = 21.5 (s, 1C, C(CH₃)₂), 22.3 (s, 1C,
C(CH₃)₂), 23.4 (s, 1C, ArCH₃), 30.2 (s, 1C, ArCCH₃), 30.3 (s, 1C, C(CH₃)₂), 72.0 (s, 2C,
CH₂CMe₂), 101.6 (s, 1C, ArCCH₃), 126.5 (s, 1C, CH₉), 128.2 (s, 1C, CH₉), 128.7 (s, 1C,
CH₉), 132.9 (s, 1C, CH₉), 136.8 (s, 1C, C⁴₉), 138.4 (s, 1C, C⁴₉).

ATR IR (ν in cm⁻¹): 2952 (w), 2865 (w), 1687 (w), 1600 (w), 1483 (w), 1471 (m), 1456 (m),
1396 (w), 1370 (m), 1318 (w), 1281 (w), 1243 (m), 1208 (m), 1179 (s), 1140 (m), 1110 (m),
1081 (s), 1053 (w), 1038 (m), 1014 (m), 950 (m), 928 (w), 912 (m), 873 (m), 866 (s), 794 (w),
760 (s), 732 (s), 689 (w), 670 (m), 608 (m).
2-(2-(bromomethyl)phenyl)-2,5,5-trimethyl-1,3-dioxane (54)

MF = C_{14}H_{19}BrO_{2}

MW = 299.20 g/mol

slightly air sensitive

To a solution of 2,5,5-trimethyl-2-(o-tolyl)-1,3-dioxane 103 (8.0 mL, 8.4 g, 38.1 mmol, 1 eq.) and NBS (7.46 g, 41.9 mmol, 1.1 eq.) in CCl\(_4\) (60 mL) was added AIBN (626 mg, 3.81 mmol, 0.1 eq.). The resulting suspension was refluxed for 1 hour then allowed to cool to room temperature. The reaction mixture was filtered then the solvent was removed under reduced pressure. The residue was dissolved in Et\(_2\)O and washed with a saturated solution of Na\(_2\)S\(_2\)O\(_3\) and brine. The organic phase was dried with Na\(_2\)SO\(_4\), filtered and concentrated. The residue was purified by column chromatography (stationary phase: neutral alumina, eluent: PET:EE 15:1) and the product was obtained as colourless oil. Yield 9.95 g, 87%

\(^1\)H-NMR (300.13 MHz, CDCl\(_3\), 298 K): \(\delta = 0.64\) (s, 3H, C(CH\(_3\))\(_2\)), 1.30 (s, 3H, C(CH\(_3\))\(_2\)), 1.66 (s, 3H, ArCCH\(_3\)), 3.47 (s, 4H, CH\(_2\)CMe\(_2\)), 4.93 (s, 2H, CH\(_2\)Br), 7.33-7.36 (m, 2H, CH\(^\beta\)), 7.49-7.56 (m, 2H, CH\(^\alpha\)).

\(^{13}\)C\(^{\{1\}H}\)-NMR (75.48 MHz, CDCl\(_3\), 298 K): \(\delta = 21.9\) (s, 1C, C(CH\(_3\))\(_2\)), 22.7 (s, 1C, C(CH\(_3\))\(_2\)), 30.0 (s, 1C, C(CH\(_3\))\(_2\)), 31.0 (s, 1C, ArCCH\(_3\)), 31.5 (s, 1C, CH\(_2\)Br), 72.2 (s, 2C, CH\(_2\)CMe\(_2\)), 100.7 (s, 1C, ArCCH\(_3\)), 128.5 (s, 1C, CH\(^\beta\)), 128.6 (s, 2C, CH\(^\alpha\)), 133.7 (s, 1C, CH\(^\beta\)), 136.0 (s, 1C, C\(^\alpha\)), 138.4 (s, 1C, C\(^\alpha\)).

ATR IR (\(\nu\) in cm\(^{-1}\)): 3070 (w), 2953 (w), 2866 (w), 1739 (w), 1471 (m), 1443 (br), 1396 (w), 1373 (m), 1321 (w), 1296 (w), 1242 (w), 1225 (w), 1208 (w), 1177 (s), 1118 (m), 1096 (w), 1077 (s), 1036 (m), 1013 (m), 949 (w), 913 (m), 871 (m), 815 (w), 795 (w), 758 (s), 672 (m), 643 (m), 615 (w), 605 (m).
diethyl 2-(2,5,5-trimethyl-1,3-dioxan-2-yl)benzylphosphonate (55)

MF = C_{19}H_{29}O_{5}P

MW = 356.39 g/mol

Air stable

A solution of 2-(2-(bromomethyl)phenyl)-2,5,5-trimethyl-1,3-dioxane 54 (2.30 g, 7.69 mmol, 1 eq.) and P(OEt)₃ (1.98 mL, 1.92 g, 11.53 mmol, 1.5 eq.) was refluxed for 3 hours then all volatiles were removed under reduced pressure. The title compound was obtained as yellowish oil. Yield: 2.53 g, 92%.

$^1$H-NMR (500.23 MHz, CDCl₃, 298 K): $\delta = 0.62$ (s, 3H, C(CH₃)₂), 1.26 (t, $^3$$J_{HH} = 7.1$ Hz, 6H, CH₂CH₃), 1.30 (s, 3H, C(CH₃)₂), 1.67 (s, 3H, ArCCCH₃), 3.40-3.50 (m, 4H, CH₂CMe₂), 3.70 (d, $^2$$J_{PH} = 23.1$ Hz, 2H, CH₂P), 4.01-4.08 (m, 4H, CH₂CH₃) 7.27-7.32 (m, 2H, CHᵐ⁺), 7.55 (d, $J = 7.6$ Hz, 1H, CHᵐ⁻), 7.67-7.70 (m, 1H, CHᵐ⁺).

$^{13}$C{¹H}-NMR (125.78 MHz, CDCl₃, 298 K): $\delta = 16.7$ (d, $^3$$J_{PC} = 6.0$ Hz, 2C, CH₂CH₃), 22.3 (s, 1C, C(CH₃)₂), 23.3 (s, 1C, C(CH₃)₂), 29.2 (d, $^1$$J_{PC} = 138.7$ Hz, 1C, CH₂P), 30.3 (s, 1C, C(CH₃)₂), 31.1 (s, 1C, ArCCH₃), 62.2 (d, $^2$$J_{PC} = 6.7$ Hz, 2C, CH₂CH₃), 72.1 (s, 2C, CH₂CMe₂), 101.5 (d, $^4$$J_{PC} = 1.2$ Hz, 1C, ArCCH₃), 127.4 (d, $J = 2.9$ Hz, 1C, CHᵐ⁺), 128.2 (d, $J = 2.9$ Hz, 1C, CHᵐ⁻), 129.3 (d, $J = 2.2$ Hz, 1C, CHᵐ⁺), 130.7 (d, $J = 7.7$ Hz, 1C, C quat), 132.6 (d, $J = 5.3$ Hz, 1C, CHᵐ⁻), 138.8 (d, $J = 9.1$ Hz, 1C, C quat).

$^{31}$P{¹H}-NMR (202.50 MHz, CDCl₃, 298 K) $\delta = 29.5$ (s).

ATR IR (in cm⁻¹): 2976 (w), 2953 (w), 2899 (w), 2863 (w), 1601 (w), 1471 (w), 1443 (w), 1396 (w), 1372 (w), 1294 (w), 1284 (w), 1247 (s), 1208 (m), 1177 (s), 1119 (w), 1098 (m), 1078 (s), 1052 (s), 1024 (s), 950 (s), 913 (m), 870 (m), 846 (s), 830 (w), 794 (m), 761 (s), 712 (w), 671 (m), 643 (m), 608 (m).
(E)-diphenyl(2-(2-(2,5,5-trimethyl-1,3-dioxan-2-yl)styryl)phenyl)phosphane (56)

\[ MF = C_{33}H_{33}O_{2}P \]

\[ MW = 492.59 \text{ g/mol} \]

\[ MP = 70-71 \degree C \]

Air stable

BuLi (1.6 M in hexane, 7.94 mL, 12.4 mmol, 1.2 eq.) was added to a solution of diethyl 2-(2,5,5-trimethyl-1,3-dioxan-2-yl)benzylphosphonate 55 (4.42 g, 12.4 mmol, 1.2 eq.) in THF (60 mL) at -78 \degree C. The resulting mixture was stirred for 20 minutes then a solution of 2-(diphenylphosphino)benzaldehyde 12 (3.00 g, 10.3 mmol, 1 eq.) in THF (10 mL) was added dropwise. The reaction mixture was stirred for 10 minutes then it was warmed to room temperature and stirred for 1 hour. Et\(_2\)O and saturated NH\(_4\)Cl were added and the aqueous phase was extracted twice with Et\(_2\)O. The combined organic phases were washed with brine, dried over Na\(_2\)SO\(_4\), filtered and concentrated. The resulting crude product was purified by column chromatography (Eluent: DCM) to give the title compound as a white solid. Yield: 4.46 g, 87%.

\[^1\text{H}-\text{NMR} \ (500.23 \text{ MHz, CDCl}_3, \ 298 \text{ K})\]: \( \delta = 0.51 \text{ (s, 3H, C(CH}_3)_2), \ 1.26 \text{ (s, 3H, C(CH}_3)_2), \ 1.61 \text{ (s, 3H, ArCCCH}_3), \ 3.20 \text{ (d, } J_{HH} = 11.2 \text{ Hz, 2H, CH}_2\text{CMe}_2), \ 3.27 \text{ (d, } J_{HH} = 11.2 \text{ Hz, 2H, CH}_2\text{CMe}_2), \ 6.88 \text{ (dd, } J = 6.6 \text{ Hz, } J = 4.6 \text{ Hz, 1H, CH}^\text{ar}), \ 7.19 \text{ (t, } J = 7.5 \text{ Hz, 1H, CH}^\text{ar}), \ 7.26-7.37 \text{ (m, 12H, CH}^\text{ar}), \ 7.40 \text{ (t, } J = 7.6 \text{ Hz, 1H, CH}^\text{ar}), \ 7.46-7.49 \text{ (m, 2H, CH}^\text{ar}, \ CH^\text{olefin}), \ 7.51 \text{ (d, } J = 4.12 \text{Hz, 1H, CH}^\text{olefin}) \]

\[^{13}\text{C}\{^1\text{H}\}-\text{NMR} \ (125.78 \text{ MHz, CDCl}_3, \ 298 \text{ K})\]: \( \delta = 22.3 \text{ (s, 1C, C(CH}_3)_2), \ 23.5 \text{ (s, 1C, C(CH}_3)_2), \ 30.1 \text{ (s, 1C, C(CH}_3)_2), \ 31.1 \text{ (s, 1C, ArCCCH}_3), \ 71.8 \text{ (s, 2C, CH}_2\text{CMe}_2), \ 101.4 \text{ (s, 1C, ArCCCH}_3), \ 126.4 \text{ (d, } J = 4.1 \text{ Hz, 1C, CH}^\text{ar}), \ 127.8 \text{ (d, } J = 0.7 \text{ Hz, 1C, CH}^\text{ar}), \ 128.1 \text{ (s, 1C, CH}^\text{ar}), \ 128.5 \text{ (d, } J = 25.2 \text{ Hz, 1C, CH}^\text{ar}), \ 128.5 \text{ (s, 1C, CH}^\text{olefin}), \ 128.5 \text{ (s, 1C, CH}^\text{olefin}), \ 128.9 \text{ (d, } J_{PC} = 7.0 \text{ Hz, 4C, CH}^\text{ar}), \ 129.1 \text{ (s, 1C, CH}^\text{ar}), \ 129.1 \text{ (s, 2C, CH}^\text{ar}), \ 129.5 \text{ (s, 1C, CH}^\text{ar}), \ 131.4 \text{ (d, } J = 2.4 \text{ Hz, 1C, CH}^\text{ar}), \ 133.5 \text{ (s, 1C, CH}^\text{ar}), \ 134.5 \text{ (d, } J_{PC} = 19.9 \text{ Hz, 4C, CH}^\text{ar}), \ 135.7 \text{ (d, } J_{PC} = 13.4 \text{ Hz, 1C, C}^\text{quat}), \ 136.9 \text{ (d, } J_{PC} = 9.8 \text{ Hz, 2C, C}^\text{quat}), \ 137.5 \text{ (s, 1C, C}^\text{quat}), \ 137.9 \text{ (s, 1C, C}^\text{quat}), \ 143.0 \text{ (d, } J_{PC} = 21.6 \text{ Hz, 1C, C}^\text{quat}). \]

\[^{31}\text{P}\{^1\text{H}\}-\text{NMR} \ (202.50 \text{ MHz, CDCl}_3, \ 298 \text{ K})\] \( \delta = -12.6 \text{ (s).} \)

ATR IR (\( \nu \text{ in cm}^{-1} \)): 3049 (w), 2950 (w), 2858 (w), 1584 (w), 1566 (w), 1475 (m), 1454 (w), 1434 (m), 1395 (w), 1371 (m), 1318 (w), 1305 (w), 1241 (m), 1204 (w), 1178 (s), 1129 (m), 1101 (w), 1078 (s), 1036 (m), 1012 (m), 949 (m), 911 (m), 868 (m), 820 (w), 794 (w), 762 (s), 743 (s), 695 (s), 672 (m), 606 (m).
(E)-1-(2-(2-(diphenylphosphino)styryl)phenyl)ethanone (53)

MF = C_{28}H_{23}OP

MW = 406.46 g/mol

MP = 137-139 °C

Air stable

To a solution of (E)-diphenyl(2-(2-(2,5,5-trimethyl-1,3-dioxan-2-yl)styryl)phenyl)phosphane 56 (3.70 g, 7.51 mmol) in THF (200 mL) was added aqueous HCl (10%, 100 mL). The resulting solution was degassed and stirred for 1 day then NaOH was added as solid until the pH of the aqueous phase was above 13. The aqueous phase was extracted 3 times with Et₂O, the combined organic phases were washed with brine, dried with Na₂SO₄ and concentrated. The title compound was obtained as white solid. Yield: 0.82 g, 100%.

^{1}H-NMR (500.23 MHz, CDCl₃, 298 K): δ = 2.57 (s, 3H, CH₃), 6.89 (dd, J = 7.0 Hz, J = 4.7 Hz, 1H, CH²Ph), 7.21 (t, J = 7.5 Hz, 1H, CH²Ph) 7.30-7.42 (m, 14H, CH²Ar), 7.55 (d, J = 15.8 Hz, 1H, CH²Ph, CH²olefin), 7.63-7.67 (m, 2H, CH²Ar, CH²olefin) 7.80 (dd, J = 7.6 Hz, J = 4.1 Hz, 1H, CH²Ph).

^{13}C{^{1}H}-NMR (125.78 MHz, CDCl₃, 298 K): δ = 30.2 (s, 1C, CH₃), 126.5 (d, J = 4.1 Hz, 1C, CH²Ph), 127.6 (s, 1C, CH²Ph), 128.2 (s, 1C, CH²Ph), 128.2 (s, 1C, CH²Ph), 129.0 (d, J_{PC} = 7.2 Hz, 4C, CH²Ph), 129.2 (s, 2C, CH²Ph), 129.3 (s, 1C, CH²olefin), 129.5 (s, 1C, CH²olefin), 129.9 (d, J = 2.4 Hz, 1C, CH²Ph), 130.6 (d, J_{PC} = 24.7 Hz, 1C, CH²Ph), 132.1 (s, 1C, CH²Ph), 133.6 (s, 1C, CH²Ph), 134.5 (d, J_{PC} = 19.9 Hz, 4C, CH²Ph), 136.1 (d, J_{PC} = 13.7 Hz, 1C, C²quat), 136.7 (d, J_{PC} = 9.8 Hz, 2C, C²quat), 137.7 (s, 1C, C²quat), 138.0 (s, 1C, C²quat), 142.3 (d, J_{PC} = 21.6 Hz, 1C, C²quat), 202.4 (s, 1C, CO).

^{31}P{^{1}H}-NMR (202.50 MHz, CDCl₃, 298 K) δ = -12.2 (s).

ATR IR (v in cm⁻¹): 3056 (w), 2965 (w), 2925 (w), 2862 (w), 1967 (w), 1678 (m), 1592 (w), 1582 (w), 1564 (m), 1506 (w), 1477 (m), 1456 (w), 1432 (m), 1390 (w), 1350 (m), 1304 (w), 1290 (w), 1273 (w), 1258 (m), 1244 (m), 1193 (w), 1179 (w), 1157 (w), 1121 (w), 1090 (m), 1053 (w), 1027 (m), 999 (m), 919 (w), 946 (s), 916 (w), 870 (w), 842 (w), 763 (s), 746 (s), 728 (w), 696 (s), 631 (w).
[RhCl(OHMe2StilbPPh2)] (57)

MF = C29H27ClOPRh

MW = 560.86 g/mol

MP = > 220 °C

Air stable

To a solution of [RhCl(COD)]2 (200 mg, 0.406 mmol, 1 eq.) in THF (3 mL) was added (E)-2-(2-(2-(diphenylphosphino)styryl)phenyl)propan-2-ol 51 (360 mg, 0.852 mmol, 2.1 eq.). The resulting solution was stirred for 30 minutes then layered with hexane. The title compound precipitated as yellow solid which was dried under high vacuum. Yield: 450 mg, 99%.

\[ \begin{align*}
\text{1H-NMR} & \quad (500.23 \text{ MHz, [D8]THF, 298 K}): \delta = 1.78 \ (s, 3H, \text{CH}_3), \ 1.87 \ (s, 3H, \text{CH}_3), \ 3.51 \ (d, \ J_{\text{HH}} = 9.9 \text{ Hz, 1H, CH}^{\text{olefin}}), \ 4.30 \ (d, \ J_{\text{HH}} = 9.9 \text{ Hz, 1H, CH}^{\text{olefin}}), \ 6.50 \ (s, 1H, \text{OH}), \ 7.00 \ (t, \ J = 7.5 \text{ Hz, 1H, CH}^{\text{ar}}), \ 7.10 \ (d, \ J = 7.1 \text{ Hz, 1H, CH}^{\text{ar}}), \ 7.14 \ (t, \ J = 7.5 \text{ Hz, 2H, CH}^{\text{ar}}), \ 7.24-7.28 \ (m, 5H, \text{CH}^{\text{ar}}), \ 7.31-7.33 \ (m, 1H, \text{CH}^{\text{ar}}), \ 7.47-7.53 \ (m, 6H, \text{CH}^{\text{ar}}), \ 8.01-8.05 \ (m, 2H, \text{CH}^{\text{ar}}).
\end{align*} \]

\[ \begin{align*}
\text{13C\{1H\}-NMR} & \quad (125.78 \text{ MHz, [D8]THF, 298 K}): \delta = 31.2 \ (d, \ J = 1.4 \text{ Hz, 1C, CH}_3), \ 35.2 \ (s, 1C, \text{CH}_3), \ 68.3 \ (dd, \ J = 16.3 \text{ Hz, 1C, CH}^{\text{olefin}}), \ 68.9 \ (d, \ J = 16.3 \text{ Hz, 1C, CH}^{\text{olefin}}), \ 76.5 \ (s, 1C, \text{CMe}_2\text{OH}), \ 125.8 \ (s, 1C, \text{CH}_3), \ 126.0 \ (s, 1C, \text{CH}_3), \ 126.1 \ (d, \ J = 7.0 \text{ Hz, 1C, CH}^{\text{ar}}), \ 126.6 \ (d, \ J = 15.6 \text{ Hz, 1C, CH}^{\text{ar}}), \ 126.8 \ (s, 1C, \text{CH}^{\text{ar}}), \ 127.6 \ (d, \ J = 10.8 \text{ Hz, 2C, CH}^{\text{ar}}), \ 128.6 \ (d, \ J = 10.1 \text{ Hz, 2C, CH}^{\text{ar}}), \ 129.6 \ (d, \ J = 2.6 \text{ Hz, 1C, CH}^{\text{ar}}), \ 129.8 \ (d, \ J = 2.4 \text{ Hz, 1C, CH}^{\text{ar}}), \ 130.2 \ (d, \ J = 2.4 \text{ Hz, 1C, CH}^{\text{ar}}), \ 132.0 \ (s, 1C, \text{CH}^{\text{ar}}), \ 132.8 \ (d, \ J = 1.2 \text{ Hz, 1C, CH}^{\text{ar}}), \ 133.1 \ (d, \ J_{\text{PC}} = 30.9 \text{ Hz, 1C, C}^{\text{quat}}), \ 133.4 \ (d, \ J = 11.0 \text{ Hz, 2C, CH}^{\text{ar}}), \ 134.1 \ (d, \ J = 11.0 \text{ Hz, 2C, CH}^{\text{ar}}), \ 134.8 \ (d, \ J_{\text{PC}} = 55.9 \text{ Hz, 2C, C}^{\text{quat}}), \ 137.5 \ (s, 1C, \text{C}^{\text{quat}}), \ 143.5 \ (s, 1C, \text{C}^{\text{quat}}), \ 158.6 \ (d, \ J_{\text{PC}} = 22.1 \text{ Hz, 1C, C}^{\text{quat}}).
\end{align*} \]

\[ \begin{align*}
\text{31P\{1H\}-NMR} & \quad (202.50 \text{ MHz, [D8]THF, 298 K}): \delta = 62.8 \ (d, \ J_{\text{RhP}} = 192.2 \text{ Hz}).
\end{align*} \]

\[ \begin{align*}
\text{1H, 103Rh-NMR} & \quad (15.81 \text{ MHz, [D8]THF, 298 K}): \delta = -7554 \ (d, \ J_{\text{PRh}} = 192.2 \text{ Hz}).
\end{align*} \]

\[ \begin{align*}
\text{ATR IR (v in cm}^{-1}) & \quad : \ 3256 \ (\text{br}), \ 2982 \ (\text{w}), \ 2902 \ (\text{w}), \ 2148 \ (\text{w}), \ 1967 \ (\text{w}), \ 1712 \ (\text{w}), \ 1694 \ (\text{w}), \ 1681 \ (\text{w}), \ 1587 \ (\text{w}), \ 1555 \ (\text{w}), \ 1541 \ (\text{w}), \ 1490 \ (\text{w}), \ 1481 \ (\text{w}), \ 1470 \ (\text{w}), \ 1437 \ (\text{m}), \ 1393 \ (\text{w}), \ 1363 \ (\text{m}), \ 1259 \ (\text{w}), \ 1236 \ (\text{w}), \ 1222 \ (\text{w}), \ 1207 \ (\text{w}), \ 1154 \ (\text{w}), \ 1127 \ (\text{w}), \ 1113 \ (\text{m}), \ 1098 \ (\text{m}), \ 1069 \ (\text{w}), \ 1050 \ (\text{w}), \ 1028 \ (\text{w}), \ 996 \ (\text{w}), \ 936 \ (\text{w}), \ 919 \ (\text{w}), \ 903 \ (\text{m}), \ 881 \ (\text{w}), \ 845 \ (\text{w}), \ 820 \ (\text{w}), \ 799 \ (\text{w}), \ 762 \ (\text{m}), \ 750 \ (\text{s}), \ 708 \ (\text{m}), \ 696 \ (\text{s}), \ 631 \ (\text{w}), \ 617 \ (\text{w}).
\end{align*} \]
[Rh(OHCHMe₂StilbPPh₂)OTf (59)

MF = C₃₀H₂₇F₃O₄PRhS

MW = 674.47 g/mol

MP = 109-111 °C (decomposition)

Slightly air sensitive

To a solution of [RhCl(OHCHMe₂StilbPPh₂)] 57 (100 mg, 0.178 mmol, 1 eq.) in THF (1 mL) and DCM (5 mL) AgOTf (50.4 mg, 0.196 mmol, 1.1 eq.) was added. The resulting mixture was stirred overnight then all solvents were removed under reduced pressure. The residue was dissolved in DCM and filtered over celite. All volatiles were removed under reduced pressure and the residue was recrystallised from THF/hexane. Yield: 80 mg, 67%.

¹H-NMR (500.23 MHz, [D₈]THF, 298 K): δ = 1.80 (s, 3H, CH₃), 1.98 (s, 3H, CH₃), 3.56 (d, 3JHH = 10.1 Hz, 1H, CH olefin), 4.50 (dd, 3JHH = 10.1 Hz, 3JHH = 1.5 Hz, 1H, CH olefin), 6.97 (s, 1H, OH), 7.09 (t, J = 8.3 Hz, 1H, CH ar), 7.18 (d, J = 7.1 Hz, 1H, CH ar), 7.22-7.32 (m, 1H, CH ar), 7.34-7.46 (m, 7H, CH ar), 7.54-7.61 (m, 5H, CH ar), 8.08-8.12 (m, 2H, CH ar).

¹³C{¹H}-NMR (125.78 MHz, [D₈]THF, 298 K): δ = 30.8 (s, 1C CH₃), 34.5 (s, 1C CH₃) 64.3 (d, J = 15.4 Hz, 1C, CH olefin), 66.1 (d, J = 19.7 Hz, 1C, CH olefin), 77.1 (s, 1C, CMe₂OH), 120.1 (q, 1JFC = 320.4 Hz, 1C, CF₃), 126.6 (s, 1C, CH ar), 126.6 (s, 1C, CH ar), 126.9 (s, 1C, CH ar), 126.9-127.1 (m, 1C, CH ar), 127.1 (d, J = 7.7 Hz, 1C, CH ar), 128.6 (s, 1C, CH ar), 128.6 (s, 1C, CH ar), 129.1 (s, 1C, CH ar), 129.2 (s, 1C, CH ar), 130.6 (d, J = 2.9 Hz, 1C, CH ar), 130.7 (d, J = 2.4 Hz, 1C, CH ar), 131.1 (d, 1JPC = 44.9 Hz, 2C, C quat), 131.3 (d, J = 2.6 Hz, 1C, CH ar) 131.9 (d, 1JPC = 52.5 Hz, 1C, C quat), 131.9 (s, 1C, CH ar), 132.6 (s, 1C, CH ar), 133.4 (d, J = 11.3 Hz, 2C, CH ar), 133.8 (d, J = 11.8 Hz, 2C, CH ar), 135.9 (d, J = 1.7 Hz, 1C, C quat), 143.4 (s, 1C, C quat), 157.4 (d, 2JPC = 22.1 Hz, 1C, C quat).

¹⁹F-NMR (188.31 MHz, [D₈]THF, 298 K): δ = -78.3 (s).

³¹P{¹H}-NMR (202.50 MHz, [D₈]THF, 298 K) δ = 60.9 (d, 1JRP = 187.6 Hz).

¹H, ¹⁰³Rh-NMR (15.81 MHz, [D₈]THF, 298 K): δ = -7323 (d, 1JPRh = 187.6 Hz).

ATR IR (v in cm⁻¹): 2963 (w), 2913 (w), 2154 (w), 1976 (w), 1649 (w), 1586 (w), 1558 (w), 1540 (w), 1483 (w), 1469 (w), 1437 (w), 1401 (w), 1284 (w), 1259 (m), 1224 (m), 1159 (m) 1093 (s), 1024 (s), 919 (w), 867 (w), 796 (s), 757 (m), 722 (w), 692 (s), 635 (s).
[RhCl(OHtripPhPPh$_2$)] (58)

MF = C$_{33}$H$_{25}$ClOPRh

MW = 606.88 g/mol

MP = >220 °C

Air stable

To a solution of [RhCl(COD)]$_2$ (200 mg, 0.406 mmol, 1 eq.) in THF (3 mL) 10-(2-(diphenylphosphane)phenyl)5H-dibenzo[a,d]cyclohepten-5-ol 32 (399 mg, 0.852 mmol, 2.1 eq.) was added. The resulting solution was stirred for 30 minutes then layered with hexane. The title compound precipitated as yellow solid which was dried under high vacuum.

Yield: 490 mg, 99%.

$^1$H-NMR (500.23 MHz, [D$_8$]THF, 298 K): $\delta = 3.80$ (s, 1H, CH$_{\text{olefin}}$), 5.91 (d, $J = 3.4$ Hz, 1H, CH$_{\text{benzyl}}$), 7.21 (dt, $J = 7.5$ Hz, $J = 1.4$ Hz, 1H, CH$_{\text{ar}}$), 7.27-7.40 (m, 9H, CH$_{\text{ar}}$), 7.44-7.51 (m, 5H, CH$_{\text{ar}}$), 7.56 (t, $J = 7.7$ Hz, 1H, CH$_{\text{ar}}$), 7.65-7.72 (m, 3H, CH$_{\text{ar}}$), 7.99 (dd, $J = 7.5$ Hz, $J = 1.7$ Hz, 1H, CH$_{\text{ar}}$), 8.04-8.08 (m, 2H, CH$_{\text{ar}}$), 8.12 (s, 1H, OH).

$^{13}$C$_{\{^1\text{H}\}}$-NMR (125.78 MHz, [D$_8$]THF, 298 K): $\delta = 66.6$ (d, $J = 2.6$ Hz, 1C, CH$_{\text{olefin}}$), 75.0 (d, $J = 15.8$ Hz, 1C, C$_{\text{quat}}$), 81.0 (s, 1C, CH$_{\text{benzyl}}$), 125.3 (s, 1C, CH$_{\text{ar}}$), 126.2 (s, 1C, CH$_{\text{ar}}$), 126.9 (d, $J = 6.5$ Hz, 1C, CH$_{\text{ar}}$), 127.7 (s, 1C, CH$_{\text{ar}}$), 127.8 (s, 2C, CH$_{\text{ar}}$), 127.8 (s, 1C, CH$_{\text{ar}}$), 128.4 (d, $J = 10.3$ Hz, 2C, CH$_{\text{ar}}$), 128.7 (d, $J = 12.7$ Hz, 2C, CH$_{\text{ar}}$), 129.3 (d, $J = 2.4$ Hz, 1C, CH$_{\text{ar}}$), 129.6 (d, $J = 2.9$ Hz, 1C, CH$_{\text{ar}}$), 129.7 (s, 1C, CH$_{\text{ar}}$), 130.4 (d, $J = 2.4$ Hz, 1C, CH$_{\text{ar}}$), 130.5 (s, 1C, CH$_{\text{ar}}$), 130.7 (d, $J = 14.9$ Hz, 1C, CH$_{\text{ar}}$), 132.9 (d, $J = 1.4$ Hz, 1C, CH$_{\text{ar}}$), 133.4 (d, $^1$J$_{\text{PH}} = 50.4$ Hz, 1C, C$_{\text{quat}}$), 134.1 (d, $J = 1.2$ Hz, 2C, CH$_{\text{ar}}$), 134.2 (s, 2C, CH$_{\text{ar}}$), 135.4 (d, $^1$J$_{\text{PH}} = 56.6$ Hz, 2C, C$_{\text{quat}}$), 137.5 (s, 1C, C$_{\text{quat}}$), 138.0 (s, 1C, C$_{\text{quat}}$), 138.1 (d, $J = 1.7$ Hz, 1C, C$_{\text{quat}}$), 139.9 (d, $J = 2.2$ Hz, 1C, C$_{\text{quat}}$), 156.9 (d, $J = 22.1$ Hz, 1C, C$_{\text{quat}}$).

$^{31}$P$_{\{^1\text{H}\}}$-NMR (202.50 MHz, [D$_8$]THF, 298 K) $\delta = 65.3$ (d, $^1$J$_{\text{RP}} = 188.4$ Hz).

$^1$H, $^{103}$Rh-NMR (15.81 MHz, [D$_8$]THF, 298 K): $\delta = -7498$ (d, $^1$J$_{\text{PRh}} = 188.4$ Hz).

ATR IR (v in cm$^{-1}$): 3056 (w), 2976 (w), 2919 (w), 2862 (w), 1967 (w), 1481 (w), 1465 (w), 1434 (m), 1333 (w), 1304 (w), 1256 (w), 1207 (w), 1179 (w), 1156 (w), 1127 (w), 1097 (m), 1065 (m), 1046 (m), 996 (w), 971 (w), 942 (w), 908 (w), 890 (w), 845 (w), 800 (w), 766 (m), 745 (s), 718 (s), 693 (s), 646 (w), 622 (m).
[Rh(OHtropPhPPh₂)]OTf (60)

MF = C₃₄H₂₅F₃O₄PRhS

MW = 720.50 g/mol

MP = 156-157 °C (decomposition)

Air stable

To a solution of [RhCl(OHtropPhPPh₂)] 58 (100 mg, 0.165 mmol, 1 eq.) in THF (1 mL) and DCM (5 mL) was added AgOTf (47 mg, 0.181 mmol, 1.1 eq.). The resulting mixture was stirred overnight then all solvents were removed under reduced pressure. The residue was dissolved in DCM and filtered over celite. All volatiles were removed under reduced pressure and the residue was recrystallised from THF/hexane. Yield: 103 mg, 87%.

¹H-NMR (500.23 MHz, [D₈]THF, 298 K): δ = 3.76 (s, 1H, CHolefin), 6.00 (s, 1H, Cbenzyl), 7.29 (td, J = 7.5 Hz, J = 1.3 Hz, 1H, CH₃), 7.33–7.64 (m, 17H, Caryl), 7.75 (dd, J = 7.7 Hz, J = 2.9 Hz, 1H, CH₃), 8.06–8.09 (m, 1H, CH₃), 8.07 (s, 1H, OH), 8.15–8.19 (m, 2H, CH₃).  

¹³C{¹H}-NMR (125.78 MHz, [D₈]THF, 298 K): δ = 61.1 (d, J = 18.7 Hz, 1C, Caryl), 70.7 (d, J = 17.5 Hz, 1C, Colefin), 80.2 (s, 1C, Caryl), 121.1 (q, JPC = 320.3 Hz, 1C, CF₃), 126.3 (s, 1C, CH₃), 126.9 (s, 1C, CH₃), 127.6 (d, J = 7.2 Hz, 1C, CH₃), 128.4 (s, 1C, CH₃), 128.7 (s, 1C, CH₃), 128.8 (s, 1C, CH₃), 128.9 (s, 1C, CH₃), 129.0 (s, 2C, CH₃), 129.2 (s, 1C, CH₃), 130.1 (s, 1C, CH₃), 130.1 (d, J = 2.2 Hz, 1C, CH₃), 130.7 (s, 1C, CH₃), 130.8 (d, J = 18.6 Hz, 1C, CH₃), 131.1 (d, JPC = 52.1 Hz, 2C, Cquat), 131.1 (s, 1C, CH₃), 131.5 (d, J = 2.6 Hz, 1C, CH₃), 132.5 (d, JPC = 54.0 Hz, 1C, Cquat), 133.7 (s, 1C, CH₃), 134.8 (d, J = 12.0 Hz, 2C, CH₃), 137.4 (d, J = 1.7 Hz, 1C, Cquat), 137.9 (s, 1C, Cquat), 138.2 (s, 1C, Cquat), 139.0 (d, J = 2.4 Hz, 1C, Cquat), 156.3 (d, JPC = 21.8 Hz, 1C, Cquat).

¹⁹F-NMR (188.31 MHz, [D₈]THF, 298 K): δ = -78.4 (s).

³¹P{¹H}-NMR (202.50 MHz, [D₈]THF, 298 K) δ = 67.5 (d, JRhP = 181.5 Hz).

¹H, ¹³⁵Rh-NMR (15.81 MHz, [D₈]THF, 298 K): δ = -7121 (d, JRhRh = 181.5 Hz).

ATR IR (v in cm⁻¹): 2965 (w), 2925 (w), 2159 (w), 1481 (w), 1464 (w), 1436 (w), 1290 (m), 1262 (w), 1228 (m), 1204 (m), 1176 (m), 1099 (m), 1067 (w), 1025 (s), 942 (w), 877 (w), 848 (w), 803 (w), 768 (m), 745 (w), 721 (m), 694 (s), 635 (s).
7.5 Compounds synthesised for chapter 3

[Rh(eq-OAc)(trop2NH)(PPh₃)] (7)

\[
\text{MF} = C_{50}H_{41}NO_2PRh \\
\text{MW} = 821.20 \text{ g/mol} \\
\text{MP} > 220^\circ C
\]

Air stable

AgOAc (42 mg, 0.25 mmol, 4 eq.) was added to a solution of [RhCl(trop2NH)(PPh₃)] (50 mg, 0.063 mmol, 1 eq.) in CH₂Cl₂ (3 mL). The resulting mixture was stirred over 3 days, filtered twice over celite and concentrated. Addition of hexane precipitated 7 as yellow powder which was dried under high vacuum. Yield: 35 mg, 68%.

The same complex 7 was extracted from the electrode with THF, filtered over Celite. The volume of the solvent was reduced and the extract analysed by 31P{1H}-NMR. The main component was complex 7, traces of P(O)Ph₃ and an unidentified impurity at 11.1 ppm (1J_{RhP} = 112.5 Hz) are present. The extract was layered with hexane and the obtained pale orange precipitate dried under vacuum. Yield of 7 from the electrode: 25 mg.

Crystals suitable for X-ray analysis were obtained by layering a concentrated solution of 7 in acetone with hexane.

1H-NMR (500 MHz, [D8]THF, 298 K): δ = 1.28 (s, 3H, CH₃), 4.82 (dt, 3J_{HH} = 9.62 Hz, 2J_{RhH} = 2.2 Hz, 3J_{PH} = 2.2 Hz, 2H, CHolefin), 4.89 (dd, 3J_{HH} = 8.1 Hz, 2J_{RhH} = 1.7 Hz, 2H, CHolefin), 4.92 (d, 4J_{PH} = 9.8 Hz, 2H, CH²benzyl), 6.54 (d, 3J_{HH} = 6.8 Hz, 2H, CH²), 6.63 (td, 3J_{HH} = 7.5 Hz, 3J_{HH} = 1.3 Hz, 2H, CH³), 6.77 (td, 3J_{HH} = 7.5 Hz, 4J_{HH} = 1.3 Hz, 2H, CH³), 6.85 (d, 3J_{HH} = 6.8 Hz, 2H, CH³), 7.03 (td, 3J_{HH} = 7.4 Hz, 4J_{HH} = 1.5 Hz, 2H, CH³), 7.08 (td, 3J_{HH} = 7.4 Hz, 4J_{HH} = 1.5 Hz, 2H, CH³), 7.15 (dd, 3J_{HH} = 7.7 Hz, 4J_{HH} = 1.3 Hz, 2H, CH³), 7.24 (dd, 3J_{HH} = 7.3 Hz, 4J_{HH} = 1.3 Hz, 2H, CH³), 7.52-7.60 (m, 9H, CH³), 8.01 (t, 3J_{HH} = 7.9 Hz, 6H, CH³), 10.90 (d, 3J_{PH} = 6.0 Hz, 1H, NH).

13C{¹H}-NMR (126 MHz, [D8]THF, 298 K): δ = 24.9 (s, 1C CH₃), 67.4 (d, 1J_{RHC} = 12.0 Hz, 2C, CHolefin), 69.0 (d, 1J_{RHC} = 7.7 Hz, 2C, CHolefin) 71.8 (s, 2C, CH²benzyl), 125.0 (s, 2C, CH³), 125.2 (s, 2C, CH⁴), 127.2 (s, 2C, CH⁴), 127.7 (s, 2C, CH⁴), 127.8 (s, 2C, CH⁴), 128.3 (s, 2C, CH⁴), 128.4 (d, 3J_{PC} = 9.6 Hz, 6C, CH³), 129.4 (s, 2C, CH⁴), 130.5 (d, 4J_{HH} = 2.4 Hz, 3C, CH⁴), 131.3 (d, 1J_{PC} = 44.1 Hz, 3C, C⁷quat), 135.1 (d, 2J_{PC} = 8.6 Hz, 6C, CH³), 136.0 (s, 2C, C⁷quat), 136.2 (s, 2C, C⁷quat), 137.2 (s, 2C, C⁷quat), 139.8 (s, 2C, C⁷quat), 178.6 (s, 1C, C⁷quat).

31P{¹H}-NMR (203 MHz, [D8]THF, 298 K): δ = 38.9 (d, 1J_{RHP} = 131.2 Hz).

1H,103Rh-NMR (15.8 MHz, [D8]THF, 298 K): δ = -6832 (d, 1J_{RHP} = 131.2 Hz).
ATR IR (ν in cm⁻¹): 2987 (w), 2970 (w), 2896 (w), 1866 (w), 1846 (w), 1712 (w), 1683 (w), 1652 (w), 1541 (m), 1487 (w), 1473 (w), 1435 (w), 1396 (m), 1338 (w), 1313 (w), 1255 (m), 1221 (w), 1185 (w), 1162 (w), 1088 (m), 1045 (m), 987 (m), 933 (w), 925 (w), 879 (w), 842 (w), 803 (m), 774 (w), 752 (m), 738 (s), 714 (w), 700 (s), 654 (m), 614 (w), 606 (w).
[\text{Rh(ax-OAc)(trop}_2\text{NH)}(\text{PPh}_3)] (\text{62})

\begin{align*}
\text{MF} & = C_{50}H_{41}NO_2PRh \\
\text{MW} & = 821.20 \text{ g/mol} \\
\text{MP} & > 220^\circ \text{C}
\end{align*}

Air stable

A solution of [\text{Rh(trop}_2\text{N})\text{PPh}_3] (50 mg, 0.07 \mu\text{mol, 1 eq.}) in \text{THF} (2 mL) was treated with degassed water (1-2 drops) and then with degassed aqueous acetic acid (5%, 3 mL) and extracted with DCM (2x 5 mL). The extract was dried over MgSO\textsubscript{4} and the solvents removed under reduced pressure. An about 1:3 mixture of \text{7} and \text{62} was obtained. The mixture was dissolved in DCM (2 mL) and layered with hexane (20 mL). \text{62} was obtained as yellow crystals of which some were suitable for X-ray diffraction. Yield: 34 mg, 62%.

\begin{align*}
\text{AgOAc} & (42 \text{ mg}, 0.25 \text{ mmol, 4 eq.}) was added to a solution of [\text{RhCl(trop}_2\text{NH)}(\text{PPh}_3)] (50 \text{ mg}, 0.063 \text{ mmol, 1 eq.}) in acetone (3 mL). The resulting mixture was stirred over 2 days, then the solvent was removed and CH\textsubscript{2}Cl\textsubscript{2} was added to the residue. The obtained mixture was filtered over Celite and concentrated. Addition of hexane precipitated \text{62} as yellow powder, which was dried under high vacuum. Yield: 38 mg, 74%.
\end{align*}

\begin{align*}
1^\text{H}-\text{NMR} (500 \text{ MHz, CDCl}_3, 298 \text{ K}): \delta & = 2.06 \ (s, 3 \text{H}, \text{CH}_3), 3.74 \ (s, 2 \text{H}, \text{CH}^{\text{benzyl}}), 5.35 \ (s, 1 \text{H}, \text{NH}), 5.52 \ (m, 2 \text{H}, \text{CH}^{\text{olefin}}) 6.50 \ (d, \ 3J_{\text{HH}} = 7.3 \text{ Hz}, 2 \text{H}, \text{CH}^{\text{ar}}), 6.62 \ (d, \ 3J_{\text{HH}} = 7.3 \text{ Hz}, 2 \text{H}, \text{CH}^{\text{ar}}), 6.67 \ (t, \ 3J_{\text{HH}} = 6.8 \text{ Hz}, 2 \text{H}, \text{CH}^{\text{ar}}), 6.68 \ (m, 2 \text{H}, \text{CH}^{\text{olefin}}), 6.78 \ (d, \ 3J_{\text{HH}} = 7.3 \text{ Hz}, 2 \text{H}, \text{CH}^{\text{ar}}), 6.86 \ (td, \ 3J_{\text{HH}} = 7.6 \text{ Hz}, 4J_{\text{HH}} = 1.3 \text{ Hz}, 2 \text{H}, \text{CH}^{\text{ar}}), 7.28 \ (d, \ 3J_{\text{HH}} = 7.3 \text{ Hz}, 2 \text{H}, \text{CH}^{\text{ar}}), 7.35-7.45 \ (m, 6 \text{H}, \text{CH}^{\text{ar}}), 7.90-8.05 \ (s, 6 \text{H}, \text{CH}^{\text{ar}}).
\end{align*}

\begin{align*}
13^\text{C}{1^\text{H}}-\text{NMR} (126 \text{ MHz, CDCl}_3, 298 \text{ K}): \delta & = 26.4 \ (s, 1 \text{C}, \text{CH}_3), 67.7-67.8 \ (m, 2 \text{C}, \text{CH}^{\text{olefin}}), 68.5 \ (dd, \ 2J_{\text{PC}} = 16.3 \text{ Hz}, \ 1J_{\text{RhC}} = 8.6 \text{ Hz}, 2 \text{C}, \text{CH}^{\text{olefin}}), 73.0 \ (s, 2 \text{C}, \text{CH}^{\text{benzyl}}), 124.6 \ (s, 2 \text{C}, \text{CH}^{\text{ar}}), 124.7 \ (s, 2 \text{C}, \text{CH}^{\text{ar}}), 127.4 \ (s, 2 \text{C}, \text{CH}^{\text{ar}}), 127.5 \ (s, 2 \text{C}, \text{CH}^{\text{ar}}), 128.6 \ (s, 2 \text{C}, \text{CH}^{\text{ar}}), 128.7 \ (s, 2 \text{C}, \text{CH}^{\text{ar}}), 128.8 \ (s, 2 \text{C} \text{CH}^{\text{ar}}), 128.8 \ (s, 6 \text{C}, \text{CH}^{\text{ar}}), 129.2 \ (s, 2 \text{C}, \text{CH}^{\text{ar}}) 129.9 \ (br \ s, 3 \text{C}, \text{CH}^{\text{ar}}), 131.8 \ (br \ s, 3 \text{C}, \text{C}^{\text{quat}}), 132.9 \ (s, 2 \text{C}, \text{C}^{\text{quat}}), 133.8 \ (s, 6 \text{C}, \text{CH}^{\text{ar}}) 135.1 \ (s, 2 \text{C}, \text{C}^{\text{quat}}), 136.8 \ (d, \ J = 4.8 \text{ Hz}, 2 \text{C}, \text{C}^{\text{quat}}), 141.0 \ (d, \ J = 2.9 \text{ Hz}, 2 \text{C}, \text{C}^{\text{quat}}), 178.6 \ (s, 1 \text{C}, \text{C}^{\text{quat}}).
\end{align*}

\begin{align*}
31^\text{P}{1^\text{H}}-\text{NMR} (203 \text{ MHz, CDCl}_3, 298 \text{ K}): \delta & = 10.3 \ (d, \ 1J_{\text{Rhp}} = 109.9 \text{ Hz}).
\end{align*}

\begin{align*}
1^\text{H}, ^{103}\text{Rh}-\text{NMR} (15.8 \text{ MHz, CDCl}_3, 298 \text{ K}): \delta & = -5769 \ (d, \ 1J_{\text{Rhp}} = 109.9 \text{ Hz}).
\end{align*}

\text{ATR IR (v in cm}^{-1}): 3193 \ (w), 3050 \ (w), 2959 \ (w), 2919 \ (w), 1712 \ (w), 1598 \ (w), 1542 \ (m), 1482 \ (w), 1433 \ (w), 1389 \ (m), 1316 \ (w), 1254 \ (w), 1222 \ (w), 1187 \ (w), 1159 \ (w), 1127 \ (w), 1092 \ (m), 1044 \ (w), 993 \ (w), 934 \ (w), 877 \ (w), 827 \ (w), 800 \ (w), 742 \ (s), 699 \ (s), 668 \ (w), 619 \ (w).
[Rh(eq-OH)(trop2NH)(PPh3)] (63)

MF = C₄₈H₃₉NOPRh

MW = 779.71 g/mol

MP = 185-187 °C (decomposition)

Air stable

To a solution of [Rh(trop2N)(PPh3)] 1 (100 mg, 0.131 mmol) in THF (3 ml) was added H₂O (0.1 ml, 5.56 mmol). The green solution turned immediately yellow. Addition of n-hexane precipitated yellow [Rh(eq-OH)(trop2NH)(PPh3)] which was collected by filtration and dried under high vacuum. Yield 91 mg (89%).

A sample suitable for NMR-measurements was prepared in-situ in a NMR-tube by adding a drop of H₂O (approximately 100 eq.) to a solution of [Rh(trop2N)(PPh3)] 1 (10 mg, 0.0131 mmol, 1 eq.) in [D₈]THF (0.5 mL). The sample was cooled immediately to prevent isomerisation.

¹H-NMR (500.23 MHz, [D₈]THF, 213 K): δ = 4.53 (d, 3J_HH = 8.9 Hz, 2H, CH^{olefin}), 4.65 (d, 3J_HH = 8.0 Hz, 2H, CH^{olefin}), 5.00 (d, J = 8.9 Hz, 2H, CH^{benzyl}), 6.52 (d, J = 7.3 Hz, 2H, CH^{ar}), 6.64 (dd, J = 7.0 Hz, 2H, CH^{ar}), 6.74 (dd, J = 7.0 Hz, 2H, CH^{ar}), 6.87 (d, J = 7.1 Hz, 2H, CH^{ar}), 7.09 (dd, J = 6.9 Hz, 2H, CH^{ar}), 7.15 (d, J = 7.1 Hz, 2H, CH^{ar}), 7.21 (dd, J = 7.0 Hz, 2H, CH^{ar}), 7.33 (d, J = 7.2 Hz, 2H, CH^{ar}), 7.61 (br, 9H, CH^{ar}), 8.02 (br, 6H, CH^{ar}). (The OH- and NH-protons undergo a fast exchange with the excess water (3.50 (s)).

¹³C{¹H}-NMR (125.78 MHz, [D₈]THF, 213 K) δ = 63.9 (d, J = 11.8 Hz, 2C, CH^{olefin}), 65.9 (d, J = 8.4 Hz, 2C, CH^{olefin}), 70.8 (s, 2C, CH^{benzyl}), 124.7 (s, 2C, CH^{ar}), 125.1 (s, 2C, CH^{ar}), 127.8 (s, 2C, CH^{ar}), 127.9 (s, 2C, CH^{ar}), 128.1 (s, 2C, CH^{ar}), 128.3 (s, 2C, CH^{ar}), 128.8 (d, J = 9.1 Hz, 6C, CH^{ar}), 129.1 (s, 2C, CH^{ar}), 129.7 (s, 2C, CH^{ar}), 130.7 (s, 3C, CH^{ar}) 131.4 (d, J = 40.3 Hz, 3C, C^{quat}), 134.8 (d, J = 6.2 Hz, 6C, CH^{ar}), 135.1 (s, 2C, C^{quat}), 136.3 (s, 2C, C^{quat}), 136.9 (s, 2C, C^{quat}), 140.0 (s, 2C, C^{quat}).

³¹P{¹H}-NMR (202.50 MHz, [D₈]THF, 213 K): δ = 41.1 (d, J_{RhP} = 134.3 Hz).

¹H, ¹⁰³Rh-NMR (15.81 MHz, [D₈]THF, 213 K): δ = -7109 (d, J_{PRh} = 134.3 Hz).

MS (HR-MALDI, m/z (%)): 762.18 (M⁺-OH, 100%), 763.18 (M⁺-OH (1³⁵C), 52.28%), 764.19 (M⁺-OH (2³⁵C), 13.35%), 756.19 (M⁺-OH (3³⁵C), 2.29%), 778.18 (M⁺-H, 5.73%), 779.18 (M⁺-H (1³⁵C), 3.04%).
ATR IR (ν in cm\(^{-1}\)): 3046 (w), 3010 (w), 2879 (w), 2850 (w), 1597 (w), 1488 (m), 1470 (m), 1435 (m), 1402 (w), 1314 (w), 1256 (w), 1223 (w), 1187 (w), 1158 (w), 1122 (w), 1093 (m), 1027 (w), 997 (m), 936 (w), 856 (w), 823 (w), 779 (w), 742 (s), 698 (s), 618 (w).
[Rh(ax-OH)(trop₂NH)(PPh₃)] (64)

MF = C₄₈H₃₉NOPRh

MW = 779.71 g/mol

Air stable

This complex was prepared in-situ in a NMR-tube by adding a drop of H₂O approximately 100 eq.) to a solution of [Rh(trop₂N)(PPh₃)] 1 (10 mg, 0.0131 mmol, 1 eq.) in [D₈]THF (0.5 ml). After 6 hours at room temperature the isomerisation of the equatorial OH-complex 63 to the axial OH-complex 64 was completed.

¹H-NMR (500.23 MHz, [D₈]THF, 298 K): δ = 1.03 (s, 1H, NH), 4.03 (s, 2H, CH benzyl), 5.06 (m, 4H, CH olefin), 6.53 (d, J = 7.3 Hz, 2H, CH²), 6.57 (d, J = 7.1 Hz, 2H, CH²), 6.70 (m, 4H, CH²), 6.76 (ddd J = 7.4 Hz, J = 7.4 Hz, J = 1.1 Hz, 2H, CH²), 6.84 (ddd J = 7.5 Hz, J = 7.5 Hz, J = 1.3 Hz, 2H, CH²), 6.93 (ddd, J = 7.5 Hz, J = 7.5 Hz, J = 1.2 Hz, 2H, CH²), 7.11 (d, J = 7.56 Hz, 2H, CH²), 7.16-7.34 (m, 13H, CH²), 7.58 (br, 1H, CH²), 7.98 (br, 1H, CH²). (The OH- and NH-protons undergo a fast exchange with the excess water (3.50 s)).

¹³C{¹H}-NMR (125.78 MHz, [D₈]THF, 298 K) δ = 67.1-67.2 (m, 2C, CH olefin), 70.8 (dd, J = 17.9 Hz, J = 9.7 Hz, 2C, CH olefin), 71.4 (s, 2C, CH benzyl), 123.9 (s, 2C, CH ar), 123.9 (s, 2C, CH ar), 124.2 (s, 2C, CH ar), 126.9 (s, 2C, CH ar), 127.8 (s, 2C, CH ar), 127.9 (s, 2C, CH ar), 128.0 (d, J = 4.8 Hz, 2C, CH ar), 128.4 (d, J = 7.4 Hz, 6C, CH ar), 128.5 (s, 3C, CH ar), 129.0 (d, J = 1.4 Hz, 2C, CH ar), 129.1 (m, 3C, C quat), 133.1 (br, 6C, CH²), 133.8 (d, J = 1.9 Hz, 2C, C quat), 136.1 (s, 2C, C quat), 137.2 (d, J = 4.6 Hz, 2C, C quat), 141.6 (d, J = 3.8 Hz, 2C, C quat).

³¹P{¹H}-NMR (202.50 MHz, [D₈]THF, 298 K): δ = 9.3 (d, ¹J_RpP = 114.4 Hz).

¹H, ¹⁰³Rh-NMR (15.81 MHz, [D₈]THF, 298 K): δ = -6239 (d, ¹J_RhR = 114.4 Hz).
[Rh(HCO₃)(trop₂NH)(PPh₃)] (65)

MF = C₄₉H₃₉NO₃PRh

MW = 823.72 g/mol

MP = 192-193 °C (decomposition)

Air stable

To a solution of [Rh(trop₂N)(PPh₃)] (54 mg, 0.071 mmol, 1 eq.) in THF (2 mL) was added H₂O (10 µL, 10 mg, 0.56 mmol, 8 eq.). Dry ice (5.0 g, 114 mmol, 1600 eq.) was added after the colour changed from green to yellow. After all CO₂ was evaporated the yellow solution was allowed to warm to room temperature while stirring. Upon layering the solution with hexane a yellow precipitate formed, which was isolated by decantation and dried under high vacuum. Yield: 48 mg (82%).

ⅧH-NMR (400.13 MHz, [D₈]THF, 298 K): δ = 4.80-4.83 (m, 4H, CHolefin, CBenzy1), 4.92 (d, J = 8.2 Hz, 2H, CHolefin), 6.52 (d, J = 7.5 Hz, 2H, CHar, trop), 6.62 (t, J = 7.3 Hz, 2H, CHar, trop), 6.75 (t, J = 7.4 Hz, 2H, CHar, trop), 6.80-6.81 (m, 2H, CHar, trop), 7.00 (t, J = 7.3 Hz, 2H, CHar, trop), 7.08 (t, J = 7.2 Hz, 2H, CHar, trop), 7.15-7.16 (m, 4H, CHar, trop), 7.52-7.62 (m, 9H, CHar, phosphane), 8.00-8.06 (m, 6H, CHar, phosphane), 10.40 (d, J = 6.0 Hz, 1H, NH).

ⅧC{1H}-NMR (100.61 MHz, [D₈]THF, 298 K): δ = 67.0-67.5 (m, 2C, CHolefin), 69.2 (d, J = 7.1 Hz, 2C, CHolefin), 72.2 (s, 2C, CBenzy1), 125.0 (s, 2C, CHar, trop), 125.2 (s, 2C, CHar, trop), 127.2 (s, 2C, CHar, trop), 127.3 (s, 2C, CHar, trop), 127.5 (s, 2C, CHar, trop), 127.7 (s, 2C, CHar, trop), 128.4 (d, JPC = 9.1 Hz, 6C, CHar, phosphane), 128.6 (s, 2C, CHar, trop), 129.3 (s, 2C, CHar, trop), 130.5 (s, 3C, CHar, phosphane), 131.2 (d, JPC = 44.5 Hz, 3C, Cquat, phosphane), 135.1 (d, JPC = 8.7 Hz, 6C, CHar, phosphane), 136.2 (d, 2C, Cquat, trop), 136.3 (s, 2C, Cquat, trop), 137.0 (s, 2C, Cquat, trop), 139.2 (s, 2C, Cquat, trop), 161.5 (s, 1C, CO₃).

ⅧP{1H}-NMR (161.98 MHz, [D₈]THF, 298 K) δ = 38.0 (d, 1JRP = 131.4 Hz).

ⅧH, ⅧRh-NMR (15.81 MHz, [D₈]THF, 298 K): δ = -6835 (d, 1JPRh = 131.4 Hz).

ATR IR (v in cm⁻¹): 3050 (w), 3016 (w), 2965 (w), 2159 (w), 1581 (m), 1489 (m), 1475 (m), 1435 (m), 1407 (m), 1313 (w), 1276 (w), 1260 (w), 1222 (w), 1188 (w), 1156 (w), 1095 (m), 1042 (w), 1020 (m), 996 (m), 985 (w), 933.40 (w), 891 (w), 871 (w), 854 (w), 820 (m), 801 (m), 765 (w), 746 (s), 697 (s), 619 (w).
[RhCl(trop2NH)(P(3,5-diMePh)3)] \( (69) \)

MF = C_{54}H_{50}ClNP\text{Rh}

MW = 882.31 g/mol

MP = 200-203°C (decomposition)

Air stable

To a suspension of [RhCl(trop2NH)]\(_2\) (700 mg, 0.653 mmol, 1 eq.) in CH\(_2\)Cl\(_2\) (5 mL) tris(3,5-dimethylphenyl)phosphane (588 mg, 1.70 mmol, 2.6 eq.) was added. The resulting orange solution was stirred for 30 minutes then the solvent was removed under reduced pressure. The residue was recrystallised from THF/hexane and the obtained orange powder was dried under high vacuum. Yield: 1.08 g, 94%. Crystals suitable for X-ray analysis were obtained by layering a concentrated solution of \( 69 \) in CDCl\(_3\) with hexane.

Rotamer 1 (84%):

\(^1\)H-NMR (500.23 MHz, CDCl\(_3\), 298 K): \( \delta = 2.01 \) (s, 6H, CH\(_3\)), 2.29 (s, 1H, NH), 2.33 (s, 12H, CH\(_3\)), 3.96 (s, 2H, CH\(_\text{benzyl}\)), 5.11 (d, \( J = 7.8 \) Hz, 2H, CH\(_\text{ar, trop}\)), 5.34 (dd, \( J = 8.5 \) Hz, \( J = 8.5 \) Hz, 2H, CH\(_\text{olefin}\)), 5.61 (dd, \( J = 9.1 \) Hz, \( J = 5.8 \) Hz, 2H, CH\(_\text{olefin}\)), 6.54 (d, \( J = 7.1 \) Hz, 2H, CH\(_\text{ar, trop}\)), 6.65-6.67 (m, 4H, CH\(_\text{ar, trop}\)), 6.73 (s, 1H, CH\(_\text{ar, phosphane}\)), 6.78 (t, \( J = 7.3 \) Hz, 2H, CH\(_\text{ar, trop}\)), 6.84 (t, \( J = 7.5 \) Hz, 2H, CH\(_\text{ar, trop}\)), 6.86-6.91 (m, 4H, CH\(_\text{ar, trop}\)), 7.04 (s, 2H, CH\(_\text{ar, phosphane}\)), 7.16 (d, \( J = 7.3 \) Hz, 2H, CH\(_\text{ar, trop}\)), 7.58 (d, \( J = 9.9 \) Hz, 4H, CH\(_\text{ar, phosphane}\)).

\(^{13}\)C\(_{\{^1H\}}\)NMR (125.78 MHz, CDCl\(_3\), 298 K): \( \delta = 21.9 \) (s, 4C, CH\(_3\)), 22.1 (s, 2C, CH\(_3\)), 66.8 (dd, \( J = 8.0 \) Hz, \( J = 5.9 \) Hz, 2C, CH\(_\text{olefin}\)), 70.7 (dd, \( J = 17.9 \) Hz, \( J = 8.8 \) Hz, 2C, CH\(_\text{olefin}\)), 73.1 (s, 2C, CH\(_\text{benzyl}\)), 124.7 (d, \( J = 1.9 \) Hz, 2C, CH\(_\text{ar, trop}\)), 125.1 (s, 2C, CH\(_\text{ar, trop}\)), 126.5 (s, 2C, CH\(_\text{ar, trop}\)), 127.8 (s, 2C, CH\(_\text{ar, trop}\)), 128.0 (s, 2C, CH\(_\text{ar, trop}\)), 128.6 (d, \( J = 5.0 \) Hz, 2C, CH\(_\text{ar, trop}\)), 128.8 (d, \( J = 1.7 \) Hz, 2C, CH\(_\text{ar, trop}\)), 129.1 (s, 2C, CH\(_\text{ar, trop}\)), 129.2 (d, 2C, \( J = 8.9 \) Hz, CH\(_\text{ar, phosphane}\)), 130.5 (s, 1C, CH\(_\text{ar, phosphane}\)), 130.9 (d, \( J = 20.9 \) Hz, 1C, C\(_\text{quat, phosphane}\)), 131.3 (d, \( J = 1.9 \) Hz, 2C, CH\(_\text{ar, phosphane}\)), 132.5 (d, \( J = 10.8 \) Hz, 4C, CH\(_\text{ar, phosphane}\)), 133.2 (d, \( J = 1.9 \) Hz, 2C, C\(_\text{quat, trop}\)), 135.1 (s, 2C, C\(_\text{quat, trop}\)), 135.3 (d, \( J = 26.2 \) Hz, 2C, C\(_\text{quat, phosphane}\)), 136.6 (d, \( J = 4.6 \) Hz, 2C, C\(_\text{quat, trop}\)), 137.4 (d, \( J = 9.6 \) Hz, 4C, C\(_\text{quat, phosphane}\)), 137.6 (d, \( J = 7.4 \) Hz, 2C, C\(_\text{quat, phosphane}\)), 140.6 (d, \( J = 3.8 \) Hz, 2C, C\(_\text{quat, trop}\)).

\(^{31}\)P\(_{\{^1H\}}\)-NMR (202.50 MHz, CDCl\(_3\), 298 K) \( \delta = 8.8 \) (d, \( J = 109.8 \) Hz).

\(^1\)H, \(^{103}\)Rh-NMR (15.81 MHz, CDCl\(_3\), 298 K): \( \delta = -6337 \) (d, \( J = 109.8 \) Hz).
Rotamer 2 (16%):

$^{31}$P{$^{1}$H}-NMR (202.50 MHz, CDCl$_3$, 298 K) $\delta = 9.3$ (d, $^{1}J_{\text{RhP}} = 113.6$ Hz).

ATR IR ($\nu$ in cm$^{-1}$): 3183 (w), 3018 (w), 2920 (w), 2853 (w), 1599 (w), 1579 (w), 1488 (m), 1467 (m), 1413 (w), 1376 (w), 1310 (w), 1271 (w), 1253 (w), 1217 (w), 1186 (w), 1155 (w), 1125 (m), 1038 (w), 970 (w), 936 (w), 887 (w), 846 (m), 763 (w), 747(s), 695 (s), 672 (w), 618 (w).
[Rh(trop2NH)(P(3,5-diMePh)_3)]OTf (77)

MF = C_{55}H_{50}F_{3}NO_{3}PRhS

MW = 995.93 g/mol

MP = 217-218 °C (decomposition)

Air stable

To a solution of [RhCl(trop2NH)(P(3,5-diMePh)_3)] 69 (350 mg, 0.397 mmol, 1 eq.) in CH_2Cl_2 (7 mL) was added AgOTf (112 mg, 0.436 mmol, 1.1 eq.). The resulting suspension was stirred overnight then filtered over celite. The solvent was removed under reduced pressure and the residue was recrystallised from THF/hexane and the obtained orange powder was dried under high vacuum. Yield: 370 mg, 94%. Crystals suitable for X-ray analysis were obtained by layering a concentrated solution of 77 in DCM with hexane.

^1H-NMR (400.13 MHz, CDCl_3, 298 K): δ = 2.44 (s, 18H, CH_3), 5.02 (m, 4H, CH_olefin, CH_benzyl), 5.46 (d, J = 7.1 Hz, 2H, CH_olefin), 5.56 (d, J = 3.8 Hz, 1H, NH), 6.68 (d, J = 7.4 Hz, 2H, CH_ar, trop), 6.78 (t, J = 6.9 Hz, 2H, CH_ar, trop), 6.89-6.94 (m, 4H, CH_ar, trop), 7.16-7.28 (m, 8H, CH_ar, trop), 7.38 (d, \text{j}_{PH} = 6.8 Hz, 3H, CH_ar, phosphane), 7.46 (d, \text{j}_{PH} = 10.4 Hz, 6H, CH_ar, phosphane).

^13C{^1H}-NMR (100.61 MHz, CDCl_3, 298 K): δ = 21.9 (s, 6C, CH_3), 72.6 (s, 2C, CH_benzyl), 74.7 (d, J = 7.3 Hz, 2C, CH_olefin), 75.1 (d, J = 13.5 Hz, 2C, CH_olefin), 120.3 (q, \text{j}_{PC} = 320.7 Hz, 1C, CF_3), 126.3 (s, 2C, CH_ar, trop), 126.7 (s, 4C, CH_ar, trop), 127.8 (s, 2C, CH_ar, trop), 128.4 (s, 4C, CH_ar, trop), 129.3 (d, \text{j}_{PC} = 46.1 Hz, 3C, C_quat, phosphane), 130.0 (s, 2C, CH_ar, trop), 130.1 (s, 2C, CH_ar, trop), 132.4 (d, \text{j}_{PC} = 9.4 Hz, 6C, C_ar, phosphane), 133.1 (d, \text{j}_{PC} = 2.1 Hz, 3C, C_ar, phosphane), 135.0 (s, 2C, C_quat, trop), 135.3 (s, 2C, C_quat, trop), 136.0 (d, J = 1.8 Hz, 2C, C_quat, trop), 137.8 (s, 2C, C_quat, trop), 138.7 (d, \text{j}_{PC} = 10.3 Hz, 3C, C_quat, phosphane).

^19F-NMR (188.31 MHz, CDCl_3, 298 K): δ = -78.9 (s).

^31P{^1H}-NMR (161.98 MHz, CDCl_3, 298 K) δ = 38.5 (d, \text{j}_{RhP} = 136.2 Hz).

^1H, ^103Rh-NMR (12.64 MHz, CDCl_3, 298 K): δ = -6772 (d, \text{j}_{PRh} = 136.2 Hz).

ATR IR (v in cm^{-1}): 2988 (s), 2971 (s), 2901 (s), 1599 (w), 1579 (w), 1473 (w), 1452 (w), 1407 (m), 1394 (m), 1381 (m), 1294 (m), 1256 (m), 1227 (s), 1170 (m), 1155 (w), 1126 (w), 1072 (s), 1066 (s), 1057 (s), 1021 (s), 940 (w), 892 (w), 879 (w), 852 (w), 825 (w), 799 (w), 779 (w), 747 (s), 697 (s), 632 (s).
[RhCl(trop2NH)(P(3,5-diCF3Ph)3)] (71)

MF = C₅₄H₃₂ClF₁₈NPRh

MW = 1206.14 g/mol

MP = >220 °C (decomposition)

Air stable

To a suspension of [RhCl(trop2NH)]₂ (1.00 g, 0.900 mmol, 1 eq.) in CH₂Cl₂ (5 mL) was added tris(3,5-bis(trifluoromethyl)phenyl)phosphane (1.45 g, 2.16 mmol, 2.4 eq.). The resulting orange solution was stirred for 30 minutes then the solvent was removed under reduced pressure. The residue was recrystallised from THF/hexane and the obtained orange powder was dried under high vacuum. Yield: 2.04 g, 94%.

¹H-NMR (400.13 MHz, CDCl₃, 298 K): δ = 2.02 (s, 1H, NH), 4.17 (s, 2H, CH benzyl), 5.17 (dd, J = 8.4 Hz, J = 8.4 Hz, 2H, CH olefin), 5.86 (dd, J = 8.8 Hz, J = 5.8 Hz, 2H, CH olefin), 6.05 (d, 3JPH = 5.4 Hz, 2H, CH ar, phosphane), 6.57-6.59 (m, 2H, CH ar, trop), 6.62 (d, J = 7.3 Hz, 2H, CH ar, trop), 7.21 (d, J = 7.3 Hz, 2H, CH ar, trop), 7.80 (s, 1H, CH ar, phosphane), 8.08 (s, 2H, CH ar, phosphane), 8.33 (d, 3JPH = 8.4 Hz, 4H, CH ar, phosphane).

¹³C{¹H}-NMR (100.61 MHz, CDCl₃, 298 K): δ = 68.4 (dd, J = 7.7 Hz, J = 5.4 Hz, 2C, CH olefin), 73.1 (s, 2C, CH benzyl), 74.7 (dd, J = 18.0 Hz, J = 8.9 Hz, 2C, CH olefin), 122.6 (q, 1JFC = 275.3 Hz, 2C, CF₃), 123.2 (q, 1JFC = 273.4 Hz, 4C, CF₃), 124.1-124.3 (m, 1C, CH ar, phosphane), 124.8-125.1 (m, 2C, CH ar, phosphane), 126.0 (s, 2C, CH ar, trop), 126.5 (d, J = 4.3 Hz, 4C, CH ar, trop), 127.0 (s, 2C, CH ar, trop), 129.0 (d, J = 5.0 Hz, 2C, CH ar, trop), 129.1 (s, 4C, CH ar, trop), 129.7 (s, 2C, CH ar, trop) 130.4-130.6 (m, 2C, CH ar, phosphane), 132.0-133.1 (m, 6C, C quat, phosphane), 132.4 (s, 2C, C quat, trop), 134.2 (s, 2C, C quat, trop) 134.3 (s, 4C, CH ar, phosphane), 135.2 (d, J = 4.6 Hz, 2C, C quat, trop) 137.0 (d, 1JPC = 20.1 Hz, 3C, C quat, phosphane), 139.9 (d, J = 3.9 Hz, 2C, C quat, trop).

¹⁹F-NMR (188.31 MHz, CDCl₃, 298 K): δ = -62.8 (s, 12F, CF₃), -61.9 (s, 6F, CF₃).

³¹P{¹H}-NMR (161.98 MHz, CDCl₃, 298 K) δ = 13.2 (d, 1JRhP = 113.2 Hz).

¹H, ¹⁰³Rh-NMR (12.64 MHz, CDCl₃, 298 K): δ = -6405 (d, 1JPRh = 113.2 Hz).

ATR IR (v in cm⁻¹): 1616 (w), 1602 (w), 1489 (w), 1473 (w), 1352 (s), 1275 (s), 1187 (m), 1173 (w), 1122 (s), 1107 (m), 1094 (s), 992 (w), 964 (w), 941 (w), 899 m, 845 (w), 826 (w), 779 (w), 766 (w), 749 (s), 704 (m), 681 (s), 619 (m).
[Rh(trop₂NH)(P(3,5-diCF₃Ph)₃)]OTf

MF = C₅₅H₃₂F₂₁NO₃PRhS

MW = 1319.76 g/mol

MP = >220 °C (decomposition)

Air stable

To a solution of [RhCl(trop₂NH)(P(3,5-diCF₃Ph)₃] 71 (400 mg, 0.332 mmol, 1 eq.) in CH₂Cl₂ (7 mL) AgOTf (94 mg, 0.365 mmol, 1.1 eq.) was added. The resulting suspension was stirred overnight then filtered over celite. The solvent was removed under reduced pressure and the residue was recrystallised from THF/hexane and the obtained orange powder was dried under high vacuum. Yield: 414 mg, 95%.

1H-NMR (400.13 MHz, CDCl₃, 298 K): δ = 4.80 (dd, 3JHH = 9.2 Hz, J = 1.8 Hz, 2H, CHᵦlefin), 4.95 (d, J = 9.2 Hz, 2H, CHᵦbenzyl), 5.41 (m, 2H, CHᵦlefin), 6.33 (d, J = 5.7 Hz, 1H, NH), 6.77 (d, J = 7.4 Hz, 2H, CHᵦar, trop), 6.86-6.90 (m, 4H, CHᵦar, trop), 7.00 (t, J = 7.4 Hz, 2H, CHᵦar, trop), 7.11 (d, J = 7.6 Hz, 2H, CHᵦar, trop), 7.29 (m, 6H, CHᵦar, trop), 8.19 (d, 3JPH = 9.3 Hz, 6H, CHᵦar, phosphane), 8.27 (s, 3H, CHᵦar, phosphane).

13C{¹H}-NMR (100.61 MHz, CDCl₃, 298 K): δ = 73.3 (s, 2C, CHᵦbenzyl), 74.1 (d, J = 12.6 Hz, 2C, CHᵦlefin), 75.0 (d, J = 7.1 Hz, 2C, CHᵦlefin), 119.8 (d, 1JFC = 318.9 Hz, 1C, CF₃OTf), 122.8 (d, 1JHC = 273.7 Hz, 6C, CF₃phosphane), 126.7 (d, J = 2.3 Hz, 3C, CHᵦar, phosphane), 126.9 (s, 2C, CHᵦar, trop), 127.7 (s, 4C, CHᵦar, trop), 128.3 (s, 2C, CHᵦar, trop), 129.2 (s, 2C, CHᵦar, trop), 129.3 (s, 2C, CHᵦar, trop), 130.0 (s, 2C, CHᵦar, trop), 130.3 (s, 2C, CHᵦar, trop), 131.1 (d, 1JFC = 42.0 Hz, 3C, Cᵦquat, phosphane), 133.6 (d, J = 9.6 Hz, 2C, Cᵦquat, trop), 134.0 (d, J = 9.6 Hz, 2C, Cᵦquat, trop), 134.2 (m, 6C, CHᵦar, phosphane), 134.2 (d, J = 1.8 Hz, 2C, Cᵦquat, trop), 134.9 (s, 6C, Cᵦquat, phosphane), 135.5 (s, 2C, Cᵦquat, trop).

19F-NMR (188.31 MHz, CDCl₃, 298 K): δ = -78.7 (s, 3F, CF₃OTf), -62.8 (s, 18F, CF₃phosphane).

31P{¹H}-NMR (161.98 MHz, CDCl₃, 298 K) δ = 48.1 (d, 1JRP = 144.8 Hz).

¹H, ¹⁰³Rh-NMR (12.64 MHz, CDCl₃, 298 K) δ = -6872 (d, 1JPRh = 144.8 Hz).

ATR IR (ν in cm⁻¹): 2160 (w), 1618 (w), 1600 (w), 1491 (w), 1352 (s), 1300 (w), 1276 (s), 1228 (m), 1173 (m), 1120 (s), 1095 (s), 1060 (w), 1021 (s), 941 (w), 901 (m), 845 (w), 823 (w), 780 (w), 750 (s), 704 (m), 682 (s), 632 (m), 623 (m).
[Rh(trop2NH)(P(3,5-di'tBuPh)3)]OTf

66

MF = C73H92F3NO3PRhS

MW = 1278.48 g/mol

MP = 96-97 °C (decomposition)

Air stable

To a suspension of [RhCl(trop2NH)]2 (965 mg, 0.900 mmol, 1 eq.) in CH2Cl2 (10 mL) tris(3,5-di-tert-butylphenyl)phosphane (3.23 g, 5.40 mmol, 3 eq.) and AgOTf (514 mg, 2.00 mmol, 2.22 eq.) were added. The reaction mixture was stirred overnight then filtered over celite. The solvent was re moved and the residue was attempted to recrystallise from THF/hexane. The obtained solid was found to contain no phosphane ligand anymore but if the solid was dissolved with the residue from the concentrated mother liquor the target complex [Rh(trop2NH)(P(3,5-di'tBu3Ph)3)]OTf 66 was found again in 31P{1H}-NMR. Therefore the solvent of this solution was just removed under reduced pressure and the complex was obtained together with the excess phosphane. Yield: 1.83 g, 86%.

1H-NMR (500.23 MHz, CDCl3, 298 K): δ = 1.32 (s, 54H, CH3), 3.93 (d, J = 4.8 Hz, 1H, NH), 4.71 (d, J = 8.7 Hz, 2H, CHolefin), 5.94 (d, J = 7.6 Hz, 2H, CHbenzyl), 6.27 (d, J = 8.7 Hz, 2H, CHolefin), 6.83 (d, J = 7.6 Hz, 2H, CHar, trop), 6.88 (t, J = 7.3 Hz, 2H, CHar, trop), 6.99 (d, J = 7.3 Hz, 2H, CHar, trop), 7.05 (t, J = 7.3 Hz, 2H, CHar, trop), 7.14 (t, J = 7.6 Hz, 2H, CHar, trop), 7.19 (m, 2H, CHar, trop), 7.29 (m, 2H, CHar, trop), 7.39 (d, J = 7.6 Hz, 2H, CHar, trop), 7.58 (dd, 3JPH = 11.0 Hz, 4JHH = 1.2 Hz, 6H, CHarp, phosphane), 7.68 (d, 4JHH = 1.2 Hz, 3H, CHar, phosphane).

13C{1H}-NMR (125.78 MHz, CDCl3, 298 K): δ = 31.8 (s, 18C, CH3), 35.6 (s, 6C, C(CH3)3), 70.8 (s, 2C, CHbenzyl), 79.8 (d, J = 7.4 Hz, 2C, CHolefin), 87.9 (d, J = 13.0 Hz, 2C, CHolefin), 121.1 (q, 1JFC = 322.7 Hz, 1C, CF3), 126.1 (s, 2C, CHar, trop), 126.1 (s, 3C, CHar, phosphane), 126.4 (s, 2C, CHar, trop), 128.5 (d, 2JPC = 10.1 Hz, 6C, CHar, phosphane), 128.7 (s, 2C, CHar, trop), 128.9 (s, 2C, CChar, trop), 129.9 (s, 2C, CHar, trop), 129.9 (s, 2C, CHar, trop), 129.5 (d, J not resolved, 3C, Cquat, phosphane), 129.9 (s, 2C, CHar, trop), 131.9 (s, 2C, CHar, trop), 135.8 (s, 2C, s, 2C, Cquat, trop), 135.9 (s, 2C, s, 2C, Cquat, trop), 136.3 (d, J = 2.2 Hz, 2C, s, 2C, Cquat, trop), 152.3 (d, 3JPC = 9.6 Hz, 6C, Cquat, phosphane).

19F-NMR (188.31 MHz, CDCl3, 298 K): δ = -77.7 (s).

31P{1H}-NMR (202.50 MHz, CDCl3, 298 K) δ = 39.9 (d, 1JRhP = 137.3 Hz).

1H, 103Rh-NMR (15.81 MHz, CDCl3, 298 K): δ = -7162 (d, 1JPRh = 137.3 Hz).
ATR IR (ν in cm⁻¹): 3059 (w), 2959 (m), 2904 (w), 2868 (w), 1591 (w), 1569 (w), 1477 (m), 1421 (m), 1394 (w), 1363 (m), 1277 (m), 1248 (s), 1224 (s), 1158 (s), 1074 (m), 1023 (s), 933 (w), 925 (w), 853 (w), 877 (m), 856 (m), 841 (w), 811 (w), 750 (s), 707 (s), 635 (s).
tris(3,5-diisopropylphenyl)phosphane

(104)

MF = C₃₆H₅₁P

MW = 514.76 g/mol

MP = 60-62 °C

Slightly air sensitive

BuLi (1.6 M in Hexane, 4.51 mL, 7.22 mmol, 3.15 eq.) was added to a solution of 1-bromo-3,5-diisopropylbenzene (1.29 mL, 1.68 g, 6.95 mmol, 3.03 eq.) in THF (20 mL) at -78 °C. The resulting solution was stirred for 5 minutes, then PCl₃ (0.20 mL, 315 mg, 2.29 mmol, 1 eq.) was added dropwise. The resulting mixture was stirred for 5 minutes then slowly allowed to warm to room temperature and stirred overnight. Water was added and the mixture was extracted 3 times with small portion of Et₂O. The combined organic phases were washed with brine, dried over Na₂SO₄, filtered and concentrated. The resulting crude product was purified by column chromatography (PET:EtOAc 10:1) to give a white oil. Ethanol (2 mL) was added and the mixture was put in the ultrasonic bath for 5 minutes then cooled to -20 °C overnight. The title compound was obtained as white solid, which was dried under high vacuum. Yield: 0.910 g, 77%.

¹H-NMR (300.13 MHz, CDCl₃, 298 K): δ = 1.20 (d, 3 J_HH = 6.9 Hz, 36H, CH₃), 2.85 (sept, 3 J_HH = 6.9 Hz, 6H, CHMe₂), 7.02 (m, 9H, C_H ar).

¹³C{¹H}-NMR (75.48 MHz, CDCl₃, 298 K): δ = 24.0 (s, 12C, CH₃), 34.1 (s, 6C, CHMe₂), 125.2 (s, 3C, C_Har), 129.2 (d, 2 J_PC = 19.2 Hz, 6C, CH₂), 137.5 (d, J = 10.0 Hz, 3C, C_quat), 148.6 (d, J = 6.7 Hz, 6C, C_quat).

³¹P{¹H}-NMR (121.49 MHz, CDCl₃, 298 K) δ = -3.63 (s)

ATR IR (ν in cm⁻¹): 3056 (w), 2955 (m), 2925 (w), 1799 (w), 1770 (w), 1589 (w), 1579 (m), 1459 (m), 1437 (w), 1424 (w), 1381 (w), 1362 (w), 1336 (w), 1310 (w), 1233 (w), 1188 (w), 1050 (w), 1124 (w), 1067 (m), 997 (w), 937 (w), 922 (w), 873 (s), 807 (w), 711 (s).
[RhCl(trop2NH)(P(3,5-di’PrPh)3)] (70)

MF = C66H74ClINPRh

MW = 1050.63 g/mol

MP = 203-204 °C (decomposition)

Air stable

To a suspension of [RhCl(trop2NH)]2 (700 mg, 0.653 mmol, 1 eq.) in CH2Cl2 (5 mL) tris(3,5-diisopropylphenyl)phosphane 104 (740 mg, 1.44 mmol, 2.2 eq.) was added. The resulting orange solution was stirred for 30 minutes then the solvent was removed under reduced pressure. The residue was recrystallised from THF/hexane and the obtained orange powder was dried under high vacuum. Yield: 1.25 g (91%). Crystals suitable for X-ray analysis were obtained by layering a concentrated solution of 70 in acetone with hexane.

1H-NMR (400.13 MHz, CDCl3, 298 K): \( \delta = 1.14 \) (d, \( J_{HH} = 6.9 \) Hz, 12H, CH(CH3)2), 1.22 (d, \( J_{HH} = 6.8 \) Hz, J = 2.2 Hz, 24H, CH(CH3)2), 2.47 (sept, \( J_{HH} = 6.9 \) Hz, 2H, CH(CH3)2), 2.50 (s, 1H, NH), 2.87 (sept, \( J_{HH} = 6.9 \) Hz, 4H, CH(CH3)2), 3.96 (s, 2H, CHbenzyl), 5.27 (d, \( J = 7.7 \) Hz, 2H, CHar, trop), 5.39 (dd, \( J = 7.76 \) Hz, J = 7.76 Hz, 2H, CHOlefin), 5.61 (dd, J = 9.0 Hz, J = 6.0 Hz, 2H, CHOlefin), 6.54 (d, J = 7.23 Hz, 2H, CHar, trop), 6.63 (dd, J = 6.5 Hz, J = 1.5 Hz, 2H, CHOlefin), 6.71 (dd, J = 6.6 Hz, J = 1.5 Hz, 2H, CHar, trop), 6.77 (t, J = 7.4 Hz, 2H, CHOlefin), 6.81-6.86 (m, 6H, CHar, trop), 6.90 (s, 1H, CHar, phosphane), 7.05 (s, 2H, CHar, phosphane), 7.16 (d, \( J_{PC} = 7.5 \) Hz, 2H, CHar, phosphane), 7.66 (d, \( J_{PC} = 9.9 \) Hz, 4H, CHOlefin, phosphane).

13C{1H}-NMR (100.61 MHz, CDCl3, 298 K): \( \delta = 24.3 \) (s, 4C, CH(CH3)2), 24.6 (s, 4C, CH(CH3)2), 24.6 (s, 4C, CH(CH3)2), 33.6 (s, 2C, CH(CH3)2), 34.7 (s, 4C, CH(CH3)2), 66.3 (dd, J = 8.3 Hz, J = 5.4 Hz, 2C, CHOlefin), 70.6 (dd, J = 18.0 Hz, J = 9.1 Hz, 2C, CHOlefin), 73.1 (s, 2C, CHbenzyl), 122.3 (s, 1C, CHar, phosphane), 124.6 (d, J = 1.6 Hz, 2C, CHar, trop), 125.0 (s, 2C, CHar, trop), 125.9 (d, J = 1.8 Hz, 2C, CHar, phosphane), 126.4 (s, 2C, CHar, trop), 127.7 (s, 2C, CHar, trop), 128.0 (s, 2C, CHar, trop), 128.6 (d, \( J_{PC} = 4.8 \) Hz, 2C, CHar, phosphane), 128.8 (d, J = 1.6 Hz, 2C, CHar, trop), 129.0-129.1 (m, 4C, CHar, trop), 130.0 (d, \( J_{PC} = 21.2 \) Hz, 1C, Cquart, phosphane), 130.2 (d, \( J_{PC} = 11.0 \) Hz, 4C, CHar, phosphane), 133.2 (d, J = 2.3 Hz, 2C, Cquart, trop), 134.8 (s, 2C, Cquart, trop), 136.4 (d, \( J_{PC} = 25.6 \) Hz, 2C, Cquart, phosphane), 136.6 (d, J = 4.8 Hz, 2C, Cquart, trop), 141.0 (d, J = 3.9 Hz, 2C, Cquart, trop), 148.3 (d, \( J_{PC} = 8.9 \) Hz, 4C, Cquart, phosphane), 148.4 (d, \( J_{PC} = 7.1 \) Hz, 2C, Cquart, phosphane).

31P{1H}-NMR (161.98 MHz, CDCl3, 298 K) \( \delta = 11.7 \) (d, \( J_{RbP} = 110.7 \) Hz).

1H, 103Rh-NMR (12.64 MHz, CDCl3, 298 K): \( \delta = -6357 \) (d, \( J_{PRh} = 110.7 \) Hz).
ATR IR (v in cm$^{-1}$): 3189 (w), 2958 (w), 2920 (w), 2868 (w), 1598 (w), 1576 (w), 1488 (m),
1459 (m), 1423 (w), 1405 (w), 1382 (w), 1362 (w), 1315 (w), 1266 (w), 1253 (w), 1214 (w),
1188 (w), 1145 (w), 1127 (w), 1103 (w), 1065 (m), 1044 (w), 969 (w), 935 (w), 883 (m),
873 (m), 828 (w), 775 (w), 763 (m), 746 (s), 732 (w), 714 (s), 675 (w).
[Rh(trop₂NH)(P(3,5-di'PrPh)₃)]OTf (80)

MF = C₆₇H₇₄F₃NO₃PRhS

MW = 1164.25 g/mol

MP = 125-130 °C (decomposition)

Air stable

To a solution of [RhCl(trop₂NH)(P(3,5-di'PrPh)₃)] 70 (300 mg, 0.340 mmol, 1 eq.) in CH₂Cl₂ (5 mL) AgOTf (96 mg, 0.374 mmol, 1.1 eq.) was added. The resulting suspension was stirred overnight then filtered over celite. The solvent was removed under reduced pressure and the residue was recrystallised from THF/hexane and the obtained orange powder was dried under high vacuum. Yield: 370 mg (93%).

¹H-NMR (500.23 MHz, CDCl₃, 298 K): δ = 1.30 (d, ³J_HH = 6.9 Hz, 36H, CH₃), 3.01 (sept, ³J_HH = 6.9 Hz, 6H, CHMe₂), 4.93 (d, J = 9.2 Hz, 2H, CHolefin), 5.18 (d, J = 7.8 Hz, 2H, CHベンジル), 5.57 (d, J = 5.0 Hz, 1H, NH), 5.67 (d, J = 9.2 Hz, 2H, CHolefin), 6.80 (d, J = 3.4 Hz, 4H, CH₄⁻, trop), 6.93-7.01 (m, 4H, CH₄⁻, trop), 7.08-7.13 (m, 4H, CH₄⁻, trop), 7.20-7.25 (m, 4H, CH₄⁻, trop), 7.31 (s, 3H, CH₃⁻, phosphane), 7.47 (d, 3J_PH = 10.5 Hz, 6H, CH₄⁻, phosphane).

¹³C{¹H}-NMR (125.78 MHz, CDCl₃, 298 K): δ = 24.5 (s, 12C, CH₃), 34.7 (s, 6C, CHMe₂), 72.3 (s, 2C, CHベンジル), 75.9 (d, J = 8.2 Hz, 2C, CHolefin), 77.2 (m, 2C, CHolefin), 120.4 (q, ¹J_FC = 320.1 Hz, 1C, CF₃), 126.6 (s, 2C, CH₄⁻, trop), 126.7 (s, 2C, CH₄⁻, trop), 127.1 (s, 2C, CH₄⁻, trop), 127.4 (d, 4J_PC = 2.4 Hz, 3C, C₄⁻, phosphane), 128.0 (s, 2C, CH₄⁻, trop), 128.3 (s, 2C, CH₄⁻, trop), 128.4 (s, 2C, CH₄⁻, trop), 129.6 (d, ¹J_PC = 45.8 Hz, 3C, C₄⁻, phosphane), 129.9 (s, 2C, CH₄⁻, trop), 130.4 (s, 2C, CH₄⁻, trop), 130.6 (d, ²J_PC = 9.4 Hz, 6C, CH₄⁻, phosphane), 135.3 (s, 2C, C₄⁻, trop), 135.5 (s, 2C, C₄⁻, trop), 136.2 (d, J = 1.9 Hz, 2C, C₄⁻, trop), 137.6 (s, 2C, C₄⁻, trop), 149.8 (d, 3J_PC = 9.6 Hz, 6C, C₄⁻, phosphane).

¹⁹F-NMR (188.31 MHz, CDCl₃, 298 K): δ = -77.7 (s).

³¹P{¹H}-NMR (202.50 MHz, CDCl₃, 298 K) δ = 41.9 (d, ¹J_RbP = 135.8 Hz).

¹H, ¹⁰⁳Rh-NMR (15.81 MHz, CDCl₃, 298 K): δ = -6856 (d, ¹J_PRh = 135.8 Hz).

ATR IR (ν in cm⁻¹): 2958 (w), 2868 (w), 1592 (w), 1576 (w), 1464 (w), 1421 (w), 1384 (w), 1362 (w), 1296 (m), 1259 (m), 1224 (m), 1160 (m), 1099 (w), 1067 (m), 1021 (s), 923 (w), 876 (w), 798 (s), 749 (m), 710 (m), 659 (w), 632 (s).
[Rh(trop2NH)(P(2-OMePh)3)]OTf (67)

MF = C52H44F3NO6PRhS

MW = 1001.85 g/mol

MP = >220 °C (decomposition)

Air stable

To a solution of tris(2-methoxyphenyl)phosphane (72 mg, 205 μmol, 2.2 eq.) in DCM (5 mL) [RhCl(trop2NH)]₂ (100 mg, 93 μmol, 1 eq.) and AgOTf (53 mg, 205 μmol, 2.2 eq.) were added. The resulting suspension was stirred overnight then filtered over celite and all volatiles were removed under reduced pressure. The residue was recrystallised from THF/hexane and dried under high vacuum. Yield: 180 mg 96%. Crystals suitable for X-ray analysis were obtained by layering a concentrated solution of 67 in acetone with hexane.

1H-NMR (500.23 MHz, CD2Cl2, 298 K): δ = 3.50 (s, 9H, OCH3), 3.60 (d, J = 4.4 Hz, 1H, NH), 4.72 (br, 2H, CHolefin), 5.34 (d, J = 7.8 Hz, 2H, CHolefin), 5.37 (s, 2H, CHbenzyl), 6.83-6.92 (m, 5H, CHar, trop, CHar, phosphane), 7.14-7.31 (m, 4H, CHar, trop), 7.41 (br, 3H, CHar, phosphane), 7.58 (d, J = 7.1 Hz, 2H, CHar, trop), 7.68 (br, 3H, CHar, phosphane).

13C{1H}-NMR (125.78 MHz, CD2Cl2, 298 K): δ = 53.8-54.0 (m, 2C, CHolefin), 56.0 (s, 3C, OCH3), 56.8 (s, 2C, CHolefin), 72.3 (s, 2C, CHbenzyl), 112.7 (d, J = 3.1 Hz, 3C, CHar, phosphane), 120.4 (q, JFC = 320.7 Hz, 1C, CF3), 122.1 (d, J = 7.7 Hz, 3C, CHar, phosphane), 127.2 (s, 2C, CHar, trop), 127.3 (s, 2C, CHar, trop), 127.5 (s, 2C, CHar, trop), 128.8 (s, 2C, CHar, trop), 129.0 (s, 2C, CHar, trop), 129.1 (s, 2C, CHar, trop), 129.2 (s, 2C, CHar, trop), 130.5 (s, 2C, CHar, trop), 134.0 (br, 3C, qquat, phosphane), 134.4 (s, 2C, Cqquat, trop), 134.6 (d, J = 11.5 Hz, 3C, CHar, phosphane), 134.6 (s, 3C, CHar, phosphane), 135.2 (s, 2C, Cqquat, trop), 135.9 (s, 2C, Cqquat, trop), 137.8 (s, 2C, Cqquat, trop), 161.7 (br, 3C, COCH3).

19F-NMR (188.31 MHz, CD2Cl2, 298 K): δ = -78.6 (s).

31P{1H}-NMR (202.50 MHz, CD2Cl2, 298 K) δ = 33.4 (d, JRhP = 143.4 Hz).

1H, 103Rh-NMR (15.81 MHz, CD2Cl2, 298 K): δ = -6951 (d, JPRh = 143.4 Hz).

ATR IR (v in cm⁻¹): 2972 (w), 2894 (w), 1585 (w), 1571 (w), 1473 (m), 1460 (w), 1430 (m), 1246 (s), 1220 (w), 1162 (m), 1132 (w), 1072 (m), 1044 (w), 1027 (s), 1014 (m), 910 (w), 864 (w), 823 (w), 793 (m), 754 (s), 728 (s), 699 (w), 667 (w), 635 (s).
bis(3,5-di-tert-butylphenyl)(phenyl) phosphane (105)

MF = $C_{34}H_{47}P$

MW = 486.71 g/mol

MP = 68-70 °C

Slightly air sensitive

To a solution of 1-bromo-3,5-di-tert-butylbenzene (401 mg, 1.49 mmol, 2.02 eq.) in THF (20 mL) a solution of BuLi (1.6 M in Hexane, 0.967 mL, 1.55 mmol, 2.10 eq.) in THF (5 mL) at -78 °C was added dropwise. The resulting solution was stirred for 60 minutes. Then a solution of PhPCl$_2$ (0.10 mL, 0.74 mmol, 1 eq.) in THF (5 mL) was added and the resulting mixture was warmed to room temperature and stirred overnight. A saturated solution of NH$_4$Cl was added and the mixture was extracted 3 times with small portion of Et$_2$O. The combined organic phases were washed with brine, dried over Na$_2$SO$_4$, filtered and concentrated. The resulting crude product was purified by column chromatography (PET:EtOAc 15:1) to give a white solid. Yield: 210 mg, 59% (not optimised).

$^1$H-NMR (300.13 MHz, CDCl$_3$, 298 K): $\delta = 1.25$ (s, 36H, CH$_3$), 7.15 (dd, $^3J_{PH} = 8.3$ Hz, $^4J_{HH} = 1.30$ Hz, 4H, CH$_{ar}$), 7.3 (m, 5H, CH$_{ar}$) 7.39 (d, $^4J_{HH} = 1.30$ Hz, 4H, 2H, CH$_{ar}$).

$^{13}$C{$^1$H}-NMR (75.48 MHz, CDCl$_3$, 298 K): $\delta = 31.4$ (s, 12C, CH$_3$), 34.9 (s, 4C, CCH$_3$), 122.5 (s, 2C, CH$_{ar}$), 128.1 (d, $J = 19.8$ Hz, 4C, CH$_{ar}$), 128.1 (d, $J = 6.7$ Hz, 2C, CH$_{ar}$), 128.3 (s, 1C, CH$_{ar}$), 133.5 (d, $J = 18.7$ Hz, 2C, CH$_{ar}$), 136.1 (d, $J$ not resolved, 2C, C$_{quat}$), 138.5 (d, $J$ not resolved, 1C, C$_{quat}$), 150.5 (d, $J = 6.9$ Hz, 4C, C$_{quat}$).

$^{31}$P{$^1$H}-NMR (121.49 MHz, CDCl$_3$, 298 K): $\delta = -2.9$(s).

ATR IR ($\nu$ in cm$^{-1}$): 3065 (w), 2961 (m), 2903 (w), 2867 (w), 2120 (w), 1770 (w), 1586 (w), 1577 (m), 1543 (w), 1476 (m), 1459 (w), 1434 (w), 1417 (m), 1393 (w), 1361 (s), 1316 (w), 1308 (w), 1287 (w), 1247 (s), 1202 (w), 1176 (w), 1129 (m), 1093 (w), 1068 (w), 1026 (w), 1000 (w), 971 (w), 923 (w), 896 (m), 874 (s), 798 (w), 773 (w), 748 (s), 710 (s), 700 (s), 669 (w), 641 (w), 618 (w).
[RhCl(trop2NH)](PPh(3,5-di'tBuPh)2)]

MF = C60H70ClNPRh

MW = 974.54 g/mol

MP = 215-217 °C (decomposition)

Air stable

To a suspension of [RhCl(trop2NH)]2 (315 mg, 0.294 mmol, 1 eq.) in CH2Cl2 (5 mL) was added bis(3,5-di-tert-butylphenyl)(phenyl)phosphane (130 mg, 0.408 mmol, 2.05 eq.). The resulting orange solution was stirred for 30 minutes then the solvent was removed under reduced pressure. The residue was recrystallised from THF/hexane and the obtained orange powder was dried under high vacuum. Yield: 568 mg (99%).

1H-NMR (400.13 MHz, CDCl3, 298 K): δ = 1.31 (s, 36H, CH3), 1.49 (br, 1H, NH), 3.80 (m, 2H, CH benzyl), 5.28 (t, J = 7.5 Hz, 2H, CH ar, phosphane), 5.35 (t, J = 8.4 Hz, 2H, CH olefin), 5.64 (dd, J = 8.8 Hz, J = 5.9 Hz, 2H, CH olefin), 6.00-7.52 (m, 4H, CH ar, trop), 6.67 (d, J = 7.3 Hz, 2H, CH ar, trop), 6.72- 6.77 (m, 4H, CH ar, trop, CH ar, phosphane) 6.80-6.84 (m, 4H, CH ar, trop), 6.93 (t, J = 9.2 Hz 2H, CH ar, trop), 7.09 (t, J = 7.3 Hz, 1H, CH ar, phosphane), 7.18 (d, J = 7.5 Hz, 2H, CH ar, trop), 7.39 (s, 2H, CH ar, phosphane), 8.08 (d, J = 10.1 Hz, 4H, CH ar, phosphane).

13C{1H}-NMR (100.61 MHz, CDCl3, 298 K): δ = 32.0 (s, 12C, CH3), 35.6 (s, 4C, C(CH3)3), 66.0 (dd, J = 8.5 Hz, J = 5.3 Hz, 2C, CH olefin), 70.8 (dd, J = 17.9 Hz, J = 9.3 Hz, 2C, CH olefin), 72.9 (s, 2C, CH benzyl), 122.7 (d, 3JPC = 2.1 Hz, 2C, CH ar, phosphane), 124.5 (s, 4C, CH ar, trop), 127.3 (s, 2C, CH ar, trop), 128.0 (s, 2C, CH ar, trop), 128.2 (s, 1C, CH ar, phosphane), 128.3 (d, J = 1.8 Hz, 2C, CH ar, trop), 128.4 (s, 2C, CH ar, trop), 128.5 (d, 3JPC = 4.8 Hz, 2C, CH ar, phosphane), 128.7 (d, 2JPC = 11.7 Hz, 4C, CH ar, phosphane), 128.8 (d, J = 1.8 Hz, 2C, CH ar, trop), 129.2 (s, 2C, CH ar, trop), 130.2 (d, 1JPC = 24.2 Hz, 1C, C quat, phosphane), 132.6 (d, 2JPC = 8.7 Hz, 2C, CH ar, phosphane), 133.0 (d, J = 2.3 Hz, 2C, C quat, trop), 135.1 (s, 2C, C quat, trop), 135.6 (d, 1JPC = 24.7 Hz, 2C, C quat, phosphane) 136.7 (d, J = 4.8 Hz, 2C, C quat, trop), 141.16 (d, J = 3.7 Hz, 2C, C quat, trop), 150.50 (d, 3JPC = 8.7 Hz, 4C, C quat, phosphane).

31P{1H}-NMR (161.98 MHz, CDCl3, 298 K) δ = 11.9 (d, 1JRhP = 110.5 Hz).

1H, 103Rh-NMR (12.64 MHz, CDCl3, 298 K): δ = -6343 (d, 1JPRh = 110.5 Hz).

ATR IR (v in cm⁻¹): 3194 (w), 3065 (w), 2960 (w), 2899 (w), 2863 (w), 1594 (w), 1576 (w), 1488 (w), 1475 (m), 1434 (w), 1420 (w), 1393 (w), 1362 (m), 1315 (w), 1290 (w), 1271 (w), 1250 (m), 1215 (w), 1200 (w), 1130 (m), 1093 (w), 1068 (m), 1026 (w), 961 (w), 935 (w), 897 (w), 880 (w), 828 (w), 777 (w), 746 (s), 707 (s), 691 (w), 674 (w), 618 (w).
[Rh(trop2NH)(PPh(3,5-di’BuPh)2)]OTf

(81)

MF = C₆₃H₇₀F₃NO₃PRhS

MW = 1136.20 g/mol

MP = 185-188 °C (decomposition)

Air stable

To a solution of [RhCl(trop2NH)(PPh(3,5-di’BuPh)2)] 72 (483 mg, 0.472 mmol, 1 eq.) in CH₂Cl₂ (10 mL) AgOTf (134 mg, 0.520 mmol, 1.1 eq.) was added. The resulting suspension was stirred overnight then filtered over celite. The solvent was removed under reduced pressure and the residue was recrystallised from THF/hexane and the obtained orange powder was dried under high vacuum. Yield: 510 mg (95%).

¹H-NMR (400.13 MHz, CDCl₃, 298 K): δ = 1.37 (s, 36H, CH₃), 4.81 (d, J = 9.0 Hz, 2H, CHolefin), 5.20 (d, J = 8.0 Hz, 2H, CHbentzy), 5.46 (d, J = 5.2 Hz, 1H, NH), 5.63 (dt, J = 9.1 Hz, J = 2.7 Hz, 2H, CHolefin), 6.79-6.84 (m, 4H, CHar, trop), 6.93-6.96 (m, 4H, CHar, trop), 7.20-7.29 (m, 6H, CHar, trop), 7.49 (m, 4H, CHar, trop; CHar, phosphane), 7.53 (dd, 4JPC = 10.9 Hz, 4JHH = 1.5 Hz, 4H, C¹H, trop; CHar, phosphane), 7.59 (dd, J = 8.1 Hz, J = 6.7 Hz, 1H, C¹H, phosphane), 7.63 (d, 4JHH = 1.5 Hz, 2H, C¹H, phosphane), 7.84 (dd, J = 10.2 Hz, J = 9.0 Hz, C¹H, phosphane).

¹³C{¹H}-NMR (100.61 MHz, CDCl₃, 298 K): δ = 31.8 (s, 12C, CH₃), 35.6 (s, 4C, C(CH₃)), 71.9 (s, 2C, CHbentzy) 75.0 (d, J = 7.5 Hz, 2C, CHolefin), 77.0-78.0 (m, 2C, CHolefin), 120.3 (d, ¹JCPC = 319.6 Hz, 1C, CF₃), 125.1 (d, J = 8.9 Hz, 2C, CHar, phosphane), 125.3 (s, 2C, CHar, trop), 126.9 (s, 2C, CHar, trop), 127.2 (s, 2C, CHar, trop), 127.5 (s, 2C, CHar, trop), 128.0 (m, 8C, CHar, phosphane, CHar, trop), 128.4 (d, ¹JPC = 33.1 Hz, 2C, C¹quat, phosphane), 128.4 (s, 2C, CHar, trop), 128.6 (d, ¹JPC = 25.7 Hz, 1C, C¹quat, phosphane), 130.1 (s, 2C, CHar, trop), 130.3 (s, 2C, CHar, trop), 131.8 (s, 1C, CHar, trop), 135.2 (s, 2C, C¹quat, trop), 135.7 (s, 2C, C¹quat, trop), 136.0 (s, 2C, C¹quat, trop), 137.5 (d, J = 10.0 Hz, 2C, CHar, trop), 138.1 (s, 2C, C¹quat, trop), 151.7 (d, ³JPC = 9.4 Hz, 4C, C¹quat, phosphane).

¹⁹F-NMR (188.31 MHz, CDCl₃, 298 K): δ = -77.4 (s).

³¹P{¹H}-NMR (161.98 MHz, CDCl₃, 298 K) δ = 44.5 (d, ¹JRP = 135.2 Hz).

¹¹H, ¹³⁵⁵Rh-NMR (12.64 MHz, CDCl₃, 298 K): δ = -6870 (d, ¹JPRh = 135.2 Hz).

ATR IR (v in cm⁻¹): 3158 (w), 2959 (w), 1286 (w), 1589 (w), 1574 (w), 1478 (w), 1437 (w), 1420 (w), 1396 (w), 1363 (w), 1301 (m), 1287 (w), 1223 (m), 1203 (s), 1171 (m), 1157 (m), 1095 (w), 1021 (s), 987 (w), 936 (w), 894 (w), 869 (w), 825 (w), 793 (m), 749 (s), 708 (w), 701 (m), 631 (s), 603 (m).
[RhCl(trop₂NH)(PPh(3,5-MePh)₂)] (73)

MF = C₅₂H₄₆ClNPRh

MW = 854.26 g/mol

MP => 220 °C (decomposition)

Air stable

To a suspension of [RhCl(trop₂NH)]₂ (213 mg, 0.199 mmol, 1 eq.) in CH₂Cl₂ (5 mL) bis(3,5-dimethylphenyl)(phenyl)phosphane (300 mg, 0.616 mmol, 2.1 eq.) was added. The resulting orange solution was stirred for 30 minutes then the solvent was removed under reduced pressure. The residue was recrystallised from THF/hexane and the obtained orange powder was dried under high vacuum. Yield: 340 mg (99%).

Isomer 1 (61%):

¹H-NMR (500.23 MHz, CDCl₃, 298 K): δ = 2.02 (s, 6H, CH₃), 2.27 (s, br, 1H, NH), 2.32 (s, 6H, CH₃), 3.98 (d, J = 10.5 Hz, 2H, CH₃benzyl), 5.13 (d, J = 7.7 Hz, 2H, CH₃), 5.32-5.42 (m, 2H, CH₃olefin), 5.60-5.66 (m, 2H, CH₃olefin), 6.50 (d, J = 7.5 Hz, 2H, CH₃), 7.04 (d, J = 7.0 Hz, 2H, CH₃), 7.17 (d, J = 7.5 Hz, 2H, CH₃), 7.36-7.42 (m, 2H, CH₃), 7.58 (d, J = 9.7 Hz, 2H, CH₃), 8.00 (t, J = 8.2 Hz, 2H, CH₃).

¹³C{¹H}-NMR (125.78 MHz, CDCl₃, 298 K): δ = 21.9 (s, 2C, CH₃), 22.1 (s, 2C, CH₃), 66.1-67.0 (m, 2C, CH₃olefin), 70.5-71.1 (m, 2C, CH₃olefin), 73.1 (d, J = 8.4 Hz, 2C, CH₃benzyl), 124.7 (s, 4C, CH₃), 125.2 (d, J = 4.3 Hz, 2C, CH₃), 126.5 (d, J = 6.0 Hz, 2C, CH₃), 127.9 (d, J = 5.3 Hz, 2C, CH₃), 128.3 (d, J = 1.9 Hz, 2C, CH₃), 128.5-128.7 (m, 2C, CH₃), 128.8 (d, J = 1.4 Hz, 1C, CH₃), 128.8 (s, 2C, CH₃), 129.2 (s, 2C, CH₃), 129.3 (d, J = 8.9 Hz, 2C, CH₃), 130.5 (d, J = 22.1 Hz, 1C, C₄quat), 130.7 (s, 1C, CH₃), 131.3 (d, J = 1.7 Hz, 1C, CH₃), 132.3 (d, J = 10.8 Hz, 2C, CH₃), 133.1 (t, J = 2.4 Hz, 2C, C₄quat), 134.9 (d, J = 10.8 Hz, 2C, CH₃), 135.1 (s, 2C, C₄quat), 135.5 (d, J = 25.7 Hz, 1C, C₄quat), 136.3 (d, J = 25.4 Hz, 1C, C₄quat), 136.5 (d, J = 4.6 Hz, 2C, C₄quat), 137.5 (d, J = 9.4 Hz, 2C, C₄quat), 137.7 (d, J = 7.4 Hz, 2C, C₄quat), 140.6 (t, J = 4.2 Hz, 2C, C₄quat).

³¹P{¹H}-NMR (202.50 MHz, CDCl₃, 298 K) δ = 8.2 (d, ¹JRhP = 110.6 Hz).

¹H, ¹⁰³Rh-NMR (15.81 MHz, CDCl₃, 298 K): δ = -6346 (d, ¹JPrh = 110.6 Hz).
Isomer 2 (39%):

$^1$H-NMR (500.23 MHz, CDCl$_3$, 298 K): $\delta = 1.56$ (s, 1H, NH), 2.35 (s, 12H, CH$_3$), 3.83 (s, 2H, CH$_{\text{benzyl}}$), 5.27 (t, $J = 7.5$ Hz, 2H, CH$_{\text{olefin}}$), 5.32-5.42 (m, 2H, CH$_{\text{olefin}}$), 5.60-5.66 (m, 2H, CH$_{\text{olefin}}$), 6.53 (d, $J = 7.5$ Hz, 2H, CH$_{\text{ar}}$), 6.63-6.96 (m, 14H, CH$_{\text{ar}}$), 7.08 (t, $J = 7.5$ Hz, 1H, CH$_{\text{ar}}$), 7.17 (d, $J = 7.5$ Hz, 2H, CH$_{\text{ar}}$), 7.36-7.42 (m, 2H, CH$_{\text{ar}}$), 7.72 (d, $J = 9.7$ Hz, 4H, CH$_{\text{ar}}$).

$^{13}$C{$^1$H}-NMR (125.78 MHz, CDCl$_3$, 298 K): $\delta = 21.9$ (s, 4C, CH$_3$), 66.1-67.0 (m, 2C, CH$_{\text{olefin}}$), 70.5-71.1 (m, 2C, CH$_{\text{olefin}}$), 72.9 (s, 2C, CH$_{\text{benzyl}}$), 127.5 (s, 2C, CH$_{\text{ar}}$), 127.8 (s, 2C, CH$_{\text{ar}}$), 128.0 (s, 2C, CH$_{\text{ar}}$), 128.1 (s, 2C, CH$_{\text{ar}}$), 128.3 (s, 2C, CH$_{\text{ar}}$) 128.5-128.7 (m, 6C, CH$_{\text{ar}}$), 129.2 (s, 2C, CH$_{\text{ar}}$), 129.6 (d, $J = 1.7$ Hz, 1C, CH$_{\text{ar}}$), 131.3 (d, $^1$J$_{PC} = 26.9$ Hz, 1C, C$_{\text{quat}}$), 131.5 (d, $J = 1.9$ Hz, 2C, CH$_{\text{ar}}$), 131.7 (d, $J = 9.1$ Hz, 2C, CH$_{\text{ar}}$), 132.1 (d, $J = 11.0$ Hz, 4C, CH$_{\text{ar}}$), 133.0 (d, $J = 1.9$ Hz, 2C, C$_{\text{quat}}$), 135.0 (s, 2C, C$_{\text{quat}}$), 135.4 (d, $^1$J$_{PC} = 24.7$ Hz, 2C, C$_{\text{quat}}$), 136.5 (d, $J = 3.1$ Hz, 2C, C$_{\text{quat}}$), 137.7 (d, $J = 9.4$ Hz, 4C, C$_{\text{quat}}$), 140.8 (d, $J = 2.9$ Hz, 2C, C$_{\text{quat}}$).

$^{31}$P{$^1$H}-NMR (202.50 MHz, CDCl$_3$, 298 K) $\delta = 6.8$ (d, $^1$J$_{RHP} = 109.1$ Hz).

$^1$H, $^{103}$Rh-NMR (15.81 MHz, CDCl$_3$, 298 K): $\delta = -6316$ (d, $^1$J$_{PRh} = 109.1$ Hz).

ATR IR (v in cm$^{-1}$): 3202 (w), 3065 (w), 3018 (w), 2920 (w), 2848 (w), 1596 (w), 1582 (w), 1486 (m), 1470 (m), 1438 (w), 1411 (w), 1372 (w), 1315 (w), 1266 (w), 1255 (w), 1219 (w), 1190 (w), 1127 (m), 1099 (w), 1065 (m), 1041 (w), 993 (w), 968 (w), 957 (w), 938 (m), 910 (w), 871 (w), 857 (w), 845 (w), 824 (w), 773 (w), 746 (s), 712 (m), 698 (s), 675 (w).
[Rh(trop$_2$NH)(PPh(di-3,5-MePh)$_2$)]OTf  
(82)  
MF = C$_{53}$H$_{46}$F$_3$NO$_3$PRhS  
MW = 967.88 g/mol  
MP = 168-170 °C (decomposition)  

Air stable  

To a solution of [RhCl(trop$_2$NH)(PPh(3,5-MePh)$_2$)] 73 (250 mg, 0.293 mmol, 1 eq.) in CH$_2$Cl$_2$ (10 mL) AgOTf (79 mg, 0.307 mmol, 1.05 eq.) was added. The resulting suspension was stirred overnight then filtered over celite. The solvent was removed under reduced pressure then the residue was recrystallised from THF/hexane and the obtained orange powder was dried under high vacuum. Yield: 275 mg (97%).

$^{1}$H-NMR (500.23 MHz, CDCl$_3$, 298 K): $\delta = 2.45$ (s, 12H, CH$_3$), 4.95 (d, $J = 8.3$ Hz, 2H, CH$^\text{benzyl}$), 5.00 (d, $J = 9.2$ Hz, 2H, CH$^\text{olefin}$), 5.46 (dt, $J = 9.3$ Hz, $J = 2.7$ Hz, 2H, CH$^\text{olefin}$), 5.64 (d, $J = 5.3$ Hz, 1H, NH), 6.70 (d, $J = 7.6$ Hz, 2H, CH$^\text{ar, trop}$), 6.78 (t, $J = 7.5$ Hz, 2H, CH$^\text{ar, trop}$), 6.86-6.87 (m, 2H, CH$^\text{ar, trop}$), 6.91 (t, $J = 6.5$ Hz, 2H, CH$^\text{ar, trop}$), 7.17 (d, $J = 7.6$ Hz, 2H, CH$^\text{ar, trop}$), 7.22 (t, $J = 6.5$ Hz, 2H, CH$^\text{ar, trop}$), 7.23 (s, 2H, CH$^\text{ar, trop}$), 7.31 (d, $J = 7.3$ Hz, 2H, CH$^\text{ar, trop}$), 7.49 (d, $^3$J$_{PH} = 10.5$ Hz, 4H, CH$^\text{quat, phosphane}$), 7.54 - 7.63 (m, 3H, CH$^\text{quat, phosphane}$), 7.83-7.87 (m, 2H, CH$^\text{quat, phosphane}$).

$^{13}$C$^\{^1\text{H}\}$-NMR (125.78 MHz, CDCl$_3$, 298 K): $\delta = 21.8$ (s, 4C, CH$_3$), 73.1 (s, 2C, CH$^\text{benzyl}$), 74.4-74.9 (m, 4C, CH$^\text{olefin}$), 120.1 (q, $^1$J$_{FC} = 320.7$ Hz, 1C, CF$_3$), 126.7 (s, 2C, CH$^\text{ar, trop}$), 126.8 (s, 2C, CH$^\text{ar, trop}$), 127.3 (s, 2C, CH$^\text{ar, trop}$), 127.9 (s, 2C, CH$^\text{ar, trop}$), 128.6 (s, 2C, CH$^\text{ar, trop}$), 128.8 (s, 2C, CH$^\text{ar, trop}$), 128.9 (d, $J = 9.8$ Hz, 2C, CH$^\text{ar, phosphane}$), 129.1 (d, $^1$J$_{PH} = 46.3$ Hz, 2C, C$^\text{quat, phosphane}$), 129.9 (s, 2C, CH$^\text{ar, trop}$), 130.0 (s, 2C, CH$^\text{ar, trop}$), 130.1 (d, $^1$J$_{PH} = 43.6$ Hz, 1C, C$^\text{quat, phosphane}$), 131.1 (d, $^3$J$_{PH} = 2.6$ Hz, 1C, CH$^\text{ar, phosphane}$), 132.6 (d, $^3$J$_{PH} = 9.6$ Hz, 4C, CH$^\text{ar, phosphane}$), 133.2 (d, $J = 2.64$ Hz, 2C, CH$^\text{ar, phosphane}$), 134.7 (d, $J = 9.4$ Hz, 2C, CH$^\text{ar, phosphane}$), 135.0 (s, 2C, C$^\text{quat, trop}$), 135.1 (s, 2C, C$^\text{quat, trop}$), 136.0 (d, $J = 1.9$ Hz, 2C, C$^\text{quat, trop}$), 137.5 (s, 2C, C$^\text{quat, trop}$), 138.8 (d, $^3$J$_{PH} = 10.3$ Hz, 4C, C$^\text{quat, phosphane}$).

$^{19}$F-NMR (188.31 MHz, CDCl$_3$, 298 K): $\delta = -78.3$ (s).

$^{31}$P$^\{^1\text{H}\}$-NMR (202.50 MHz, CDCl$_3$, 298 K) $\delta = 39.3$ (d, $^1$J$_{RP} = 136.7$ Hz).

$^1$H, $^{103}$Rh-NMR (15.81 MHz, CDCl$_3$, 298 K): $\delta = -6779$ (d, $^1$J$_{PRh} = 136.7$ Hz).

ATR IR (v in cm$^{-1}$): 3059 (w), 2925 (w), 2858 (w), 1598 (w), 1492 (w), 1458 (w), 1433 (w), 1377 (w), 1352 (w), 1312 (w), 1275 (m), 1258 (s), 1223 (m), 1192 (w), 1147 (m), 1124 (w), 1080 (w), 1063 (w), 1030 (s), 982 (w), 950 (w), 892 (w), 854 (w), 824 (w), 804 (w), 782 (w), 767 (m), 751 (s), 696 (s), 636 (s).
[RhCl(trop2NH)(PPh(di-3,5-CF3Ph)2)]

(74)

MF = C52H34ClF12NPRh

MW = 1070.15 g/mol

MP =>220 °C (decomposition)

Air stable

To a suspension of [RhCl(trop2NH)]2 (162 mg, 0.150 mmol, 1 eq.) in CH2Cl2 (5 mL) bis(3,5-bis(trifluoromethyl)phenyl)(phenyl)phosphane (290 mg, 0.543 mmol, 3.6 eq.) was added. The resulting orange solution was stirred for 30 minutes then the solvent was removed under reduced pressure. The residue was recrystallised from THF/hexane and the obtained orange powder was dried under high vacuum. Yield: 320 mg (99%).

1H-NMR (500.23 MHz, CDCl3, 298 K): \( \delta = 1.50 \) (br, 1H, NH), 3.93 (s, 2H, \( CH_{\text{benzyl}} \)), 5.10-5.22 (m, 4H, \( CH_{\text{olefin}}, CH_{\text{ar}}, \text{phosphane} \)), 5.78 (dd, \( J = 9.1 \text{ Hz}, J = 6.3 \text{ Hz}, 2H, CH_{\text{olefin}} \)), 6.53 (d, \( J = 7.6 \text{ Hz}, 2H, CH_{\text{ar}}, \text{trop} \)), 6.62-6.96 (m, 6H, \( CH_{\text{ar}}, \text{trop}, CH_{\text{ar}}, \text{phosphane} \)), 7.01 (dd, \( J = 7.6 \text{ Hz}, J = 7.3 \text{ Hz}, 2H, CH_{\text{ar}}, \text{trop} \)), 7.25 (t, \( J = 7.5 \text{ Hz}, 1H, CH_{\text{ar}}, \text{phosphane} \)), 8.01 (s, 2H, \( CH_{\text{ar}}, \text{phosphane} \)), 8.71 (d, \( J_{PH} = 8.5 \text{ Hz}, 4H, CH_{\text{ar}}, \text{phosphane} \)).

13C\{1H\}-NMR (125.78 MHz, CDCl3, 298 K): \( \delta = 67.5 \) (dd, \( J = 8.4 \text{ Hz}, J = 5.3 \text{ Hz}, 2C, CH_{\text{olefin}} \)), 72.8 (s, 2C, \( CH_{\text{benzyl}} \)), 73.3 (dd, \( J = 18.1 \text{ Hz}, J = 8.8 \text{ Hz}, 2C, CH_{\text{olefin}} \)), 123.4 (q, \( J_{PC} = 273.3 \text{ Hz}, 4C, CF_3 \)), 124.3 (br, 2C, \( CH_{\text{ar}}, \text{phosphane} \)), 125.5 (s, 4C, \( CH_{\text{ar}}, \text{trop} \)), 126.6 (s, 2C, \( CH_{\text{ar}}, \text{trop} \)), 127.0 (d, \( J_{PC} = 22.6 \text{ Hz}, 1C, C_{\text{quat}}, \text{phosphane} \)), 128.1 (s, 2C, \( CH_{\text{ar}}, \text{phosphane} \)), 128.7-129.0 (m, 6C, \( CH_{\text{ar}}, \text{trop} \)), 129.5 (s, 2C, \( CH_{\text{ar}}, \text{phosphane} \)) 129.8-130.0 (m, 3C, \( CH_{\text{ar}}, \text{trop}, CH_{\text{ar}}, \text{phosphane} \)), 131.0 (d, \( J_{PC} = 10.1 \text{ Hz}, 2C, \text{ar}, \text{phosphane} \)), 132.3 (qd, \( J_{PC} = 33.3 \text{ Hz}, J_{PC} = 8.6 \text{ Hz} \)), 135.2 (s, 2C, \( CH_{\text{quat}}, \text{trop} \)), 135.6 (d, \( J = 5.0 \text{ Hz}, 2C, C_{\text{quat}}, \text{trop} \)), 138.8 (d, \( J_{PC} = 18.0 \text{ Hz}, 2C, C_{\text{quat}}, \text{phosphane} \)), 140.4 (d, \( J = 4.1 \text{ Hz}, 2C, C_{\text{quat}}, \text{trop} \)).

19F-NMR (188.31 MHz, CDCl3, 298 K): \( \delta = -62.6 \) (s, 12F).

31P\{1H\}-NMR (202.50 MHz, CDCl3, 298 K) \( \delta = 11.5 \) (d, \( J_{RBP} = 114.4 \text{ Hz} \)).

1H, 103Rh-NMR (15.81 MHz, CDCl3, 298 K) \( \delta = -6405 \) (d, \( J_{PRh} = 114.4 \text{ Hz} \)).

ATR IR (\( \nu \) in cm\(^{-1}\)): 3194 (w), 2988 (w), 2899 (w), 1618 (w), 1600 (w), 1489 (w), 1473 (w), 1438 (w), 1408 (w), 1353 (s), 1276 (s), 1189 (m), 1175 (m), 1118 (s), 1092 (m), 999 (w), 970 (w), 960 (w), 942 (w), 906 (m), 876 (w), 843 (w), 827 (w), 780 (w), 767 (w), 751 (s), 731 (w), 714 (w), 706 (m), 681 (s), 621 (m).
[Rh(trop₂NH)(PPh(di-3,5-CF₃Ph)₂)]OTf (83)

MF = C₅₃H₃₄F₁₅NO₃PRhS

MW = 1183.76 g/mol

MP = 190-193 °C (decomposition)

Air stable

To a solution of [RhCl(trop₂NH)(PPh(di-3,5-CF₃Ph)₂)] (74) (250 mg, 0.234 mmol, 1 eq.) in CH₂Cl₂ (10 mL) AgOTf (63 mg, 0.245 mmol, 1.05 eq.) was added. The resulting suspension was stirred overnight then filtered over celite. The solvent was removed under reduced pressure then the residue was recrystallised from THF/hexane and the obtained orange powder was dried under high vacuum. Yield: 250 mg (90%).

¹H-NMR (500.23 MHz, CDCl₃, 298 K): δ = 4.88 (dd, J = 9.2 Hz, 3JHH = 1.4 Hz, 2H, CHolefin), 4.94 (d, J = 8.9 Hz, 2H, CHBenzyl), 5.37 (dd, J = 9.2 Hz, J = 2.8 Hz, J = 2.8 Hz, 2H, CHolefin), 6.17 (d, J = 5.7 Hz, 1H, NH), 6.73 (d, J = 7.3 Hz, 2H, CHar, trop), 6.84 (t, J = 7.3 Hz, 2H, CHar, trop), 6.87 (d, J = 7.8 Hz, 2H, CHar, trop), 6.97 (t, J = 7.5 Hz, 2H, CHar, trop), 7.19 (d, J = 7.6 Hz, 2H, CHar, trop), 7.28 (m, 6H, CHar, trop), 7.76 (m, 5H, CHar, phosphane), 8.20 (s, 2H, CHar, phosphane), 8.24 (d, 3JPH = 9.4 Hz, 4H, CHar, phosphane).

¹³C{¹H}-NMR (125.78 MHz, CDCl₃, 298 K): δ = 73.3 (d, J = 1.4 Hz, 2C, CHBenzyl), 74.0 (d, J = 13.0 Hz, 2C, CHolefin), 74.3 (d, J = 7.2 Hz, 2C, CHolefin), 119.9 (eq, 1JFC = 319.6 Hz, 1C, CF₃OTf), 123.0 (d, 1JFC = 274.5 Hz, 4C, ArCF₃), 126.0 (br; s, 2C, CHar, phosphane), 126.9 (s, 2C, CHar, trop), 127.4 (s, 2C, CHar, trop), 127.8 (s, 2C, CHar, trop), 127.9 (s, 2C, CHar, trop), 129.0 (s, 2C, CHar, trop), 129.1 (s, 2C, CHar, trop), 129.9 (s, 2C, CHar, trop), 130.2 (d, J = 10.1 Hz, 2C, CHar, phosphane), 130.2 (s, 2C, CHar, trop), 132.7 (d, 1JPC = 41.5 Hz, 2C, Cquat, phosphane), 132.9 (d, 1JPC = 34.5 Hz, 1C, Cquat, phosphane), 133.1 (d, 4JPC = 2.2 Hz, 1C, CHar, phosphane), 133.4 (br; d, J = 9.4 Hz, 4C, CHar, phosphane), 134.3 (d, 3JPC = 9.8 Hz, 4C, Cquat, phosphane), 134.7 (d, J = 9.8 Hz, 2C, CHar, phosphane), 134.8 (d, J = 1.9 Hz, 2C, Cquat, trop), 135.0 (d, J = 0.7 Hz, 2C, Cquat, trop), 135.0 (s, 2C, Cquat, trop), 136.2 (s, 2C, Cquat, trop).

¹⁹F-NMR (188.31 MHz, CDCl₃, 298 K): δ = -78.7 (s, 3F, CF₃OTf), -62.6 (s, 12F, CF₃phosphane).

³¹P{¹H}-NMR (202.50 MHz, CDCl₃, 298 K) δ = 45.9 (d, 1JRhP = 141.9 Hz).

¹H, ¹⁰³Rh-NMR (15.81 MHz, CDCl₃, 298 K): δ = -6832 (d, 1JRhRh = 141.9 Hz).

ATR IR (v in cm⁻¹): 2988 (w), 2894 (w), 1618 (w), 1492 (w), 1434 (w), 1353 (m), 1308 (w), 1276 (s), 1226 (w), 1177 (m), 1123 (s), 1106 (w), 1092 (s), 1017 (s), 980 (w), 903 (m), 844 (w), 825 (w), 770 (w), 746 (s), 715 (w), 702 (m), 682 (s), 634 (s).
[RhCl(trop2NH)(DBP)] (75)

MF = C₄₈H₃₅ClNPRh

MW = 795.13 g/mol

MP = >220 °C (decomposition)

Air stable

To a suspension of [RhCl(trop2NH)]₂ (100 mg, 0.093 mmol, 1 eq.) in CH₂Cl² (5 mL) 5-phenyl-5H-dibenzophosphole (DBP) (53 mg, 0.205 mmol, 2.2 eq.) was added. The resulting orange solution was stirred for 30 minutes then the solvent was removed under reduced pressure. The residue was recrystallised from THF/hexane and the obtained orange powder was dried under high vacuum. Yield: 140 mg (94%).

Isomer 1 (50%):

¹H-NMR (500.23 MHz, CDCl₃, 223 K): δ = 2.63 (s, 1H, NH), 4.09 (s, 2H, CH benzyl), 4.36 (t, J = 8.6 Hz, 2H, CH olefin), 5.26 (dd, J = 9.3 Hz, J = 5.8 Hz, 2H, CH olefin), 5.77-5.78 (m, 2H, CH₂), 6.26-6.28 (m, 2H, CH₆), 6.62-7.63 (m, 21H, CH₆), 7.79 (t, J = 8.8 Hz, 2H, CH₆), 8.51 (t, J = 6.7 Hz, 2H, CH₆).

¹³C{¹H}-NMR (125.78 MHz, CDCl₃, 223 K): δ = 67.9 (s, 2C, CH olefin), 68.7 (d, J = 18.7 Hz, 2C, CH olefin), 72.3 (s, 2C, CH benzyl), 121.4-132.4 (m, 32C, CH₂, C quat, phosphole), 132.3 (m, 2C, C quat, trop), 134.3 (s, 2C, C quat, trop), 136.2 (m, 2C, C quat, trop), 138.1 (s, 2C, C quat, trop), 142.0 (d, J³PC = 5.8 Hz, 2C, C quat, phosphole).

³¹P{¹H}-NMR (202.50 MHz, CDCl₃, 223 K) δ = 3.8 (d, J RHp = 111.3 Hz).

¹H, ¹⁰³Rh-NMR (15.81 MHz, CDCl₃, 223 K): δ = -6531 (d, J PRh = 111.3 Hz).

Isomer 2 (50%):

¹H-NMR (500.23 MHz, CDCl₃, 223 K): δ = 2.63 (s, 1H, NH), 4.49 (s, 2H, CH benzyl), 4.95 (t, J = 8.9 Hz, 2H, CH olefin), 5.36-5.38 (m, 2H, CH₂), 5.57 (dd, J = 9.4 Hz, J = 5.6 Hz, 2H, CH olefin), 6.31 (d, J = 7.6 Hz, 2H, CH₂), 6.62-7.63 (m, 23H, CH₂), 7.79 (t, J = 8.8 Hz, 2H, CH₂).

¹³C{¹H}-NMR (125.78 MHz, CDCl₃, 223 K): δ = 67.3 (s, 2C, CH olefin), 70.9-71.1 (m, 2C, CH olefin), 72.9 (s, 2C, CH benzyl), 121.4-132.4 (m, 32C, CH₂, C quat, phosphole), 132.3 (m, 2C, C quat, trop), 134.8 (s, 2C, C quat, trop), 136.2 (m, 2C, C quat, trop), 140.6 (s, 2C, C quat, trop), 143.0 (d, J³PC = 7.2 Hz, 2C, C quat, phosphole).
$^{31}\text{P}$\{}$^{1}\text{H}$\}-\text{NMR (202.50 MHz, CDCl}_3$, 223 K) $\delta = 3.8$ (d, $^{1}J_{\text{RhP}} = 111.3$ Hz).

$^{1}\text{H}$, $^{103}\text{Rh}$-NMR (15.81 MHz, CDCl$_3$, 223 K): $\delta = -6531$ (d, $^{1}J_{\text{PRh}} = 111.3$ Hz).

ATR IR ($\nu$ in cm$^{-1}$): 3204 (w), 3062 (w), 3039 (w), 3016 (w), 2159 (w), 1597 (w), 1487 (m), 1467 (m), 1437 (m), 1413 (w), 1398 (w), 1318 (w), 1299 (w), 1270 (w), 1256 (w), 1220 (w), 1196 (w), 1187 (w), 1159 (w), 1125 (w), 1107 (w), 1093 (w), 1065 (w), 1073 (w), 1065 (w), 1045 (w), 1028 (w), 1002 (w), 988 (w), 968 (w), 961 (m), 939 (m), 882 (w), 840 (w), 828 (w), 781 (w), 748 (s), 721 (s), 700 (m), 687 (s), 668 (w), 619 (w).
[Rh(trop2NH)(DBP)]OTf (78)

MF = C_{49}H_{36}F_{3}NO_{3}PRhS

MW = 909.75 g/mol

MP = 205-206 °C (decomposition)

Air stable

To a solution of [RhCl(trop2NH)(P(n-BuPh)₃)] (122 mg, 0.153 mmol, 1 eq.) in CH₂Cl₂ (5 mL) AgOTf (43 mg, 0.169 mmol, 1.1 eq.) was added. The resulting suspension was stirred overnight then filtered over celite. The solvent was removed under reduced pressure then the residue was recrystallised from THF/hexane and the obtained orange powder was dried under high vacuum. Yield: 138 mg (99%). Crystals suitable for X-ray analysis were obtained by layering a concentrated solution of 78 in acetone with hexane.

$^{1}$H-NMR (500.23 MHz, CDCl₃, 298 K): $\delta = 4.58$ (d, $J = 8.7$ Hz, 2H, $CH_{\text{olefin}}$), 4.89 (d, $J = 8.0$ Hz, 2H, $CH_{\text{benzyl}}$), 5.57 (d, $J = 5.0$ Hz, 1H, NH), 5.66 (d, $J = 9.2$ Hz, 2H, $CH_{\text{olefin}}$), 6.79 (d, $J = 3.9$ Hz, 4H, $CH_{\text{ar, trop}}$), 6.84-6.91 (m, 6H, $CH_{\text{ar, trop}}$), 7.15-7.20 (m, 4H, $CH_{\text{ar, trop}}$), 7.24 (d, $J = 6.9$ Hz, 2H, $CH_{\text{ar, trop}}$), 7.51-7.55 (m, 3H, $CH_{\text{phosphole}}$), 7.69-7.72 (m, 2H, $CH_{\text{ar, phosphole}}$), 7.76 (t, $J = 7.3$ Hz, 2H, $CH_{\text{ar, phosphole}}$), 7.96-8.00 (m, 2H, $CH_{\text{ar, phosphole}}$), 8.02 (d, $J = 7.6$ Hz, 2H, $CH_{\text{ar, phosphole}}$), 8.41 (t, $J = 7.2$ Hz, 2H, $CH_{\text{ar, phosphole}}$).

$^{13}$C{1H}-NMR (125.78 MHz, CDCl₃, 298 K): $\delta = 71.7$ (d, $J = 12.5$ Hz, 2C, $CH_{\text{olefin}}$), 73.2 (s, 2C, $CH_{\text{benzyl}}$), 74.4 (d, $J = 7.2$ Hz, 2C $CH_{\text{olefin}}$), 119.9 (q, $^{1}J_{FC} = 319.6$ Hz, 1C, CF₃), 122.4 (d, $J = 6.2$ Hz, 2C, $CH_{\text{ar, phosphole}}$), 126.7 (s, 2C, $CH_{\text{ar, trop}}$), 127.1 (s, 2C, $CH_{\text{ar, trop}}$), 127.2 (s, 2C, $CH_{\text{ar, trop}}$), 127.6 (s, 2C, $CH_{\text{ar, trop}}$), 128.7 (s, 2C, $CH_{\text{ar, trop}}$), 128.8 (s, 2C, $CH_{\text{ar, trop}}$), 129.5 (d, $J = 10.6$ Hz, 2C, $CH_{\text{ar, phosphole}}$), 129.8 (d, $J = 9.6$ Hz, 2C, $CH_{\text{ar, phosphole}}$), 130.1 (s, 2C, $CH_{\text{ar, trop}}$), 130.1 (s, 2C, $CH_{\text{ar, trop}}$), 131.4 (s, 1C, $CH_{\text{ar, phosphole}}$), 132.4-132.6 (m, 7C, $CH_{\text{ar, phosphole}}$, $C_{\text{quat, phosphole}}$), 133.6 (d, $^{1}J_{PC} = 51.5$ Hz, 2C, $C_{\text{quat, phosphole}}$), 134.8 (s, 2C, $C_{\text{quat, trop}}$), 134.9 (s, 2C, $C_{\text{quat, trop}}$), 135.7 (s, 2C, $C_{\text{quat, trop}}$), 137.4 (s, 2C, $C_{\text{quat, trop}}$), 143.3 (d, $^{2}J_{PC} = 9.6$ Hz, 2C, $C_{\text{quat, phosphole}}$).

$^{19}$F-NMR (188.31 MHz, CDCl₃, 298 K): $\delta = -78.2$ (s).

$^{31}$P{1H}-NMR (202.50 MHz, CDCl₃, 298 K) $\delta = 40.0$ (d, $^{1}J_{RhP} = 135.8$ Hz).

$^{1}$H, $^{103}$Rh-NMR (15.81 MHz, CDCl₃, 298 K): $\delta = -6884$ (d, $^{1}J_{Prh} = 135.8$ Hz).
ATR IR (v in cm\(^{-1}\)):
3130 (w), 2993 (w), 2908 (w), 2154 (w), 1976 (w), 1601 (w), 1490 (w),
1473 (w), 1438 (w), 1398 (w), 1338 (w), 1294 (m), 1241 (w), 1223 (m), 1215 (m), 1190 (w),
1152 (m), 1110 (w), 1093 (w), 1073 (w), 1051 (w), 1022 (s), 1002 (w), 993 (w), 972 (w),
936 (w), 911 (w), 891 (w), 874 (w), 836 (w), 826 (w), 756 (m), 744 (s), 731 (w), 720 (s),
694 (m), 632 (s).
[\text{RhCl(trop}_2\text{NH})(P(py)_3)] (68)

MF = C$_{42}$H$_{35}$ClN$_4$PRh

MW = 801.12 g/mol

MP = > 220 °C (decomposition)

Air stable

To a suspension of [\text{RhCl(trop}_2\text{NH})]$_2$ (200 mg, 0.187 mmol, 1 eq.) in DCM (5 mL) tri(pyridin-2-yl)phosphane (104 mg, 0.392 mmol, 2.1 eq.) was added. The [\text{RhCl(trop}_2\text{NH})]$_2$ dissolved slowly then a yellow precipitate was formed. After stirring for 2 hours the reaction mixture was layered with hexane. The title compound precipitated as yellow powder, which was isolated by decantation and dried under high vacuum. Yield: 267 mg, 86%.

$^1$H-NMR (400.13 MHz, CDCl$_3$, 298 K): $\delta$ = 4.31 (s, 2H, $\text{CH}^{\text{benzyl}}$), 5.21 (t, $J$ = 8.5 Hz, 2H, $\text{CH}^{\text{olefin}}$), 5.58 (dd, $J$ = 8.5 Hz, $J$ = 6.3 Hz, 2H, $\text{CH}^{\text{olefin}}$), 6.61-6.69 (m, 6H, $\text{CH}^{\text{ar, trop}}$), 6.74 (d, $J$ = 7.4 Hz, 2H, $\text{CH}^{\text{ar, trop}}$), 6.79-6.85 (m, 6H, $\text{CH}^{\text{ar, trop}}$), 7.14 (d, $J$ = 6.6 Hz, 2H, $\text{CH}^{\text{ar, trop}}$), 7.20 (br, 3H, $\text{CH}^{\text{ar, phosphane}}$), 7.40 (br, 3H, $\text{CH}^{\text{ar, phosphane}}$), 7.55 (br, 3H, $\text{CH}^{\text{ar, phosphane}}$), 8.39 (br, 1H, NH), 8.48 (br, 3H, $\text{CH}^{\text{ar, phosphane}}$).

$^{13}$C$\{^1$H$\}$-NMR (100.61 MHz, CDCl$_3$, 298 K): $\delta$ = 68.3 (dd, $J$ = 8.0 Hz, $J$ = 5.7 Hz, 2C, $\text{CH}^{\text{olefin}}$), 71.2 (dd, $J$ = 17.9 Hz, $J$ = 9.3 Hz, 2C, $\text{CH}^{\text{olefin}}$), 73.1 (s, 2C, $\text{CH}^{\text{benzyl}}$), 123.4 (s, 3C, $\text{CH}^{\text{ar, phosphane}}$), 124.6 (s, 2C, $\text{CH}^{\text{ar, trop}}$), 124.6 (s, 2C, $\text{CH}^{\text{ar, trop}}$), 126.1 (s, 2C, $\text{CH}^{\text{ar, trop}}$), 127.1 (s, 2C, $\text{CH}^{\text{ar, trop}}$), 128.0 (s, 2C, $\text{CH}^{\text{ar, trop}}$), 128.2 (d, $J$ = 5.0 Hz, 2C, $\text{CH}^{\text{ar, trop}}$), 128.8 (d, $J$ = 1.1 Hz, 2C, $\text{CH}^{\text{ar, trop}}$), 128.9 (d, $J$ = 1.8 Hz, 2C, $\text{CH}^{\text{ar, trop}}$), 130.4 (d, $J$ = 15.1 Hz, 3C, $\text{CH}^{\text{ar, phosphane}}$), 133.9 (d, $J$ = 2.1 Hz, 2C, $\text{C}^{\text{quat, trop}}$), 135.7 (d, $J$ = 5.3 Hz, 3C, $\text{CH}^{\text{ar, phosphane}}$), 136.3 (s, 2C, $\text{C}^{\text{quat, trop}}$), 136.5 (d, $J$ = 5.5 Hz, 2C, $\text{C}^{\text{quat, trop}}$), 140.4 (d, $J$ = 3.7 Hz, 2C, $\text{C}^{\text{quat, trop}}$), 149.0 (d, $J$ = 16.4 Hz, 3C, $\text{CH}^{\text{ar, phosphane}}$), 159.2 (d, $^1$J$_{\text{PC}}$ = 45.9 Hz 3 C).

$^{31}$P$\{^1$H$\}$-NMR (161.98 MHz, CDCl$_3$, 298 K) $\delta$ = 15.6 (d, $^1$J$_{\text{Rhp}}$ = 112.9 Hz).

$^1$H, $^{103}$Rh-NMR (12.64 MHz, CDCl$_3$, 298 K): $\delta$ = -6445 (d, $^1$J$_{\text{PRh}}$ = 112.9 Hz).

ATR IR (ν in cm$^{-1}$): 2987 (w), 2965 (w), 2868 (w), 1967 (w), 1746 (w), 1715 (w), 1684 (w), 1652 (w), 1597 (w), 1575 (m), 1559 (w), 1538 (w), 1489 (m), 1451 (m), 1418 (m), 1396 (w), 1338 (w), 1260 (m), 1222 (w), 1187 (w), 1153 (w), 1088 (m), 1042 (m), 999 (w), 989 (m), 946 (w), 911 (w), 891 (w), 880 (w), 800 (m), 764 (m), 742 (s), 694 (w), 626 (w).
[Rh(trop2NH)(P(py)3)]OTf (85)

MF = C_{40}H_{35}F_{3}N_{4}O_{3}PRhS

MW = 914.73 g/mol

MP = > 220 °C (decomposition)

Air stable

To a degased solution of [RhCl(trop2NH)(P(py)3)] 68 (100 mg, 0.125 mmol, 1 eq.) in acetonitrile (5 mL) AgOTf (35 mg, 0.137 mmol, 1.1 eq.) was added. The resulting suspension was stirred for 1.5 months then all volatiles were removed under reduce pressure. DCM was added to the residue then the mixture was filtered over celite. The solvent was removed under reduced pressure then the residue was recrystallised from THF/hexane and the obtained orange powder was dried under high vacuum. Yield: 55 mg (48%).

$^{1}$H-NMR (500.23 MHz, [D6]DMSO, 298 K): $\delta = 5.15$ (d, $J = 8.9$ Hz, 2H, $CH_benzyl$), 5.25 (d, $J = 4.6$ Hz, 1H, $NH$), 5.84-5.88 (m, 4H, $CH_{olefin}$), 6.78 (d, $J = 7.6$ Hz, 2H, $CH_{ar, trop}$), 6.84-6.87 (m, 2H, $CH_{ar, trop}$), 6.90 (d, $J = 4.6$ Hz, 1H, $NH$), 7.16-7.30 (m, 5H, $CH_{ar, trop}$, $CH_{ar, phosphane}$), 7.37 (d, $J = 7.4$ Hz, 2H, $CH_{ar, trop}$), 7.38 (d, $J = 8.1$ Hz, 2H, $CH_{ar, trop}$), 7.38 (d, $J = 8.1$ Hz, 2H, $CH_{ar, trop}$), 7.83 (d, $J = 8.1$ Hz, 2H, $CH_{ar, trop}$), 8.01-8.05 (m, 3H, $CH_{ar, phosphane}$), 9.30 (d, $J = 3.7$ Hz, 3H, $CH_{ar, phosphane}$).

$^{13}$C {$^{1}$H} NMR (125.78 MHz, [D6]DMSO, 298 K): $\delta = 68.2$ (d, $J = 7.2$ Hz, 2C, $CH_{olefin}$), 70.4 (s, 2C, $CH_{benzyl}$), 72.2 (d, $J = 10.1$ Hz, 2C, $CH_{olefin}$), 127.0 (s, 2C, $CH_{ar, trop}$), 127.1 (d, $J = 1.9$ Hz, 3C, $CH_{ar, phosphane}$), 127.7 (s, 2C, $CH_{ar, trop}$), 128.4 (s, 2C, $CH_{ar, trop}$), 128.7 (s, 2C, $CH_{ar, trop}$), 129.1 (s, 2C, $CH_{ar, trop}$), 129.1 (s, 2C, $CH_{ar, trop}$), 129.3 (s, 2C, $CH_{ar, trop}$), 130.2 (s, 2C, $CH_{ar, trop}$), 130.9 (d, $J = 13.7$ Hz, 3C, $CH_{ar, phosphane}$), 134.4 (s, 2C, $C_{quat, trop}$), 135.9 (s, 2C, $C_{quat, trop}$), 137.3 (s, 2C, $C_{quat, trop}$), 137.8 (s, 2C, $C_{quat, trop}$), 138.8 (d, $J = 6.0$ Hz, 3C, $CH_{ar, phosphane}$), 152.0 (d, $J = 17.5$ Hz, 3C, $CH_{ar, phosphane}$), 153.3 (d, $J_{PC} = 70.8$ Hz, 3C, $C_{quat, phosphane}$).

$^{19}$F-NMR (188.31 MHz, [D6]DMSO, 298 K): $\delta = -77.7$ (s).

$^{31}$P {$^{1}$H} NMR (202.50 MHz, [D6]DMSO, 298 K) $\delta = 26.2$ (d, $J_{RhP} = 131.9$ Hz).

$^{1}$H, $^{103}$Rh NMR (15.81 MHz, [D6]DMSO, 298 K): $\delta = -7328$ (d, $J_{PRh} = 131.9$ Hz).

ATR IR (v in cm$^{-1}$): 3410 (br), 3159 (w), 3050 (w), 2982 (w), 1595 (w), 1572 (w), 1561 (w), 1491 (w), 1451 (w), 1426 (w), 1344 (w), 1291 (m), 1254 (s), 1224 (m), 1155 (m), 1091 (w), 1035 (s), 998 (w), 986 (w), 945 (w), 891 (w), 881 (w), 862 (w), 826 (w), 778 (w), 765 (m), 752 (s), 730 (m), 718 (w), 668 (w), 637 (s).
[RhCl(trop$_2$NH)(P(p-BuPh)$_3$)] (76)

MF = C$_{60}$H$_{62}$ClNPRh

MW = 966.47 g/mol

MP = 208-209°C (decomposition)

Air stable

To a suspension of [RhCl(trop$_2$NH)$_2$] (2.50 mg, 2.33 mmol, 1 eq.) in CH$_2$Cl$_2$ (10 mL) tris(4-butylphenyl)phosphane (2.61 mg, 6.06 mmol, 2.6 eq.) was added. The resulting orange solution was stirred for 30 minutes then the solution was concentrated to approximately 5 mL and layered with hexane. An orange precipitate formed which was collected by decantation and washed twice with small portion of methanol (10 mL). The obtained orange powder was dried under high vacuum. Yield: 4.30 g (95%).

$^1$H-NMR (500.23 MHz, CDCl$_3$, 298 K): δ = 0.97 (t, $^3$J$_{HH}$ = 7.3 Hz, 6H, CH$_3$), 1.07 (t, $^3$J$_{HH}$ = 7.5 Hz, 3H, CH$_3$), 1.41 (m, 6H, CH$_2$CH$_3$), 1.64 (m, 7H, CH$_2$CH$_2$CH$_3$; NH), 2.55 (t, $^3$J$_{HH}$ = 7.7 Hz, 2H, CH$_2$CH$_2$CH$_2$CH$_3$), 2.65 (t, $^3$J$_{HH}$ = 7.6 Hz, 4H, CH$_2$CH$_2$CH$_2$CH$_3$), 3.78 (s, 2H, CH$_{benzyl}$), 5.18 (t, $^1$J = 7.8 Hz, 2H, CH$_{ar, phosphane}$), 5.40 (m, 2H, CH$_{olefin}$), 5.61 (dd, $^1$J = 9.4 Hz, $^1$J = 6.0 Hz, 2H, CH$_{olefin}$), 6.53 (d, $^1$J = 7.3 Hz, 2H, CH$_{ar, trop}$), 6.57 (d, $^1$J = 6.4 Hz, 2H, CH$_{ar, trop}$), 6.85 (m, 4H, CH$_{ar, trop}$), 6.95 (t, $^1$J = 7.2 Hz, 2H, CH$_{ar, trop}$), 7.18 (m, 6H, CH$_{ar, trop}$; CH$_{ar, phosphane}$) 8.02 (t, $^1$J = 8.7 Hz, 4H, CH$_{ar, phosphane}$).

$^{13}$C{$^1$H}-NMR (125.78 MHz, CDCl$_3$, 298 K): δ = 14.4 (s, 2C, CH$_3$), 14.5 (s, 1C, CH$_3$), 22.7 (s, 2C, CH$_2$CH$_3$), 22.8 (s, 1C, CH$_2$CH$_3$), 33.8 (s, 1C, CH$_2$CH$_2$CH$_3$), 33.8 (s, 2C, CH$_2$CH$_2$CH$_3$), 35.6 (s, 1C, CH$_2$CH$_2$CH$_2$CH$_3$), 35.9 (s, 2C, CH$_2$CH$_2$CH$_2$CH$_3$), 66.2 (dd, $^2$J$_{PC}$ = 8.4 Hz, $^1$J = 5.5 Hz, 2C, CH$_{olefin}$), 70.7 (dd, $^2$J$_{PC}$ = 18.4 Hz, $^1$J = 9.2 Hz, 2C, CH$_{olefin}$), 73.2 (s, 2C, CH$_{enzyl}$), 124.6 (d, $^1$J = 1.9 Hz, 2C, CH$_{ar, trop}$), 124.7 (s, 2C, CH$_{ar, trop}$), 127.4 (d, $^2$J$_{PC}$ = 26.9 Hz, 1C, C$_{quat, phosphane}$), 127.5 (s, 2C, CH$_{ar, trop}$), 127.7 (s, 2C, CH$_{ar, trop}$), 128.6 (m, 8C, CH$_{ar, trop}$, CH$_{ar, phosphane}$), 128.8 (m, 4C, CH$_{ar, trop}$, CH$_{ar, phosphane}$), 129.2 (s, 2C, CH$_{ar, trop}$), 131.8 (d, $^2$J$_{PC}$ = 9.1 Hz, 2C, CH$_{ar, phosphane}$), 133.0 (d, $^2$J$_{PC}$ = 2.4 Hz, 2C, C$_{quat, trop}$), 133.3 (d, $^2$J$_{PC}$ = 25.9 Hz, 2C, C$_{quat, phosphane}$), 134.3 (d, $^2$J$_{PC}$ = 11.0 Hz, 4C, CH$_{ar, phosphane}$), 135.1 (s, 2C, C$_{quat, trop}$), 136.5 (d, $^2$J$_{PC}$ = 4.6 Hz, 2C, C$_{quat, trop}$), 140.8 (d, $^2$J$_{PC}$ = 3.8 Hz, 2C, C$_{quat, trop}$), 143.0 (s, 1C, C$_{quat, phosphane}$), 144.7 (d, $^2$J$_{PC}$ = 2.2 Hz, 2C, C$_{quat, phosphane}$).

$^{31}$P{$^1$H}-NMR (202.50 MHz, CDCl$_3$, 298 K) δ = 6.9 (d, $^3$J$_{RhP}$ = 111.3 Hz).

$^1$H, $^{103}$Rh-NMR (15.81 MHz, CDCl$_3$, 298 K): δ = -6328 (d, $^1$J$_{PRh}$ = 111.3 Hz).
ATR IR (v in cm$^{-1}$): 3188 (w), 3012 (w), 2951 (w), 2925 (w), 2853 (w), 1598 (m), 1560 (w), 1488 (w), 1467 (m), 1401 (m), 1375 (w), 1339 (w), 1314 (w), 1270 (w), 1252 (w), 1217 (w), 1188 (m), 1158 (w), 1124 (w), 1089 (m), 1042 (w), 1018 (w), 995 (w), 966 (w), 954 (w), 932 (w), 887 (w), 870 (w), 843 (w), 826 (m), 810 (w), 778 (m), 764 (m), 748 (s), 731 (m), 685 (w), 653 (m), 640 (w), 622 (m).
[Rh(trop2N)(P(p-BuPh)3)] (86)

MF = C₆₀H₆₁NPRh

MW = 930.01 g/mol

MP = 119-120 °C (decomposition)

Air sensitive

t-BuOK (93 mg, 0.828 mmol, 1 eq) was added to a solution of [RhCl(trop:NH)(P(n-BuPh)3)] 76 (800 mg, 0.828 mmol, 1 eq) in THF (5 mL) and toluene (2 mL). After stirring for 30 minutes all volatiles were removed under reduced pressure then toluene (2 mL) was added. The volatiles were removed again and the residue was suspended in THF. The green suspension was filtered over a plug of celite then the volatiles were removed under reduced pressure and the residue was dried under high vacuum. Yield: 761 mg (99%).

1H-NMR (500.23 MHz, [D8]THF, 213 K): δ = 0.99 (t, 3J_HH = 7.2 Hz, 9H, CH₂CH₂CH₂CH₃), 1.44 (m, 6H, CH₂CH₂CH₂CH₃), 1.66 (m, 6H, CH₂CH₂CH₂CH₃), 2.73 (t, 3J_HH = 7.6 Hz, 6H, CH₂CH₂CH₂CH₃), 4.70 (br, 2H, CHolefin), 4.93 (d, 2J_HH = 13.3 Hz, 2H, CHbenzyl), 5.63 (d, 2J_HH = 5.0 Hz, 2H, CHolefin), 6.61 (br, 2H, CHar₃, trop), 6.70 (br, 2H, CHar₃, trop), 6.81 (br, 2H, CHar₃, trop), 6.91 (br, 2H, CHar₃, trop), 6.98 (br, 2H, CHar₃, trop), 7.05 (br, 4H, CHar₃, trop), 7.24 (br, 2H, CHar₃, trop), 7.42 (d, 2J_HH = 7.1 Hz, 6H, CHar₃, phosphane), 7.57 (t, 2J_HH = 8.5 Hz, 6H, CHar₃, phosphane).

13C{¹H}-NMR (125.78 MHz, [D8]THF, 213 K): δ = 14.2 (s, 3C, CH₂CH₂CH₂CH₃), 23.3 (s, 3C, CH₂CH₂CH₂CH₃), 34.6 (s, 3C, CH₂CH₂CH₂CH₃), 36.1 (s, 3C, CH₂CH₂CH₂CH₃), 75.8 (d, 2J_HH = 9.4 Hz, 2C, CHolefin), 81.9 (s, 2C, CHbenzyl), 83.8 (d, 2J_HH = 16.6 Hz, 2C, CHolefin), 125.3 (br, 2C, CHar₃, trop), 125.5 (br, 2C, CHar₃, trop), 125.7 (br, 2C, CHar₃, trop), 125.9 (br, 4C, CHar₃, trop), 126.8 (br, 2C, CHar₃, trop), 127.4 (br, 2C, CHar₃, trop), 128.2 (br, 2C, CHar₃, trop), 128.8 (d, 2J_PC = 37.0 Hz, 3C, Cquat, phosphane), 128.9 (d, 2J_PC = 8.9 Hz, 6C, CHar₃, phosphane), 135.0 (d, 2J_PC = 10.8 Hz, 6C, CHar₃, phosphane), 136.3 (br, 2C, Cquat, trop), 137.3 (br, 2C, Cquat, trop), 143.3 (br, 2C, Cquat, trop), 145.5 (s, 3C, Cquat, phosphane), 146.3 (br, 2C, Cquat, trop).

31P{¹H}-NMR (202.50 MHz, [D8]THF, 213 K) δ = 38.7 (d, 2J_RhP = 122.8 Hz).

1H, 103Rh-NMR (15.81 MHz, [D8]THF, 213 K): δ = -7452 (d, 1J_RhP = 122.8 Hz).

ATR IR (ν in cm⁻¹): 3013 (w), 2951 (w), 2927 (w), 2858 (w) 1598 (w), 1573 (w), 1560 (w), 1490 (m), 1466 (m), 1400 (m), 1375 (w), 1313 (w), 1256 (w), 1223 (w), 1189 (w), 1155 (w), 1091 (m), 1067 (w), 1042 (w), 1018 (w), 980 (w), 933 (w), 825 (w), 806 (w), 778 (w), 744 (s), 656 (m), 620 (m).
\[ \text{[Rh(trop}_2\text{NH})(\text{P}(p-\text{BuPh})_3)]OTf (84) } \]

\[ \text{MF} = \text{C}_{61}\text{H}_{62}\text{F}_3\text{NO}_3\text{PRhS} \]

\[ \text{MW} = 1080.09 \text{ g/mol} \]

\[ \text{MP} = 123-125^\circ \text{C} \]

Air stable

Standard procedure: To a solution of \[ \text{[RhCl(trop}_2\text{NH})(\text{P}(n-\text{BuPh})_3)] } \] 76 (3.00 g, 3.10 mmol, 1 eq.) in \( \text{CH}_2\text{Cl}_2 \) (15 mL) was added AgOTf (837 mg, 3.26 mmol, 1.05 eq.). The resulting suspension was stirred overnight then filtered over celite. The solvent was removed under reduced pressure and the residue dissolved in THF then hexane was added. An oily dark orange precipitate formed which was isolated by decantation and dried under high vacuum. While drying the product solidified and was obtained as dark orange powder. Yield: 3.30 g (98%).

AgOTf free procedure: Triethyl ammonium triflate (97 mg, 0.39 mmol, 1.2 eq.) was added to a solution of \[ \text{[Rh(trop}_2\text{N})(\text{P}(n-\text{BuPh})_3)] } \] 86 (300 mg, 0.32 mmol, 1 eq.) in THF (5 mL). The colour changes immediately from dark green to orange. After stirring for 15 minutes all volatiles were removed under reduced pressure. The residue was dissolved in \( \text{CH}_2\text{Cl}_2 \) (10 mL) and washed with water. The aqueous phase was extracted once with a small portion of \( \text{CH}_2\text{Cl}_2 \) then the combined organic phases were dried over Na\(_2\)SO\(_4\) and filtered. The solvent was removed under reduced pressure and the residue dissolved in THF, then hexane was added. An oily dark orange precipitate formed which was isolated by decantation and dried under high vacuum. While drying, the product solidified and was obtained as dark orange powder. Yield: 329 mg (94%).

\(^1\text{H}-\text{NMR} \) (500.23 MHz, CDCl\(_3\), 298 K): \( \delta = 0.99 \) (\( t, 3^J_{\text{HH}} = 7.3 \text{ Hz} \), 9H, \( \text{CH}_3 \)), 1.44 (m, 6H, \( \text{CH}_2\text{CH}_3 \)), 1.71 (m, 6H, \( \text{CH}_2\text{CH}_2\text{CH}_3 \)), 2.75 (\( t, 3^J_{\text{HH}} = 7.7 \text{ Hz} \), 6H, \( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)), 4.89 (d, \( J = 9.2 \text{ Hz} \), 2H, \( \text{CH}^{\text{olefin}} \)), 5.01 (d, \( J = 8.0 \text{ Hz} \), 2H, \( \text{CH}^{\text{benzyl}} \)), 5.52 (m, 3H, \( \text{CH}^{\text{olefin}} \), \( \text{NH} \)), 6.78 (m, 4H, \( \text{CH}^{\text{ar, trop}} \)), 6.91 (m, 4H, \( \text{CH}^{\text{ar, trop}} \)), 7.14 (d, \( J = 6.9 \text{ Hz} \), 2H, \( \text{CH}^{\text{ar, trop}} \)), 7.23 (m, 4H, \( \text{CH}^{\text{ar, trop}} \)), 7.35 (d, \( J = 7.6 \text{ Hz} \), 2H, \( \text{CH}^{\text{ar, trop}} \)), 7.39 (d, \( 3^J_{\text{HH}} = 6.4 \text{ Hz} \), 6H, \( \text{CH}^{\text{ar, phosphane}} \)), 7.74 (m, 6H, \( \text{CH}^{\text{ar, phosphane}} \)).

\(^{13}\text{C}\{\text{^1\text{H}}\}\text{-NMR} \) (125.78 MHz, CDCl\(_3\), 298 K): \( \delta = 14.4 \) (s, 3C, \( \text{CH}_3 \)), 22.8 (s, 3C, \( \text{CH}_2\text{CH}_3 \)), 33.7 (s, 3C, \( \text{CH}_2\text{CH}_2\text{CH}_3 \)), 35.9 (s, 3C, \( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)), 72.9 (s, 2C, \( \text{CH}^{\text{benzil}} \)), 74.8 (m, 4C, \( \text{CH}^{\text{olefin}} \)), 120.3 (q, \( 1^J_{\text{PC}} = 319.1 \text{ Hz} \), 1C, \( \text{CF}_3 \)), 126.3 (d, \( 1^J_{\text{PC}} = 48.7 \text{ Hz} \), 3C, \( \text{C}^{\text{quat, phosphane}} \)), 126.7 (s, 2C, \( \text{CH}^{\text{ar, trop}} \)), 126.7 (s, 2C, \( \text{CH}^{\text{ar, trop}} \)), 126.9 (s, 2C, \( \text{CH}^{\text{ar, trop}} \)), 127.8 (s, 2C, \( \text{CH}^{\text{ar, trop}} \)), 128.5 (s, 2C, \( \text{CH}^{\text{ar, trop}} \)), 128.7 (s, 2C, \( \text{CH}^{\text{ar, trop}} \)), 129.1 (d, \( 1^J_{\text{PC}} = 10.3 \text{ Hz} \), 6C, \( \text{CH}^{\text{ar, phosphane}} \)), 129.9 (s, 2C, \( \text{CH}^{\text{ar, trop}} \)), 130.2 (s, 2C, \( \text{CH}^{\text{ar, trop}} \)), 134.9 (d, \( 2^J_{\text{PC}} = 9.4 \text{ Hz} \), 6C, \( \text{CH}^{\text{ar, phosphane}} \)), 135.1 (s, 2C, \( \text{C}^{\text{quat, trop}} \)), 135.1 (s, 2C, \( \text{C}^{\text{quat, phosphane}} \)), 136.1 (d, \( J = 1.9 \text{ Hz} \), 2C, \( \text{C}^{\text{quat, phosphane}} \)), 137.7 (s, 2C, \( \text{C}^{\text{quat, phosphane}} \)), 146.7 (d, \( 4^J_{\text{PC}} = 2.4 \text{ Hz} \), 3C, \( \text{C}^{\text{quat, phosphane}} \)).
$^{19}\text{F-NMR (188.31 MHz, CDCl}_3, 298 \text{ K)}: \delta = -78.0 \text{ (s).}$

$^{31}\text{P}\{^1\text{H}\}-\text{NMR (202.50 MHz, CDCl}_3, 298 \text{ K)} \delta = 38.7 \text{ (d, } ^1J_{\text{RhP}} = 136.5 \text{ Hz).}$

$^1\text{H}, ^{103}\text{Rh-NMR (15.81 MHz, CDCl}_3, 298 \text{ K)}: \delta = -6808 \text{ (d, } ^1J_{\text{PRh}} = 136.5 \text{ Hz).}$

ATR IR (ν in cm$^{-1}$): 2951 (w), 2927 (m), 1599 (m), 1561 (w), 1492 (m), 1466 (m), 1402 (m), 1377 (w), 1290 (m), 1277 (w), 1259 (w), 1224 (s), 1189 (w), 1157 (s), 1091 (m), 1023 (s), 977 (w), 938 (w), 884 (w), 824 (m), 809 (w), 778 (w), 748 (s), 729 (w), 698 (w), 662 (m), 631 (s).
[RhH(trop2NH)(P(p-BuPh)3)] (87)

MF = C60H63NPRh

MW = 932.03 g/mol

Air stable

A solution of [Rh(trop2N)(P(p-BuPh)3)] 86 (10 mg, 11 µmol, 1 eq.) in [D8]-THF (0.5 mL) was put in a Young-NMR tube and degassed by 3 pump freeze thaw cycles. Hydrogen was filled in the evacuated Young-NMR tube and the formed hydride complex was analysed in-situ by NMR.

1H-NMR (500.23 MHz, [D8]THF, 298 K): δ = -8.19 (t, 1J_RhH = 23.5 Hz, RhH), 1.00 (t, 3J_HH = 7.2 Hz, 9H, CH2CH2CH2CH3), 1.45 (m, 6H, CH2CH2CH2CH3), 1.71 (m, 6H, CH2CH2CH2CH3), 2.73 (t, 3J_HH = 7.1 Hz, 6H, CH2CH2CH2CH3), 3.62 (d, J = 8.3 Hz, 2H, CHolefin), 3.94 (m, 2H, CHolefin), 4.51 (d, J = 7.3 Hz, 2H, CH_benzyl), 5.03 (s, 1H, NH), 6.35 (d, J = 7.6 Hz, 2H, CHar^tr, trop), 6.56 (t, J = 7.0 Hz, 2H, CHar^tr, trop), 6.62 (m, 4H, CHar^tr, trop), 6.90 (t, J = 7.2 Hz, 2H, CHar^tr, trop), 7.05 (m, 4H, CHar^tr, trop), 7.12 (d, J = 7.1 Hz, 2H, CHar^tr, trop), 7.31 (d, J = 7.3 Hz, 6H, CHar^tr, phosphane), 7.75 (t, J = 8.7 Hz, 6H, CHar^tr, phosphane).

13C{1H}-NMR (125.78 MHz, [D8]THF, 298 K): δ = 13.7 (s, 3C, CH2CH2CH2CH3), 22.8 (s, 3C, CH2CH2CH2CH3), 33.8 (s, 3C, CH2CH2CH2CH3), 35.7 (s, 3C, CH2CH2CH2CH3), 57.2 (d, J = 8.2 Hz, 2C, CHolefin), 60.3 (d, J = 8.9 Hz, 2C, CHolefin), 72.5 (s, 2C, CH_benzyl), 121.4 (s, 2C, CHar^tr, trop), 123.5 (s, 2C, CHar^tr, trop), 126.8 (s, 2C, CHar^tr, trop), 127.4 (s, 2C, CHar^tr, trop), 127.5 (s, 2C, CHar^tr, trop), 127.8 (s, 2C, CHar^tr, trop), 128.0 (d, 2J_PC = 10.1 Hz, 6C, CHar^tr, phosphane), 128.1 (s, 2C, CHar^tr, trop), 129.5 (s, 2C, CHar^tr, trop), 131.7 (d, 1J_PC = 48.9 Hz, 3C, C^quat, phosphane), 132.2 (s, 2C, C^quat, trop), 134.3 (d, 2J_PC = 10.1 Hz, 6C, CHar^tr, phosphane), 137.2 (s, 2C, C^quat, trop), 137.9 (s, 2C, C^quat, trop), 143.8 (s, 2C, C^quat, trop), 144.7 (d, 1J_PC = 2.2 Hz, 3C, C^quat, phosphane).

31P{1H}-NMR (202.50 MHz, [D8]THF, 298 K) δ = 62.1 (d, 1J_RhP = 144.2 Hz).

1H, 103Rh-NMR (15.81 MHz, [D8]THF, 298 K): δ = -8470 (dd, 1J_Rh = 144.2 Hz, d, 1J_HRh = 23.5 Hz).
[Rh(OAc)(trop2NH)(P(p-BuPh)3)] (89)

MF = C62H65NO2Prh

MW = 990.06 g/mol

MP = 88-90 °C

Air stable

To a solution of [Rh(trop2N)(P(n-BuPh)3)] 86 (65 mg, 0.070 mmol, 1 eq.) in THF (3 mL) a solution of acetic acid (2.5%vol in THF, 0.160 mL, 0.070 mmol, 1 eq.) was added. The green solution turned yellow immediately then all volatiles were removed under reduced pressure and the residue dried under high vacuum. Yield: 66 mg, 95%.

1H-NMR (500.23 MHz, CDCl3, 298 K): δ = 1.00 (t, 3JHH = 7.3 Hz, 9H, CH2CH2CH2CH3), 1.44 (m, 6H, CH2CH2C2H5), 1.70 (m, 6H, CH2CH2CH2CH3), 1.74 (s, 3H, CO2CH3), 2.74 (t, 3JHH = 7.7 Hz, 6H, CH2CH2CH2CH3), 4.77 (m, 4H, CHolefin, CHbenzyl), 4.88 (d, J = 9.4 Hz, 2H, CHolefin), 6.58 (d, J = 7.6 Hz, 2H, CHar, trop), 6.70 (m, 2H, CHar, trop), 7.11 (m, 6H, CHar, trop), 7.20 (d, J = 7.1 Hz, 2H, CHar, trop), 7.34 (d, J = 7.1 Hz, 6H, CHar, phosphane), 7.78 (t, J = 8.8 Hz, 6H, CHar, phosphane), 9.83 (s, 1H, NH).

13C{1H}-NMR (125.78 MHz, CDCl3, 298 K): δ = 14.4 (s, 3C, CH2CH2CH2CH3), 22.8 (s, 3C, CH2CH2CH2CH3), 23.4 (s, 1C, CO2CH3), 33.7 (s, 3C, CH2CH2CH2CH3), 36.0 (s, 3C, CH2CH2CH2CH3), 67.9 (d, J = 12.7 Hz, 2C, CHolefin), 69.9 (d, J = 6.2 Hz, 2C, CHolefin), 72.6 (s, 2C, CHbenzyl), 125.4 (s, 2C, CHar, trop), 125.9 (s, 2C, CHar, trop), 127.3 (s, 2C, CHar, trop), 127.8 (d, JPC = 48.7 Hz, 3C, Cquat, phosphane), 127.9 (s, 2C, CHar, trop), 128.1 (s, 2C, CHar, trop), 128.2 (s, 2C, CHar, trop), 128.6 (d, 3JPC = 10.1 Hz, 6C, CHar, phosphane), 128.6 (s, 2C, CHar, trop), 129.6 (s, 2C, CHar, trop), 134.9 (d, 2JPC = 9.1 Hz, 6C, CHar, phosphane), 135.4 (s, 2C, Cquat, trop), 136.2 (d, J = 0.7 Hz, 2C, Cquat, trop), 136.3 (s, 2C, Cquat, trop), 139.5 (s, 2C, Cquat, trop), 145.9 (d, 4JPC = 2.4 Hz, 3C, Cquat, phosphane), 177.3 (s, 1C, CO2CH3).

31P{1H}-NMR (202.50 MHz, CDCl3, 298 K) δ = 37.8 (d, 1JRhP = 132.0 Hz).

1H, 103Rh-NMR (15.81 MHz, CDCl3, 298 K) δ = -6819 (d, 1JRhP = 132.0 Hz).

ATR IR (v in cm⁻¹): 3013 (w), 2051 (w), 2926 (w), 2858 (w), 1707 (w), 1599 (w), 1552 (m), 1491 (m), 1466 (w), 1400 (m), 1315 (w), 1257 (w), 1190 (m), 1158 (w), 1091 (m), 1044 (w), 1016 (w), 990 (m), 935 (w), 884 (w), 826 (m), 780 (w) 745 (s), 654 (m), 620 (w).
[Rh(OH)(trop₂NH)(P(ρ-BuPh)₃)] (88)

MF = C₆₀H₆₃NOPRh

MW = 948.03 g/mol

Air stable

To a solution of [Rh(trop₂N)(P(n-BuPh)₃)] (86) (10 mg, 11 μmol, 1 eq.) in [D₈]THF (0.5 mL) a drop of water (approximately 65 eq.) was added. The colour changes immediately from dark green to yellow and the formed hydroxide complex was analysed in-situ by NMR.

¹H-NMR (500.23 MHz, [D₈]THF, 238 K): δ = 0.99 (t, 3J_HH = 7.2 Hz, 9H, CH₂CH₂CH₂CH₃), 1.44 (m, 6H, CH₂CH₂CH₂CH₃), 1.69 (m, 6H, CH₂CH₂CH₂CH₃), 2.74 (t, 3J_HH = 7.1 Hz, 6H, CH₂CH₂CH₂CH₃), 4.55 (d, J = 8.3 Hz, 2H, CḦ_olefin), 4.60 (d, J = 9.1 Hz, 2H, CḦ_olefin), 4.99 (d, J = 8.9 Hz, 2H, CḦ_benzyl), 6.59 (d, J = 7.3 Hz, 2H, CḦ_ar, trop), 6.66 (t, J = 7.2 Hz, 2H, CḦ_ar, trop), 6.74 (t, J = 7.0 Hz, 2H, CḦ_ar, trop), 6.88 (d, J = 7.3 Hz, 2H, CḦ_ar, trop), 7.07 (t, J = 7.4 Hz, 2H, CḦ_ar, trop), 7.11 (d, J = 7.3 Hz, 2H, CḦ_ar, trop), 7.18 (d, J = 6.9 Hz, 2H, CḦ_ar, trop), 7.33 (d, J = 7.3 Hz, 2H, CḦ_ar, trop), 7.44 (d, J = 6.9 Hz, 2H, CḦ_ar, phosphane), 7.87 (t, J = 8.0 Hz, 6H, CḦ_ar, phosphane). (The OH- and NH-protons undergo a fast exchange with the excess water (3.50 (s)).

¹³C{¹H}-NMR (125.78 MHz, [D₈]THF, 238 K): δ = 14.1 (s, 3C, CH₂CH₂CH₂CH₃), 23.1 (s, 3C, CH₂CH₂CH₂CH₃), 34.4 (s, 3C, CH₂CH₂CH₂CH₃), 35.9 (s, 3C, CH₂CH₂CH₂CH₃), 63.3 (d, J = 9.8 Hz, 2C, CḦ_olefin), 66.4 (m, 2C, CḦ_olefin), 70.9 (d, J = 1.2 Hz, 2C, CḦ_benzyl), 124.5 (s, 2C, CḦ_ar, trop), 125.0 (s, 2C, CḦ_ar, trop), 127.6 (s, 2C, CḦ_ar, trop), 127.8 (s, 2C, CḦ_ar, trop), 128.0 (s, 2C, CḦ_ar, trop), 128.3 (s, 2C, CḦ_ar, trop), 128.5 (m, 3C, C̈_quat, phosphane), 128.7 (d, 3J_PC = 9.8 Hz, 6C, CḦ_ar, phosphane), 129.1 (s, 2C, CḦ_ar, trop), 129.7 (s, 2C, CḦ_ar, trop) 135.0 (d, 2J_PC = 8.9 Hz, 6C, CḦ_ar, phosphane), 135.1 (s, 2C, C̈_quat, trop), 136.4 (s, 2C, C̈_quat, trop), 137.1 (s, 2C, C̈_quat, trop), 140.2 (s, 2C, C̈_quat, trop), 145.7 (d, 4J_PC = 1.7 Hz, 3C, C̈_quat, phosphane).

³¹P{¹H}-NMR (202.50 MHz, [D₈]THF, 238 K) δ = 40.1 (d, 1J_RhP = 133.5 Hz).

¹H, ¹⁰³ Rh-NMR (15.81 MHz, [D₈]THF, 238 K): δ = -7050 (d, 1J_Rh = 133.5 Hz).
7.6 Compounds synthesised for chapters 4, 5 and 6

[Rh(trop2N)(TMIY)] (95)

MF = C_{37}H_{35}N_{3}Rh

MW = 624.60 g/mol

MP = >220 °C (decomposition)

Slightly air sensitive

To a suspension of [RhCl(TMIY)(trop2NH)] (100 mg, 160 µmol, 1 eq.) in THF (10 mL) t-BuOK (90 mg, 0.8 mmol, 5 eq.) was added. After stirring the reaction mixture for 5 minutes, water (10 mL) and KOH (1 g) were added. The two-phasic mixture was stirred for another hour then the aqueous phase was separated off. From the organic phase all volatiles were removed under reduced pressure and the residue dried under high vacuum overnight. Yield: 91 mg, 91%. Crystals suitable for X-ray analysis were grown from a solution of 95 in wet THF and slow vacuum application. After a few hours an oily material was obtained, which after standing for 24h in a closed schlenk tube, produced suitable crystals.

$^1$H-NMR (400.13 MHz, [D8]THF, 200 K): $\delta = 2.21$ (s, 3H, CH$_3$), 2.26 (s, 3H, CH$_3$), 3.52 (s, 3H, CH$_3$), 3.95 (s, 3H, CH$_3$), 4.77 (s, 2H, CH$_2^{\text{benzyl}}$), 4.78 (d, $^3$J$_{HH} = 8.2$ Hz, 2H, CH$_2^{\text{olefin}}$), 6.02 (d, $^3$J$_{HH} = 8.2$ Hz, 2H, CH$_2^{\text{olefin}}$), 6.60 (t, $^3$J$_{HH} = 7.2$ Hz, 2H, CH$_2^{\text{ar}}$), 6.68 (t, $^3$J$_{HH} = 7.0$ Hz, 2H, CH$_2^{\text{ar}}$), 6.89 (d, $^3$J$_{HH} = 7.3$ Hz, 2H, CH$_2^{\text{ar}}$), 6.92-7.03 (m, 6H, CH$_2^{\text{ar}}$), 7.16 (br s, 4H, CH$_2^{\text{ar}}$).

$^{13}$C{$^1$H}-NMR (100.61 MHz, [D8]THF, 200 K): $\delta = 8.3$ (s, 1C, CH$_3$), 8.6 (s, 1C, CH$_3$), 34.2 (s, 1C, CH$_3$), 34.9 (s, 1C, CH$_3$), 75.7 (br s, 2C, CH$_2^{\text{olefin}}$), 81.3 (br s, 2C, CH$_2^{\text{benzyl}}$), 81.3 (br s, 2C, CH$_2^{\text{olefin}}$), 124.4 (s, 2C, CH$_2^{\text{ar}}$), 124.8 (s, 2C, CH$_2^{\text{ar}}$), 124.9 (s, 2C, CH$_2^{\text{ar}}$), 125.2 (s, 2C, C$_{\text{quat}}$), 125.5 (s, 2C, CH$_2^{\text{ar}}$), 125.7 (s, 2C, CH$_2^{\text{ar}}$), 126.8 (s, 2C, CH$_2^{\text{ar}}$), 127.0 (s, 2C, CH$_2^{\text{ar}}$), 128.3 (s, 2C, CH$_2^{\text{ar}}$), 138.0 (s, 2C, C$_{\text{quat}}$), 138.7 (s, 2C, C$_{\text{quat}}$), 144.6 (s, 2C, C$_{\text{quat}}$), 147.2 (s, 2C, C$_{\text{quat}}$), 179.3 (d, J not resolved, C$_{\text{quat}}$).

$^1$H, $^{103}$Rh-NMR (12.64 MHz, [D8]THF, 200 K): $\delta = -6969$ (s).

ATR IR (v in cm$^{-1}$): 3587 (w), 3003 (w), 2914 (w), 2852 (w), 1656 (w), 1596 (w), 1489 (w), 1427 (br), 1367 (w), 1297 (w), 1251 (w), 1217 (w), 1184 (w), 1155 (w), 1142 (w), 1124 (w), 1082 (w), 1041 (w), 1026 (w), 976 (w), 931 (w), 878 (m), 845 (w), 817 (w), 743 (s), 690 (m), 657 (w), 640 (m).
[\text{RhH}(\text{trop}_2\text{NH})(\text{TMIY})] (94)

\text{MF} = C_{37}H_{37}N_3\text{Rh}

\text{MW} = 624.60 \text{ g/mol}

\text{MP} = >220 ^\circ \text{C (decomposition)}

Air sensitive

The hydride was prepared \textit{in-situ} in a young-NMR tube in [D6]DMSO. LiHDMS (2.3 mg, 0.014 mmol, 1.05 eq.) was added to a solution of [\text{Rh}(\text{trop}_2\text{NH})(\text{TMIY})]\text{OTf} 8 (10 mg, 0.013 mmol, 1 eq.) in [D6]DMSO (0.5 mL). The resulting dark green solution was degassed by 3 pump freeze thaw cycles then the NMR tube was repeatedly filled with hydrogen gas (2 bar) and shacked until a yellow solution was obtained.

$^1\text{H}$-NMR (300.13 MHz, [D6]DMSO, 298 K): $\delta = -6.30$ (d, $^1J_{\text{RhH}} = 34.8$ Hz, 1H, RhH), 2.01 (s, 3H, CH$_3$), 2.05 (s, 3H, CH$_3$), 3.29 (d, $J = 9.0$ Hz, 2H, CH$^\text{olefin}$), 3.79 (d, $J = 9.0$ Hz, 2H, CH$^\text{olefin}$), 3.81 (s, 3H, CH$_3$), 4.19 (s, 3H, CH$_3$), 4.38 (s, 2H, CH$^\text{benzyl}$), 6.60-6.68 (m, 8H, CH$^\text{ar}$), 6.81-6.86 (m, 2H, CH$^\text{ar}$), 6.90-6.93 (m, 2H, CH$^\text{ar}$), 6.99-7.07 (m, 2H, CH$^\text{ar}$), 7.18-7.21 (m, 2H, CH$^\text{ar}$).

$^{13}\text{C}\{^1\text{H}\}$-NMR (75.48 MHz, [D6]DMSO, 298 K): $\delta = 9.7$ (s, 1C, CH$_3$), 10.3 (s, 1C, CH$_3$), 36.2 (s, 1C, CH$_3$), 38.2 (s, 1C, CH$_3$), 52.3 (d, $J = 8.7$ Hz, 2C, CH$^\text{olefin}$), 54.1 (, $J = 7.9$ Hz, 2C, CH$^\text{olefin}$), 71.1 (s, 2C, CH$^\text{benzyl}$), 119.2 (s, 2C, CH$^\text{ar}$), 123.1 (s, 2C, CH$^\text{ar}$), 124.8 (s, 1C, C$^\text{quat}$), 125.1 (s, 1C, C$^\text{quat}$), 125.2 (s, 2C, CH$^\text{ar}$), 126.2 (s, 2C, CH$^\text{ar}$), 127.6 (s, 2C, CH$^\text{ar}$), 128.4 (s, 2C, CH$^\text{ar}$), 130.2 (s, 2C, CH$^\text{ar}$), 130.8 (s, 2C, C$^\text{quat}$), 137.3 (s, 2C, C$^\text{quat}$), 138.8 (s, 2C, C$^\text{quat}$), 145.3 (s, 2C, C$^\text{quat}$), 171.7 (d, $^1J_{\text{RhC}} = 51.2$ Hz, 1C, C$^\text{quat}$).

$^1\text{H}$, $^{103}\text{Rh}$-NMR (12.64 MHz, [D6]DMSO, 298 K): $\delta = -7937$ (d, $^1J_{\text{HRh}} = 34.8$ Hz).
[Rh(OH)(TMIY)(trop₂NH)] (96)

MF = C₃₇H₇₇N₃Rh

MW = 624.60 g/mol

MP = >220 °C (decomposition)

Air stable

H₂O (0.16 mL, 9 mmol, 600 eq.) was added to a suspension of [Rh(TMIY)(trop₂N)] 94 (10 mg, 0.015 mmol, 1 eq.) in [D₈]THF (0.5 mL). A yellow solution was immediately obtained.

¹H-NMR (500.23 MHz, [D₈]THF, 298 K): δ = 2.24 (s, 3H, CH₃), 2.30 (s, 3H, CH₃), 3.85 (s, 3H, CH₃), 4.12 (s, 3H, CH₃), 4.99 (d, J = 7.8 Hz, 2H, CH olefin), 5.31 (s, 2H, CH benzyl), 6.18 (br, 2H, CH olefin), 6.87 (t, J = 6.9 Hz, 2H, CH₈), 6.96 (t, J = 7.3 Hz, 2H, CH₈), 7.14 (d, J = 6.9 Hz, 2H, CH₈), 7.22 (m, 6H, CH₈), 7.36 (d, J = 5.7 Hz, 2H, CH₈), 7.44 (d, J = 5.5 Hz, 2H, CH₈). The OH- and NH-protons undergo a fast exchange with the excess water (3.50 (s))

¹³C{¹H}-NMR (125.78 MHz, [D₈]THF, 298 K): δ = 8.3 (s, 1C, CH₃), 8.8 (s, 1C, CH₃), 34.5 (s, 1C, CH₃), 35.4 (s, 1C, CH₃), 71.6 (s, 2C, CH benzyl), 76.6 (br, 2C, CH olefin), 80.2 (s, 2C, CH olefin), 126.3 (s, 2C, CH₈), 126.6 (s, 2C, CH₈), 126.8 (s, 1C, C quat), 126.9 (s, 1C, C quat), 127.1 (s, 2C, CH₈), 128.3 (s, 2C, CH₈), 128.5 (s, 4C, CH₈), 128.8 (s, 2C, CH₈), 130.9 (s, 2C, CH₈), 135.7 (s, 2C, C quat), 136.2 (s, 2C, C quat), 137.8 (s, 2C, C quat), 138.5 (s, 2C, C quat) 163.9 (d, 1JRbC = 48.2 Hz, 1C, C quat).

¹H, ¹⁰³Rh-NMR (15.81 MHz, [D₈]THF, 298 K): δ = -6730 (s).
\[ \text{[Rh(trop_2N)(eq-PPh_3)(ax-PhN=N(O)Ph)] (97)} \]

**MF = C_{60}H_{48}N_3OPRh**

**MW = 960.92 g/mol**

**MP = 74-76°C (decomposition)**

Air stable

To a solution of \([\text{RhCl(PPh}_3\text{(trop}_2\text{NH)}\text{)}]_6\) (100 mg, 0.125 mmol, 1 eq.) in THF (2 mL) and toluene (1 mL) \(\text{t-BuOK}\) (14 mg, 0.125 mmol, 1 eq.) was added. The reaction mixture was stirred for 30 minutes then all volatiles were removed under reduced pressure. Toluene (1 mL) was added to the residue and removed again under reduced pressure. The residue was dissolved in THF and filtrated then azoxybenzene (26 mg, 0.132 mmol, 1.05 eq.) was added. The resulting solution was stirred overnight then the solvent was removed in vacuum. Yield: 101 mg, 84%.

\(^1\)H-NMR (400.13 MHz, [D\(_8\)]THF, 273 K): \(\delta = 0.86\) (s, 1H, N\(\text{H}\)), 4.06 (s, 2H, CH\(_{\text{benzyl}}\)), 4.80 (dd, \(J = 9.2\) Hz, \(J = 5.0\) Hz, 2H, CH\(_{\text{olefin}}\)), 4.92 (t, \(J = 7.4\) Hz, 2H, CH\(_{\text{olefin}}\)), 5.49 (t, \(J = 7.60\) Hz, 2H, CH\(_{\text{ar}}\)), 6.42 (d, \(J = 7.5\) Hz, 2H, CH\(_{\text{ar}}\)), 6.56 (d, \(J = 7.3\) Hz, 2H, CH\(_{\text{ar}}\)), 6.67-6.73 (m, 4H, CH\(_{\text{ar}}\)), 6.75-6.81 (m, 4H, CH\(_{\text{ar}}\)), 6.86 (t, \(J = 7.4\) Hz, 1H, CH\(_{\text{ar}}\)), 6.94 (t, \(J = 7.3\) Hz, 2H, CH\(_{\text{ar}}\)), 7.05 (d, \(J = 7.6\) Hz, 2H, CH\(_{\text{ar}}\)), 7.15 (t, \(J = 7.3\) Hz, 1H, CH\(_{\text{ar}}\)), 7.30-7.37 (m, 6H, CH\(_{\text{ar}}\)), 7.45 (t, \(J = 7.4\) Hz, 1H, CH\(_{\text{ar}}\)), 7.53 (t, \(J = 7.7\) Hz, 3H, CH\(_{\text{ar}}\)), 7.59-7.65 (m, 2H, CH\(_{\text{ar}}\)), 8.28 (d, \(J = 7.9\) Hz, 2H, CH\(_{\text{ar}}\)), 8.33-8.39 (m, 6H, CH\(_{\text{ar}}\)).

\(^{13}\)C\(_{\{^1\}H}\)-NMR (100.61 MHz, [D\(_8\)]THF, 273 K): \(\delta = 67.6-67.7\) (m, 1C, CH\(_{\text{olefin}}\)), 70.0 (dd, \(J = 17.6\) Hz, \(J = 10.3\) Hz, 2C, CH\(_{\text{olefin}}\)), 71.0 (s, 2C, CH\(_{\text{benzyl}}\)), 122.4 (s, 2C, CH\(_{\text{ar}}\)), 123.7 (d, \(J = 1.6\) Hz, 2C, CH\(_{\text{ar}}\)), 124.1 (s, 2C, CH\(_{\text{ar}}\)), 125.9 (s, 2C, CH\(_{\text{ar}}\)), 126.6 (s, 2C, CH\(_{\text{ar}}\)), 127.7 (d, \(J = 4.3\) Hz, 2C, CH\(_{\text{ar}}\)), 127.9-128.0 (m, 8C, CH\(_{\text{ar}}\)), 128.5 (s, 2C, CH\(_{\text{ar}}\)), 128.5-128.7 (m, 3C, CH\(_{\text{ar}}\)), 128.9 (s, 2C, CH\(_{\text{ar}}\)), 129.1-129.2 (m, 4C, CH\(_{\text{ar}}\)), 129.2 (s, 2C, CH\(_{\text{ar}}\)), 130.0 (s, 1C, CH\(_{\text{ar}}\)), 131.4 (d, \(J = 8.7\) Hz, 2C, CH\(_{\text{ar}}\)), 131.8 (d, \(J = 2.5\) Hz, 1C, C\(_{\text{quat, azoxybenzene}}\)), 132.0 (s, 1C, CH\(_{\text{ar}}\)), 132.2 (d, \(J_{PC} = 9.4\) Hz, 1C, C\(_{\text{quat, phosphane}}\)), 133.6 (d, \(J = 10.5\) Hz, 4C, CH\(_{\text{ar}}\)), 133.9 (d, \(J = 2.1\) Hz, 2C, C\(_{\text{quat, trop}}\)), 136.2 (s, 2C, C\(_{\text{quat, trop}}\)), 137.5 (d, \(J = 4.6\) Hz, 2C, C\(_{\text{quat, trop}}\)), 138.0 (d, \(J_{PC} = 24.7\) Hz, C\(_{\text{quat, phosphane}}\)), 142.0 (d, \(J = 4.1\) Hz, 2C, C\(_{\text{quat, trop}}\)), 144.5 (s, 1C, C\(_{\text{quat, azoxybenzene}}\)).

\(^{31}\)P\(_{\{^1\}H}\)-NMR (161.98 MHz, [D\(_8\)]THF, 273 K) \(\delta = 7.9\) (d, \(J_{\text{Rhp}} = 118.8\) Hz).

\(^1\)H, \(^{103}\)Rh-NMR (15.81 MHz, [D\(_8\)]THF, 273 K): \(\delta = -6508\) (d, \(J_{\text{Prh}} = 118.8\) Hz).
ATR IR (ν in cm⁻¹): 3199 (w), 3039 (w), 2953 (w), 1598 (w), 1569 (w), 1472 (m), 1435 (m), 1413 (w), 1396 (w), 1324 (w), 1300 (w), 1258 (w), 1216 (w), 1188 (w), 1159 (w), 1119 (w), 1088 (w), 1069 (m), 1025 (m), 999 (w), 971 (w), 925 (w), 906 (w), 859 (w), 810 (m), 763 (m), 745 (s), 698 (s), 684 (s), 618 (w).
[Rh(trop2NH)(PPh3)(ONHPh)] (98)

MF = C54H44N2OPRh

MW = 870.82 g/mol

MP = 170-175°C (decomposition)

Slightly air sensitive

To a solution of [Rh(trop2N)(PPh3)] 1 (42 mg, 55 μmol, 1 eq.) in THF (1 mL) N-phenyl hydroxylamine (6.3 mg, 58 μmol, 1.05 eq.) was added. After 15 minutes the orange precipitate was filtered off, washed with a small portion of Et2O (2 mL) and dried under high vacuum. Yield: 38 mg, 79%.

Alternative procedure: Hydrogen gas was bubbled through a solution of [Rh(trop2N)(PPh3)] 1 (84 mg, 0.11 mmol, 1 eq.) in THF (1 mL) until the colour of the solution changed from deep green to yellow and the 31P{1H}-NMR confirmed complete reaction to the hydride complex [RhH(trop2NH)(PPh3)] 2. To this solution nitrosobenzene (11.8 mg, 0.11 μmol, 1 eq.) was added and after 15 minutes the precipitate was filtered off, washed with a small portion of Et2O (2 mL) and dried under high vacuum. Yield: 25 mg, 26%.

1H-NMR (500.23 MHz, CDCl3, 298 K): δ = 4.59 (d, J = 6.4 Hz, 1H, NHtrop), 4.67 (d, J = 8.7 Hz, 2H, CH benzyl), 4.80 (d, J = 9.2 Hz, 2H, CHOlef), 4.87 (d, J = 9.4 Hz, 2H, CH olef), 6.64 (d, J = 7.3 Hz, 2H, CHar, trop), 6.75 (t, J = 7.33 Hz, 2H, CHar, trop), 6.77 (d, J = 8.3 Hz, 2H, CHar, trop), 6.83 (t, J = 7.1 Hz, 2H, CHar, trop), 7.07-7.10 (m, 2H, CHar, trop), 7.16 (d, J = 7.3 Hz, 2H, CHar, trop), 7.19-7.21 (m, 4H, CHar, trop), 7.56 (m, 13H, CHar, phosphane, CHar, PhNHO, NHPhNHO), 8.02 (br, 6H, CHar, phosphane), 8.20 (d, J = 7.6 Hz, 1H, CHar, PhNHO), 8.35 (d, J = 8.0 Hz, 1H, CHar, PhNHO).

13C{1H}-NMR (125.78 MHz, CDCl3, 298 K): δ = 67.4 (d, J = 12.0 Hz, 2C, CHOlef), 69.7 (d, J = 7.4 Hz, 2C, CHOlef), 73.0 (s, 2C, CH benzyl), 122.8 (s, 1C, CHar, PhNHO), 125.5 (s, 2C, CHar, trop), 125.9 (m, 3C, CHar, trop, CHar, PhNHO), 125.9 (s, 2C, CHar, trop), 127.4 (s, 2C, CHar, trop), 127.7 (s, 2C, CHar, trop), 128.5 (s, 2C, CChar, trop), 128.6 (s, 2C, CChar, trop), 128.7 (d, J = 9.6 Hz, 6C, CChar, phosphane), 129.1 (s, 1C, CChar, PhNHO), 129.2 (s, 1C, CChar, PhNHO), 129.5 (s, 2C, CChar, trop), 129.6 (s, 2C, CChar, trop), 130.0 (s, 1C, CChar, PhNHO), 130.9 (s, 3C, CChar, phosphane), 131.1 (d, JPC = 45.6 Hz, 3C, CChar, trop), 132.0 (s, 1C, CChar, trop), 134.6 (s, 2C, CChar, trop), 134.7 (s, 2C, CChar, trop), 135.1 (d, J = 8.9 Hz, 6C, CChar, phosphane) 136.4 (s, 2C, CChar, trop), 139.8 (s, 2C, CChar, trop).

31P{1H}-NMR (202.50 MHz, CDCl3, 298 K) δ = 43.1 (d, JRhP = 135.0 Hz).

1H, 103Rh-NMR (15.81 MHz, CDCl3, 298 K): δ = -7147 (d, JPhRh = 135.0 Hz).

ATR IR (v in cm⁻¹): 3147 (w), 3044 (w), 2848 (w), 1719 (w), 1636 (w), 159 (w), 1474 (m), 1435 (m), 1403 (w), 1341 (w), 1297 (w), 1258 (w), 1223 (w), 1186 (w), 1157 (w), 1114 (w),
1092 (m), 1064 (w), 1042 (w), 1024 (w), 998 (w), 984 (m), 936 (w), 887 (w), 879 (w), 856 (w), 840 (w), 825 (w), 801 (w), 742 (s), 714 (w), 699 (s) 683 (s), 618 (m).
8 Appendix
8.1 List of abbreviation

acac acetylacetonate
ADAFC alkaline direct alcohol fuel cell
AIBN 2,2'-(diazene-1,2-diyl)bis(2-methylpropanenitrile)
Ar aryl
ATR attenuated total reflection
Boc \( t \)-butyloxycarbonyl
BSE back-scattered electrons
Bu \( n \)-butyl
t ct centroid
Cv Vulcan XC-72
CV cyclic voltammetry
COD cyclooctadiene
DCM dichloromethane
DIPEA \( N \)-ethyl-\( N,N \)-diisopropylamine
DME dimethoxyethane
DMF dimethyl formamide
DMSO dimethyl sulfoxide
dppe 1,2-bis(diphenylphosphino)ethane
EA elemental analysis
EBFC enzymatic bio fuel cell
EDXS energy-dispersive X-ray spectroscopy
Eq. equation
eq equivalent
ESI electronspray-ionisation
Et ethyl
GC gas chromatography
HAADF high-angle annular dark field detector
HMDS hexamethyldisilazide
\( i \)-Pr \( i \)-propyl
IR infra-red
LDA lithium diisopropylamide
MALDI matrix-assisted laser desorption/ionization
<table>
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<th>Abbreviation</th>
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<td>Me</td>
<td>methyl</td>
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<tr>
<td>MEA</td>
<td>membrane electrode assembly</td>
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<tr>
<td>MF</td>
<td>molecular formula</td>
</tr>
<tr>
<td>MMA</td>
<td>methyl methacrylate</td>
</tr>
<tr>
<td>MOM</td>
<td>methoxymethyl ether</td>
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<tr>
<td>MP</td>
<td>melting point</td>
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<tr>
<td>MS</td>
<td>mass spectrometry</td>
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<tr>
<td>MW</td>
<td>molecular weight</td>
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<tr>
<td>NBS</td>
<td>N-bromosuccinimide</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>OAc</td>
<td>acetate</td>
</tr>
<tr>
<td>OMFC</td>
<td>organometallic fuel cell</td>
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<td>phenyl</td>
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<td>n-propyl</td>
</tr>
<tr>
<td>py</td>
<td>pyridine</td>
</tr>
<tr>
<td>RHE</td>
<td>reversible hydrogen electrode</td>
</tr>
<tr>
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<td>ratio of substrate to catalyst</td>
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<td>secondary electrons</td>
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<td>scanning electron microscopy</td>
</tr>
<tr>
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<td>scanning transmission electron microscopy</td>
</tr>
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<td>T</td>
<td>temperature</td>
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<td>t-butyl</td>
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<tr>
<td>TBAF</td>
<td>tetrabutyl ammonium fluoride</td>
</tr>
<tr>
<td>Tf</td>
<td>CF$_3$SO$_2$</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMIY</td>
<td>1,3,4,5-tetramethylimidazole-2-ylidene</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilyl</td>
</tr>
<tr>
<td>TOF$_{50}$</td>
<td>turnover frequency at 50% conversion</td>
</tr>
<tr>
<td>TON</td>
<td>turnover number</td>
</tr>
<tr>
<td>TPP</td>
<td>1,2,5-triphenylphophole</td>
</tr>
<tr>
<td>trop</td>
<td>5-H-dibenzo[a,d]cyclohepten-5-yl</td>
</tr>
<tr>
<td>Ts</td>
<td>tosyl</td>
</tr>
</tbody>
</table>
XPS  X-ray photoelectron spectroscopy
Z. P. E.  zero point energy
## 8.2 Crystallographic data

Crystallographic data and structure refinement for [Rh(tropNHCH₂StilbPPh₂)]OTf (5)

<table>
<thead>
<tr>
<th>Identification code</th>
<th>[Rh(tropNHCH₂StilbPPh₂)]OTf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₄₃H₃₄F₃NO₃PRhS</td>
</tr>
<tr>
<td>Formula weight</td>
<td>835.68 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>100 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/c</td>
</tr>
<tr>
<td>Unit cell dimension</td>
<td>a = 13.9885(8) Å  (\alpha = 90^\circ)</td>
</tr>
<tr>
<td></td>
<td>b = 15.0054(9) Å  (\beta = 102.072(1)^\circ)</td>
</tr>
<tr>
<td></td>
<td>c = 15.0054(11) Å (\gamma = 90^\circ)</td>
</tr>
<tr>
<td>Volume</td>
<td>3963.2(4) Å(^3)</td>
</tr>
<tr>
<td>Cell formula units Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.458 g/cm(^3)</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.58 mm(^{-1})</td>
</tr>
<tr>
<td>F(000)</td>
<td>1792.0</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.09 mm × 0.05 mm × 0.05 mm</td>
</tr>
<tr>
<td>Data collection</td>
<td>Bruker SMART Apex</td>
</tr>
<tr>
<td></td>
<td>with CCD detector</td>
</tr>
<tr>
<td></td>
<td>Mo K(\alpha), graphite monochromator</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>20 = 56.73°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-18 ≤ h ≤ 18</td>
</tr>
<tr>
<td></td>
<td>-20 ≤ k ≤ 20</td>
</tr>
<tr>
<td></td>
<td>-25 ≤ l ≤ 25</td>
</tr>
<tr>
<td>Reflection collected</td>
<td>41652</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>9895 [R(int) = 0.0649]</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F(^2)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>9895 / 0 / 590</td>
</tr>
<tr>
<td>Goodness-of-fit on F(^2)</td>
<td>1.168</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0689, wR2 = 0.1445</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0865, wR2 = 0.1517</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.42 and -0.79e.Å(^3)</td>
</tr>
<tr>
<td>Operator</td>
<td>Matthias Vogt</td>
</tr>
<tr>
<td>Crystallographic data and structure refinement for [Rh(eq-OAc)(trop2NH)(PPh3)] (7)</td>
<td></td>
</tr>
<tr>
<td>--------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td><strong>Identification code</strong></td>
<td>[Rh(eq-OAc)(trop2NH)(PPh3)]</td>
</tr>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C₅₀H₄₁NO₂PRh</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>821.20 g/mol</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>250 K</td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
<td>0.71073 Å</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P₁</td>
</tr>
<tr>
<td><strong>Unit cell dimension</strong></td>
<td></td>
</tr>
<tr>
<td>a = 11.189(2) Å</td>
<td>α = 97.77(3)°</td>
</tr>
<tr>
<td>b = 13.369(3) Å</td>
<td>β = 93.26(3)°</td>
</tr>
<tr>
<td>c = 13.548(3) Å</td>
<td>γ = 103.67(3)°</td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td>1942.7(7) Å³</td>
</tr>
<tr>
<td><strong>Cell formula units Z</strong></td>
<td>2</td>
</tr>
<tr>
<td><strong>Density (calculated)</strong></td>
<td>1.405 g/cm³</td>
</tr>
<tr>
<td><strong>Absorption coefficient</strong></td>
<td>0.52 mm⁻¹</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>848.0</td>
</tr>
<tr>
<td><strong>Crystal size</strong></td>
<td>0.19 mm × 0.10 mm × 0.60 mm</td>
</tr>
<tr>
<td><strong>Data collection</strong></td>
<td>Bruker SMART Apex</td>
</tr>
<tr>
<td></td>
<td>with CCD detector</td>
</tr>
<tr>
<td></td>
<td>Mo Kα, graphite monochromator</td>
</tr>
<tr>
<td><strong>Theta range for data collection</strong></td>
<td>2θ = 56.63°</td>
</tr>
<tr>
<td><strong>Limiting indices</strong></td>
<td>-14 ≤ h ≤ 14</td>
</tr>
<tr>
<td></td>
<td>-17 ≤ k ≤ 17</td>
</tr>
<tr>
<td></td>
<td>-17 ≤ l ≤ 18</td>
</tr>
<tr>
<td><strong>Reflection collected</strong></td>
<td>20308</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>9560 [R(int) = 0.0354]</td>
</tr>
<tr>
<td><strong>Refinement method</strong></td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td><strong>Data / restraints / parameters</strong></td>
<td>9560 / 0 / 649</td>
</tr>
<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
<td>1.023</td>
</tr>
<tr>
<td><strong>Final R indices [I&gt;2σ(I)]</strong></td>
<td>R₁ = 0.0432, wR₂ = 0.0935</td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
<td>R₁ = 0.0559, wR₂ = 0.0994</td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole</strong></td>
<td>0.79 and -0.35 e.Å³</td>
</tr>
<tr>
<td><strong>Operator</strong></td>
<td>Matthias Vogt</td>
</tr>
</tbody>
</table>
Crystallographic data and structure refinement for [RhCl(trop2NH)(PPh3)] (61)

<table>
<thead>
<tr>
<th>Identification code</th>
<th>[RhCl(trop2NH)(PPh3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{48}H_{38}ClNPRh</td>
</tr>
<tr>
<td>Formula weight</td>
<td>798.15 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>100 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_1/n</td>
</tr>
<tr>
<td>Unit cell dimension</td>
<td>a = 9.9277(6) Å, α = 90°</td>
</tr>
<tr>
<td></td>
<td>b = 22.1115(12) Å, β = 101.1020(10)°</td>
</tr>
<tr>
<td></td>
<td>c = 16.6664(9) Å, γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>3590.1(4) Å³</td>
</tr>
<tr>
<td>Cell formula units Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.477 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.63 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1640.0</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.17 mm × 0.18 mm × 0.33 mm</td>
</tr>
<tr>
<td>Data collection</td>
<td>Bruker SMART Apex</td>
</tr>
<tr>
<td></td>
<td>with CCD detector</td>
</tr>
<tr>
<td></td>
<td>Mo Kα, graphite monochromator</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2θ = 56.47°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-13 ≤ h ≤ 13</td>
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<tr>
<td></td>
<td>-29 ≤ k ≤ 29</td>
</tr>
<tr>
<td></td>
<td>-22 ≤ l ≤ 22</td>
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<tr>
<td>Reflection collected</td>
<td>37432</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>8856 [R(int) = 0.0476]</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>8856 / 0 / 469</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.002</td>
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<tr>
<td>Final R indices [I&gt;2σ(I)]</td>
<td>R1 = 0.0312, wR2 = 0.0722</td>
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<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0385, wR2 = 0.0749</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.70 and -0.32 e.Å³</td>
</tr>
<tr>
<td>Operator</td>
<td>Amos Rosenthal</td>
</tr>
</tbody>
</table>
Crystallographic data and structure refinement for [Rh(ax-OAc)(trop2NH)(PPh3)] (62)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>[Rh(ax-OAc)(trop2NH)(PPh3)]</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C50H41NO2PRh</td>
</tr>
<tr>
<td>Formula weight</td>
<td>821.20 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>100 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_1/m</td>
</tr>
<tr>
<td>Unit cell dimension</td>
<td>a = 13.5948(5) Å, ( \alpha = 90^\circ )</td>
</tr>
<tr>
<td></td>
<td>b = 17.6192(6) Å, ( \beta = 90.7110(10) ) °</td>
</tr>
<tr>
<td></td>
<td>c = 16.0760(5) Å, ( \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Volume</td>
<td>3850.4(2) Å³</td>
</tr>
<tr>
<td>Cell formula units Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.418 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.53 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1696.0</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.20 mm × 0.14 mm × 0.09 mm</td>
</tr>
<tr>
<td>Data collection</td>
<td>Bruker SMART Apex</td>
</tr>
<tr>
<td></td>
<td>with CCD detector</td>
</tr>
<tr>
<td></td>
<td>Mo Kα, graphite monochromator</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>20 = 87.82°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-26 ≤ h ≤ 26</td>
</tr>
<tr>
<td></td>
<td>-32 ≤ k ≤ 34</td>
</tr>
<tr>
<td></td>
<td>-31 ≤ l ≤ 29</td>
</tr>
<tr>
<td>Reflection collected</td>
<td>123107</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>29059 [R(int) = 0.0406]</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>29059 / 0 / 687</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.090</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0440, wR2 = 0.1009</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0532, wR2 = 0.1055</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>3.12 and -0.75 e.Å³</td>
</tr>
<tr>
<td>Operator</td>
<td>Matthias Vogt</td>
</tr>
</tbody>
</table>
Crystallographic data and structure refinement for [Rh(trop₂NH)(P(2-OMePh)₃)]OTf

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>[Rh(trop₂NH)(P(2-OMePh)₃)]OTf</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₅₂H₄₄F₃NO₆PRhS</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1001.85 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>100 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P1¯</td>
</tr>
<tr>
<td>Unit cell dimension</td>
<td>(a = 15.567(5) \text{ Å} \quad \alpha = 61.768(6)°)</td>
</tr>
<tr>
<td></td>
<td>(b = 18.868(7) \text{ Å} \quad \beta = 74.932(7)°)</td>
</tr>
<tr>
<td></td>
<td>(c = 19.444(7) \text{ Å} \quad \gamma = 77.346(7)°)</td>
</tr>
<tr>
<td>Volume</td>
<td>4828(3) Å³</td>
</tr>
<tr>
<td>Cell formula units Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.454 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.49 mm⁻¹</td>
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<tr>
<td>F(000)</td>
<td>2108.0</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.58 mm × 0.50 mm × 0.33 mm</td>
</tr>
<tr>
<td>Data collection</td>
<td>Bruker SMART Apex</td>
</tr>
<tr>
<td></td>
<td>with CCD detector</td>
</tr>
<tr>
<td></td>
<td>Mo Kα, graphite monochromator</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>20 = 56.99°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-20 ≤ h ≤ 20</td>
</tr>
<tr>
<td></td>
<td>-25 ≤ k ≤ 25</td>
</tr>
<tr>
<td></td>
<td>-26 ≤ l ≤ 25</td>
</tr>
<tr>
<td>Reflection collected</td>
<td>50767</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>24044 [R(int) = 0.0531]</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>24044 / 0 / 1251</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>0.983</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0441, wR2 = 0.1044</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0626, wR2 = 0.1118</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.40 and -1.43 e.Å³</td>
</tr>
<tr>
<td>Operator</td>
<td>Amos Rosenthal</td>
</tr>
</tbody>
</table>
Crystallographic data and structure refinement for \([\text{RhCl(trop}_2\text{NH)}(\text{P(3,5-diMePh)}_3)]\) (69)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>([\text{RhCl(trop}_2\text{NH)}(\text{P(3,5-diMePh)}_3)])</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>(\text{C}<em>{54}\text{H}</em>{50}\text{ClNPRh} )</td>
</tr>
<tr>
<td>Formula weight</td>
<td>882.31 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>100 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>(P\bar{1})</td>
</tr>
<tr>
<td>Unit cell dimension</td>
<td>(a = 15.469(3) \text{ Å} \quad \alpha = 86.89(3)^\circ )</td>
</tr>
<tr>
<td></td>
<td>(b = 17.700(4) \text{ Å} \quad \beta = 71.13(3)^\circ )</td>
</tr>
<tr>
<td></td>
<td>(c = 18.068(4) \text{ Å} \quad \gamma = 83.96(3)^\circ )</td>
</tr>
<tr>
<td>Volume</td>
<td>4654(2) \text{ Å}^3</td>
</tr>
<tr>
<td>Cell formula units Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.333 g/cm(^3)</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.50 mm(^{-1})</td>
</tr>
<tr>
<td>F(000)</td>
<td>1936.0</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.40 mm \times 0.37 mm \times 0.22 mm</td>
</tr>
<tr>
<td>Data collection</td>
<td>Bruker SMART Apex</td>
</tr>
<tr>
<td>with CCD detector</td>
<td></td>
</tr>
<tr>
<td>Mo K(\alpha), graphite monochromator</td>
<td></td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>20 = 56.71^\circ</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-20 \leq h \leq 20</td>
</tr>
<tr>
<td></td>
<td>-23 \leq k \leq 23</td>
</tr>
<tr>
<td></td>
<td>-24 \leq l \leq 24</td>
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<tr>
<td>Reflection collected</td>
<td>39459</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>15673 [R(int) = 0.0568]</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on (F^2)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>15673 / 0 / 1127</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.985</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0608, wR2 = 0.1906</td>
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<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0989, wR2 = 0.2497</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>2.98 and -2.77 e.Å(^3)</td>
</tr>
<tr>
<td>Temperature</td>
<td>(K)</td>
</tr>
<tr>
<td>Operator</td>
<td>Amos Rosenthal</td>
</tr>
</tbody>
</table>
Crystallographic data and structure refinement for $[\text{RhCl(trop}_2\text{NH})(\text{P(3,5-di}'\text{PrPh})_3)]$ (70)

<table>
<thead>
<tr>
<th>Identification code</th>
<th>$[\text{RhCl(trop}_2\text{NH})(\text{P(3,5-di}'\text{PrPh})_3]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>$\text{C}<em>{66}\text{H}</em>{74}\text{ClNPRh}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1050.63 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>100 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P$\bar{T}$</td>
</tr>
<tr>
<td>Unit cell dimension</td>
<td>$a = 12.1046(5) \text{ Å}$ $\alpha = 86.179(1)^\circ$</td>
</tr>
<tr>
<td></td>
<td>$b = 12.6967(5) \text{ Å}$ $\beta = 83.945(1)^\circ$</td>
</tr>
<tr>
<td></td>
<td>$c = 18.9956(8) \text{ Å}$ $\gamma = 66.218(1)^\circ$</td>
</tr>
<tr>
<td>Volume</td>
<td>2655.7(2) Å$^3$</td>
</tr>
<tr>
<td>Cell formula units Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.314 g/cm$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.44 mm$^{-1}$</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>1108.0</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.43 mm $\times$ 0.42 mm $\times$ 0.22 mm</td>
</tr>
<tr>
<td>Data collection</td>
<td>Bruker SMART Apex</td>
</tr>
<tr>
<td></td>
<td>with CCD detector</td>
</tr>
<tr>
<td></td>
<td>Mo K$\alpha$, graphite monochromator</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>56.58$^\circ$</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>$-16 \leq h \leq 16$</td>
</tr>
<tr>
<td></td>
<td>$-16 \leq k \leq 16$</td>
</tr>
<tr>
<td></td>
<td>$-25 \leq l \leq 25$</td>
</tr>
<tr>
<td>Reflection collected</td>
<td>27701</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>13068 $[R(\text{int}) = 0.0460]$</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>13068 / 0 / 643</td>
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<td>Goodness-of-fit on $F^2$</td>
<td>0.990</td>
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<tr>
<td>Final R indices [$I&gt;2\sigma(I)$]</td>
<td>R1 = 0.0364, wR2 = 0.0818</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0448, wR2 = 0.0906</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.82 and -0.98 e.Å$^3$</td>
</tr>
<tr>
<td>Operator</td>
<td>Amos Rosenthal</td>
</tr>
</tbody>
</table>
Crystallographic data and structure refinement for [Rh(trop2NH)(P(3,5-diMePh)3]OTf (77)

<table>
<thead>
<tr>
<th>Identification code</th>
<th>[Rh(trop2NH)(P(3,5-diMePh)3]OTf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C55H50F3NO3PRhS</td>
</tr>
<tr>
<td>Formula weight</td>
<td>995.93 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>100 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
</tr>
<tr>
<td>Unit cell dimension</td>
<td>a = 27.866(2) Å, α = 90°</td>
</tr>
<tr>
<td></td>
<td>b = 18.798(1) Å, β = 121.962(1)°</td>
</tr>
<tr>
<td></td>
<td>c = 23.968(2) Å, γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>10652(1) Å³</td>
</tr>
<tr>
<td>Cell formula units Z</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.449 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.63 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>4766.0</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.39 mm × 0.37 mm × 0.14 mm</td>
</tr>
<tr>
<td>Data collection</td>
<td>Bruker SMART Apex</td>
</tr>
<tr>
<td></td>
<td>with CCD detector</td>
</tr>
<tr>
<td></td>
<td>Mo Kα, graphite monochromator</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>20 = 60.37°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-39 ≤ h ≤ 38</td>
</tr>
<tr>
<td></td>
<td>-26 ≤ k ≤ 26</td>
</tr>
<tr>
<td></td>
<td>-33 ≤ l ≤ 33</td>
</tr>
<tr>
<td>Reflection collected</td>
<td>58512</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>15264 [R(int) = 0.0370]</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>15264 / 0 / 660</td>
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<td>Goodness-of-fit on F²</td>
<td>1.038678</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.067898, wR2 = 0.1612</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.055756, wR2 = 0.1914</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>2.33 and -1.84e.Å³</td>
</tr>
<tr>
<td>Operator</td>
<td>Amos Rosenthal</td>
</tr>
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Crystallographic data and structure refinement for [Rh(trop$_2$NH)(DBP)]OTf (78)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Identification code</td>
<td>[Rh(trop$_2$NH)(DBP)]OTf</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C$<em>{49}$H$</em>{36}$F$_3$NO$_3$PRhS</td>
</tr>
<tr>
<td>Formula weight</td>
<td>909.75 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>100 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2$_1$/c</td>
</tr>
<tr>
<td>Unit cell dimension</td>
<td>a = 18.507(3) Å, $\alpha$ = 90°</td>
</tr>
<tr>
<td></td>
<td>b = 10.203(1) Å, $\beta$ = 101.724(3)$^\circ$</td>
</tr>
<tr>
<td></td>
<td>c = 23.604(3) Å, $\gamma$ = 90$^\circ$</td>
</tr>
<tr>
<td>Volume</td>
<td>4364(1)Å$^3$</td>
</tr>
<tr>
<td>Cell formula units Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.473 g/cm$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.54 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>1984.0</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.56 mm × 0.44 mm × 0.39 mm</td>
</tr>
<tr>
<td>Data collection</td>
<td>Bruker SMART Apex</td>
</tr>
<tr>
<td></td>
<td>with CCD detector</td>
</tr>
<tr>
<td></td>
<td>Mo K$\alpha$, graphite monochromator</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>$2\theta$ = 56.76$^\circ$</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-24 ≤ h ≤ 24</td>
</tr>
<tr>
<td></td>
<td>-13 ≤ k ≤ 13</td>
</tr>
<tr>
<td></td>
<td>-31 ≤ l ≤ 31</td>
</tr>
<tr>
<td>Reflection collected</td>
<td>45787</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>10887 [R(int) = 0.0601]</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>10887 / 0 / 570</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.003</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0405, wR2 = 0.1047</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0523, wR2 = 0.1104</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>2.03 and -1.07 e.Å$^3$</td>
</tr>
<tr>
<td>Operator</td>
<td>Amos Rosenthal</td>
</tr>
</tbody>
</table>
Crystallographic data and structure refinement for [Rh(TMIY)(trop₂N)] (95)

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>[Rh(TMIY)(trop₂N)]</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₃₇H₃₅N₃Rh</td>
</tr>
<tr>
<td>Formula weight</td>
<td>624.60 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>100 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.70173 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pnma</td>
</tr>
<tr>
<td>Unit cell dimension</td>
<td>a = 14.420(1) Å, b = 15.495(1) Å, c = 12.3729(9) Å, α = 90°, β = 90°, γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>2764.7(3) Å³</td>
</tr>
<tr>
<td>Cell formula units Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.498 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.65 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1288.0</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.07 mm × 0.04 mm × 0.02 mm</td>
</tr>
<tr>
<td>Data collection</td>
<td>Bruker SMART Apex</td>
</tr>
<tr>
<td></td>
<td>with CCD detector</td>
</tr>
<tr>
<td></td>
<td>Mo Kα, graphite monochromator</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>20 = 50.05°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-17 ≤ h ≤ 17, -18 ≤ k ≤ 18, -11 ≤ l ≤ 14</td>
</tr>
<tr>
<td>Reflection collected</td>
<td>17835</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2541 [R(int) = 0.1079]</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2541 / 0 / 254</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>0.899</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0391, wR2 = 0.0635</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0661, wR2 = 0.0690</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.60 and -0.75 e.Å³</td>
</tr>
<tr>
<td>Operator</td>
<td>Gustavo Santiso-Quinones</td>
</tr>
</tbody>
</table>

- 301 -
8.3 Curriculum Vitae

Personal Information

Name: Annen
First Names: Samuel Philipp
Address: Schueppwiesenstrasse 4
9152 Glattebrugg
Telephone (office): +41 44 633 48 15
E-mail: annen@inorg.chem.ethz.ch
Date of Birth: 07 October 1984
Marital Status: married
Nationality: Switzerland

Education

Dehydrogenations with Rhodium(I) Amino Olefin Complexes
using O₂, N₂O and Nitrosoarenes as Hydrogen Acceptors” (Prof.
Dr. H. Grützmacher) Defence: 24th October 2012
09. 2007 – 09. 2008 Master of Science in Chemistry; ETHZ, Zurich: Master thesis:
“Transfer Hydrogenation of C=C and C=O Double Bonds and
Catalytic Aerobic Oxidation of Alcohols using
[Rh(trop2NH)L]X-systems as Catalyst” (Prof. Dr. H.
Grützmacher); grade 6e
10. 2004 – 09. 2007 Bachelor of Science in Chemistry; ETHZ, Zurich: grade point
average: 5.13e
08. 1999 – 06. 2003 General qualification for university entrance; Kantonsschule
Kollegium Schwyz (KKS)

* Referred to the Swiss grading scale reaching from 6 (very good) to 1 (very weak).
Professional Experience

10. 2008 – present  Scientific assistance; ETHZ, Laboratory of Inorganic Chemistry, Zurich:
  - Operation and maintenance of GC-FID and GC-MS devices
  - Assistance for undergraduate research
  - Assistance for the basic inorganic laboratory courses

Further Education

<table>
<thead>
<tr>
<th>Year</th>
<th>Course Details</th>
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</thead>
<tbody>
<tr>
<td>2011</td>
<td>Dutch for Advanced, Lic. Phil C. De Wulf, University of Zurich</td>
</tr>
<tr>
<td>2010</td>
<td>EndNote X4 Introduction, A. Venakis, ETHZ</td>
</tr>
<tr>
<td>2010</td>
<td>Word 2010 optimal Application 1, K. Stephan, ETHZ</td>
</tr>
<tr>
<td>2010</td>
<td>Introduction in the Dutch Language, Dr. M. Clement, University of Zurich</td>
</tr>
<tr>
<td>2010</td>
<td>Chemistry Information for the Advanced, Dr. E. Zass, ETHZ</td>
</tr>
<tr>
<td>2009</td>
<td>Radiochemistry, Dr. M. Badertscher, ETHZ</td>
</tr>
<tr>
<td>2009</td>
<td>Word 2007 for Scientific Publication, E. Spier, ETHZ</td>
</tr>
<tr>
<td>2009</td>
<td>Basic Presentation Skills Course for Scientists (in Englisch), Dr. B. Hellermann, ETHZ</td>
</tr>
<tr>
<td>2007</td>
<td>Patent- and Licensing Law II, Dr. H. Laederach</td>
</tr>
<tr>
<td>2006</td>
<td>Patent- and Licensing Law I, Dr. H. Laederach</td>
</tr>
</tbody>
</table>
### Further Professional Engagement

<table>
<thead>
<tr>
<th>Date</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Since 2010</td>
<td>Packaging of pharmaceutical products according to GMP standards on behalf of the Swiss Army Pharmacy during the annual repetition course of the Swiss Army.</td>
</tr>
</tbody>
</table>
| 12. 2003 – 08. 2004 | Internship: Swiss Holiday Park, Bureau of reservation, Morschach:  
  - General correspondence (German, English, French)  
  - Working with Word, Excel, Outlook and Sales & Catering  
  - Registration of group reservations with Sales & Catering  
  - Office organisation and filing  
  - General administrative tasks |
| 07. 2003 – 10. 2003 | Military service, basic training |

### Languages

<table>
<thead>
<tr>
<th>Language</th>
<th>Skill</th>
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</thead>
<tbody>
<tr>
<td>German:</td>
<td>First language</td>
</tr>
<tr>
<td>English:</td>
<td>very good writing and oral skills</td>
</tr>
<tr>
<td>Dutch:</td>
<td>good writing and oral skills</td>
</tr>
<tr>
<td>French:</td>
<td>knowledge existing</td>
</tr>
</tbody>
</table>

### DP Expertise

<table>
<thead>
<tr>
<th>Software</th>
<th>Skill</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS Word:</td>
<td>very good</td>
</tr>
<tr>
<td>ChemDraw:</td>
<td>very good</td>
</tr>
<tr>
<td>MS Excel:</td>
<td>good</td>
</tr>
<tr>
<td>EndNote:</td>
<td>good</td>
</tr>
<tr>
<td>Xcalibur:</td>
<td>good</td>
</tr>
<tr>
<td>ACD Labs</td>
<td>knowledge existing</td>
</tr>
<tr>
<td>Origin Labs:</td>
<td>knowledge existing</td>
</tr>
<tr>
<td>Corel Draw:</td>
<td>knowledge existing</td>
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</table>
9 Literature


