Doctoral Thesis

**Iridium-catalyzed dehydrogenation of alcohols**

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Iridium-Catalyzed
Dehydrogenation of Alcohols

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Für Elke und Franz
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Abstract

Aldehydes are valuable synthetic intermediates, commonly prepared by the dehydrogenation of primary alcohols. Due to the increasing structural complexity of target molecules, the development of catalysts able to chemoselectively oxidize primary hydroxyl groups in polyols is a key challenge. In an earlier work, the chemoselective dehydrogenation of primary alcohols based on the homogeneous amino-olefin catalyst \([\text{Ir(trop}_2\text{DACH})\text{OTf}]\) (trop_2DACH = \(N,N\)-bis(5-H-dibenzo[\(a,d\]cycloheptene-5-yl]-1,2-diamino-cyclohexane) was explored.\(^{[1-3]}\) The mechanism for this catalysis, however, was speculative and its scope limited to substrates with insensitive functional groups. This new work offers a deeper insight into the mechanism, including the successful isolation and characterization of the reactive intermediates of the catalytic cycle by NMR and EPR spectroscopy. Furthermore, a 2\(^{nd}\) generation catalyst is introduced, which exhibits low catalyst loading and higher reaction rates under milder conditions. This new catalyst improves the functional group tolerance of the system and enlarges its scope to include primary alcohols with more sensitive and therefore more challenging functional groups.

The mechanistic studies revealed that \([\text{Ir(trop}_2\text{DACH})\text{OTf}]\) and the amino-olefin complexes newly synthesized in this work behave non-innocently under catalytic conditions and are only catalyst precursors: the true catalytically active species are the corresponding diazadiene-olefin complexes formed by oxidative dehydrogenation prior to catalysis (Scheme I). During the assessment of diazadiene complexes and co-oxidants, the highest catalytic activity was observed using \([\text{Ir(trop}_2\text{DAD})\text{OTf}]\) (trop_2DAD = \(N,N\)-bis(5-H-dibenzo[\(a,d\]cycloheptene-5-yl]-1,4-diazabuta-1,3-diene) as the catalyst in combination with \(p\)-benzoquinone. Under mild, almost base free reaction conditions and low catalyst loadings (0.01 mol%), a wide range of primary aliphatic, benzylic, allylic alcohols were oxidized to the corresponding aldehydes. Aside from unactivated alcohols, the oxidation of naturally occurring alcohols such as lavandulol, geraniol and even a partially protected carbohydrate was possible. The most remarkable aspect of the catalytic system is its high group tolerance and selectivity, e.g. despite the unprotected secondary hydroxy group, 1,3-butanediol was selectively oxidized to 3-hydroxybutanal.

The investigation of the catalytic cycle showed that the diazadiene ligand behaves as a cooperative ligand, as it actively contributes to the bond activation and is reversibly reduced and oxidized. Upon reaction with alcohols, \([\text{Ir(trop}_2\text{DAD})\text{OTf}]\) was reduced to the mono(imino)mono(amino) complex \([\text{Ir(trop}_2\text{MIMA})\text{OTf}]\) under formation of the aldehyde. In the last step of the catalytic cycle,
[Ir(trop₂MIMA)]OTf was reoxidized by p-benzoquinone to regenerate the diazadiene complex. Based on these results, the following catalytic cycle was proposed (Scheme I).

Scheme I: Proposed simplified mechanism for the dehydrogenation of alcohols with amino-olein complexes.

The chemoselective dehydrogenation of alcohols with [Ir(trop₂DAD)]OTf is an attractive preparative method; in particular, as it reduces the need for a sophisticated group protection strategy.
Zusammenfassung

Aldehyde sind wichtige Zwischenprodukte in der organischen Synthese und werden üblicherweise durch Oxidation der entsprechenden Alkohole hergestellt. Aufgrund immer komplexeren Zielmoleküle, ist die Entwicklung neuer Katalysatoren, die in Polyolen selektiv die primäre Hydroxylgruppen zu Aldehyden oxidieren eine der derzeitigen Herausforderungen. Mit dem homogenen Amino-Olefin Katalysator \( [\text{Ir}(\text{trop}_2\text{DACH})]OTf \) (\( \text{trop}_2\text{DACH} = N,N\text{-bis}(5\text{-H-dibenzo}[a,d]\text{cyclohepten-5-yl})-1,2\text{-diamino-cyclohexan} \)) konnten gute Ergebnisse für die chemoselektive Dehydrierung von primären Alkoholen erzielt werden.\(^{1-3}\) Der Anwendungsbereich war jedoch auf Substrate mit unempfindlichen funktionellen Gruppen beschränkt und über den Mechanismus konnte bisher nur spekuliert werden. Aufgrund der erfolgreichen Isolierung der Zwischenprodukte und deren Charakterisierung per NMR- und EPR Spektroskopie, konnte in dieser Arbeit ein tiefer Einblick in den Katalysezyklus erhalten werden. Ausgehend von diesen Erkenntnissen, wurde ein Katalysator der zweiten Generation entwickelt, welcher sich durch mildere Reaktionsbedingungen, schnellere Reaktionsgeschwindigkeiten und eine höhere Toleranz gegenüber funktionellen Gruppen auszeichnet.

Die mechanistischen Untersuchungen haben gezeigt, dass \( [\text{Ir}(\text{trop}_2\text{DACH})]OTf \) und die im Zuge dieser Doktorarbeit hergestellten Amino-Olefin Komplexe nur Katalysator-Vorläufer sind. Unter katalytischen Bedingungen verhalten sie sich "non-innocent" und wandeln sich durch oxidative Dehydrierung in die katalytisch aktiven Diazadien-Olefin Komplexe um (Schema II). Von den untersuchten Diazadien-Olefin Komplexen und Co-Oxidationsmitteln wurde die besten Ergebnisse mit \( [\text{Ir}(\text{trop}_2\text{DAD})]OTf \) (\( \text{trop}_2\text{DAD} = N,N\text{-bis}(5\text{-H-dibenzo}[a,d]\text{cyclohepten-5-yl})-1,4\text{-diazabuta-1,3-dien} \)) und p-Benzoquinon erzielt. Unter milden, fast basenfreien Reaktionsbedingungen (0.01 mol%) und mit geringen Katalysatormengen (0.01 mol%), konnten die verschiedensten primären aliphatischen, benzyllischen und allyllischen Alkohole zu den entsprechenden Aldehyde umgesetzt werden. Neben der Oxidation von unaktivierten Alkoholen war auch die Oxidation von natürlich vorkommenden Alkoholen wie Lavandulol, Geraniol und teilweise geschützten Kohlenhydraten möglich. Die Methode zeichnet sich vor allem durch die hohe Toleranz gegenüber verschiedenen funktionellen Gruppen und die gleichzeitiger Selektivität der Oxidation von primären Hydroxylgruppen aus z.B. konnte 1,3-Butandiol trotz der ungeschützten sekundären Hydroxylgruppe ausschließlich zu 3-Hydroxybutanal dehydriert werden.

Ausgehend vom Diazadien-Olefin Katalysator \( [\text{Ir}(\text{trop}_2\text{DAD})]OTf \) wurde der Mechanismus des Katalysezyklus für die Dehydrierung von Alkoholen eingehend untersucht. Es konnte gezeigt werden, dass es sich bei dem Diazadien-Olefin Liganden um einen kooperativen Liganden handelt, der während
der Katalyse aktiv an der Bindungsaktivierung beteiligt ist und reversibel reduziert und oxidiert wird. Durch die Reaktion mit Alkoholen wird \([\text{Ir(trop}_2\text{DAD})]\text{OTf}\) unter Bildung des entsprechenden Aldehyds zum mono(imino)mono(amo) Komplex \([\text{Ir(trop}_2\text{MIMA})]\text{OTf}\) reduziert. Im nächsten Schritt schließt sich der Katalyse-Zyklus durch die Reoxidation mit \(p\)-Benzoquinon zum Ausgangskomplex (Schema II).

![Diagram](attachment:diagram.png)


Insgesamt, ist mit dem \([\text{Ir(trop}_2\text{DAD})]\text{OTf}\)-System eine attraktive, universelle Methode zur Dehydrierung von Alkoholen gelungen, insbesondere da auf die Verwendung von Schutzgruppen weitgehend verzichtet werden kann.
Public Presentations

Oral presentation at the PhD Students Symposium of the Laboratory of Inorganic Chemistry 2008, ETH Zürich, *Highly Efficient Iridium-Catalyzed Oxidation of Alcohols*.

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I. Introduction
Target molecules of increasing structural complexity and levels of sophistication are the central focus of modern organic synthesis. As a result, one of the most important challenges is the development of reagents that satisfy the demand for higher selectivity and function group tolerance. Despite substantial progress in this field, even the simple transformation of an alcohol to a carbonyl group can still cause synthetic problems.[4]

1 Oxidation of Alcohols

The oxidation of alcohols is traditionally performed using stoichiometric amounts of strong acidic or strong basic chromium salts.[5-10] Milder procedures use activated dimethyl sulfoxide reagents[11-13] or hypervalent iodine compounds[14, 15] of which the Dess-Martin periodinane reagent is the most common example. These stoichiometric oxidants are relatively expensive and some, such as chromium salts, generate large amounts of heavy metal waste. Given today’s demand for highly efficient and environmentally sound processes, the replacement of stoichiometric oxidants by the combined use of a catalyst with a terminal oxidant is becoming increasingly important. Prominent examples include the use of TPAP with stoichiometric amounts of NMO[4, 16] and the use of TEMPO with sodium hypochlorite[17, 18] as co-oxidant for the oxidation of alcohols. Ideally, molecular oxygen is used as the terminal oxidant, as it is readily available, inexpensive and, most importantly, produces benign by-products (water and/or hydrogen peroxide). In nature, this concept of aerobic oxidation is found in metalloenzymes such as galactose-, glucose- and pyranose oxidase, which selectively oxidize carbohydrates in the presence of oxygen.[19] For example, galactose oxidase (GOase), a mononuclear copper-containing enzyme, uses a modified tyrosyl radical to exclusively oxidize the primary alcohol group of galactose to the corresponding aldehyde. The proposed catalytic cycle is outlined in Scheme 1.
Mechanistic studies have shown that the square pyramidal coordination of the copper serves to position the methylene hydrogen of the alcohol in close proximity to the oxygen atom of the tyrosyl radical.\[^{20, 21}\] The rate-determining step is the formation of a coordinated ketyl radical anion by hydrogen abstraction from the α-carbon. Rapid intramolecular reduction of copper(II) to copper(I) leads to the formation of the aldehyde. In the last step of the catalytic cycle, the active radical cofactor is regenerated by the reaction of the reduced enzyme with oxygen. Despite the advantages of metalloenzymes, such as mild reaction conditions and excellent regio- and chemoselectivity, they are seldom used for the industrial oxidation of alcohols, largely due to their narrow substrate specificity.\[^{19}\]

Although the mechanistic understanding of GOase has initiated many studies with model systems, they remain of limited practical use for the oxidation of alcohols.\[^{21-26}\]

In contrast to metalloenzymes, homogeneous palladium catalysts have been found to be extremely useful for the oxidation of a wide range of alcohols,\[^{27-32}\] such as the Pd(OAc)$_2$/pyridine system reported by Uemura et al.\[^{33, 34}\] and the water-soluble Pd(OAc)$_2$/phenantroline system by Sheldon et al.\[^{35-37}\]. Both of these catalytic systems serve as benchmarks for the development of new aerobic catalysts: Uemura’s primarily due to the simplicity of the procedure and Sheldon’s due to the effective use of low catalyst loadings (≥0.25 mol%), in comparison to other aerobic catalysts. Aside from
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Palladium catalysts, a diverse range of transition metal complexes have been used for the aerobic oxidation of alcohols,\[38, 39\] including ruthenium,\[40-44\] cobalt,\[45-48\] vanadium,\[49-54\] rhodium,\[55\] platinum\[56-58\] and gold.\[59\] When reoxidation of the catalyst with oxygen is impossible, electron transfer mediators (ETMs) can be inserted into the catalytic cycle.\[60\] Bäckvall et al. reported the oxidation of alcohols by the ruthenium catalyst $1$ in combination with benzoquinone and a $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ system as ETM (Scheme 2).\[61-63\]

![Scheme 2: Biometric aerobic oxidation of alcohols reported by Bäckvall et al.][60]

The role of the cyclopentadienone ligand is particularly noteworthy: it behaves as a *cooperating ligand*, participating directly in the bond activation and undergoing a reversible chemical transformation in the catalysis.\[64\]

While many of these aerobic systems are synthetically useful, significant drawbacks remain, such as high catalyst loadings (up to 5 mol%), lack of substrate scope and poor chemoselectivity. For use in target-orientated synthesis, the functional group tolerance of the individual systems must be broadened to include more complex alcohols that are synthetically relevant. In addition to minimizing by-products, enhancing the selectivity of these oxidation methods is also crucial.\[65\] Scheme 3 illustrates problems with the selective oxidation of alcohols to which no satisfactory solution exists.
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Scheme 3: Problems with selective alcohol oxidation to which no satisfactory solution exists include i) asymmetric oxidation of secondary alcohols to ketones (kinetic resolution), ii) enantiotoposelective oxidation of meso-diols (desymmetrization) and iii) chemoselective oxidation of primary alcohols to aldehydes in the presence of secondary alcohols.\[^{[65]}\]

One of the most prominent issues in pharmaceutical and natural product synthesis is the enrichment of enantiomerically pure alcohols. Of the many methods used to synthesize chiral alcohols, kinetic resolution is of particular interest since racemic alcohols are readily available and inexpensive (Scheme 3 i). A related enantioselective oxidation of significance is the oxidative desymmetrization of meso-diols (Scheme 3 ii). When choosing an oxidizing reagent, chemoselectivity (Scheme 3 iii) is an important consideration; neglecting this aspect can result in side reactions with other functional groups, loss of protecting groups, oxidative bond fragmentation, rearrangement and epimerization. Consequently, it is important to develop catalysts that can discriminate between two different secondary alcohols within the same molecule on the basis of their steric environment and at the same time being able to distinguish between several oxygen-containing functional groups at different oxidation states.
Prominent catalysts for the aerobic kinetic resolution and desymmetrization are displayed in Figure 1.

Figure 1: Prominent catalysts for the aerobic kinetic resolution and the desymmetrization of meso-diols.

An important breakthrough in the aerobic enantioselective oxidation of alcohols was simultaneously disclosed by Sigman et al.\(^{66-71}\) and Stolz et al.\(^{72,73}\). Both groups found that the palladium (-)-sparteine complex 2 is able to enrich the unreacted alcohol in high enantiomeric purity in the presence of oxygen. Furthermore, 2 can also be used for the desymmetrization of meso-diols. Unfortunately, as sparteine is only available as (-)-antipode, the synthesis is restricted to one enantiomeric series of alcohols. This shortcoming has recently been overcome by the preparation of complex 3, in which the diamine ligand acts as the (+)-sparteine mimic.\(^{74}\) In addition to the chiral palladium(II) catalysts, it has been demonstrated that the iridium(III) complex 4\(^{75,76}\) and ruthenium(II) complex 5\(^{65,77}\) are efficient aerobic catalysts for the kinetic resolution and desymmetrization of alcohols. The approach of Katsuki et al. is of particular interest: desymmetrization of meso-diols was achieved in the presence of air and light by employing the chiral ruthenium(II) salen complex 5.\(^{78}\)

While good approaches for the kinetic resolution and desymmetrization of alcohols have been reported, hardly any chemoselective methods exist where the reagent or catalyst selectively oxidizes the secondary alcohol in the presence of a primary or vice versa.\(^{43,79-81}\) In particular, the selective oxidation of carbohydrates is considered one of the most challenging disciplines in oxidation chemistry. Due to the thermal instability and high polarity of carbohydrates, mild reaction conditions in polar solvents, preferably water, are necessary. Recently, Ramström et al. reported the chemoselective organocatalytic oxidation of unprotected glycosides (Scheme 4).\(^{82}\)
The synthesis of dialdo-glycosides in good to excellent yields was achieved by using TEMPO with TTC as co-oxidant. However, this method necessitates high catalyst loadings (2.5 mol% TEMPO) and long reaction times.

Recently, our group reported the first transition metal catalyzed chemoselective oxidation of a primary alcohol in the presence of a secondary alcohol within the same molecule using [Ir(trop_2DACH)]OTf 6b\(^\text{1}\) (Scheme 5).

\[ \text{OH} \quad \text{OH} + \quad \text{O} \quad \text{O} \quad \text{OTf} \]

\[ \text{0.03 mol\% KO}^\text{Bu} \quad \text{chlorobenzene, 80 °C} \quad \text{60 min, } >98\% \]

Scheme 5: Chemoselective catalytic oxidation of 1,3-butanediol to 3-hydroxybutanal with [Ir(trop_2DACH)]OTf 6b.

The oxidation of 1,3-butanediol with p-benzoquinone as co-oxidant under basic conditions exclusively forms 3-hydroxybutanal. In this competition experiment, the primary alcohol reacts whereas the secondary remains unchanged. This observation implies that a metal-alkoxide is a key intermediate in the catalytic cycle. The reduced steric hindrance of the coordinated primary alkoxide and the higher acidity of the primary alcohol form the basis of this conjecture.\(^{[83-85]}\)

Previous mechanistic studies showed that a paramagnetic species is formed upon the double deprotonation and subsequent oxidation of [Ir(trop_2DACH)]OTf 6b.\(^{[2, 3]}\) Based on intensive EPR studies, the species was assigned as the amyl radical complex 8a, analogous to the corresponding rhodium(I) radical complex 8a.\(^{[86]}\) The synthesis of the radical complexes 8a,b and the proposed catalytic cycle for the dehydrogenation of primary alcohols are displayed in Scheme 6.\(^{[2]}\)

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\(^{1}\) In order to distinguish between metal complexes with the same ligand, we use following letters: a for rhodium and b for the iridium complexes, e.g. [Rh(trop_2DACH)]OTf will be referred to as 6a and [Ir(trop_2DACH)]OTf as 6b.
Inspired by the mechanism of GOase, the aminyl radical complex 8b has been proposed as the catalytic active species.\textsuperscript{[2, 3]} The cationic di(amino) complex 6a,b is doubly deprotonated by potassium tert-butoxide to give the anionic di(amido) complex 7a,b.\textsuperscript{[1, 87]} This resulting complex is subsequently oxidized by \( p \)-benzoquinone to the iridium aminyl radical complex 8a,b.\textsuperscript{[2, 86]} In the next stage, the alkoxide coordinates to the iridium centre, positioning the \( \alpha \)-hydrogen in close proximity to the nitrogen centred radical I-1. Intramolecular hydrogen-transfer then results in the formation of an iridium coordinated ketyl radical anion I-2. In the final stage of the catalytic cycle, I-2 is oxidized by the semiquinone radical anion, yielding 6b, \( p \)-hydroquinone and the corresponding aldehyde. Despite its ability to form aminyl radical complex 8a, the corresponding rhodium complex 6a is unable to catalyze the alcohol oxidation.

While the initial goal of developing an effective, highly chemoselective catalytic oxidation method was met, several concerning observations undermine the validity of the proposed mechanism. Firstly, despite the use of an enantiomerically pure catalyst 6b, no chiral induction was observed.\textsuperscript{[88]} Furthermore, contrary to the hypothesis that chemoselectivity results from the favoured binding of a primary alcohol to the metal centre, the structurally related \( cis \)-[Ir(tropNH\(_2\))]OTf 9b is unable to bind a
fifth ligand. This result strongly suggest that the catalytic cycle cannot proceed over an iridium alkoxide intermediate, at least, not if the di(amino) 6b, the di(amido) 7b or the aminyl-radical complex 8b is the catalytically active species. Finally, a poor fit between the experimental EPR and computed DFT data for the rhodium and iridium aminyl radical complexes 8a,b implies that the assignment is incorrect.

2 Oxidative Dehydrogenation of Coordinated Amines

The absence of chiral induction of the enantiomerically pure catalyst 6b can be readily explained by the loss of chirality at the backbone of the ligand by oxidative dehydrogenation. In the literature, the phenomenon of oxidative dehydrogenation has been well known since the early 50s for transition metal coordinated amine ligands. Although the first oxidative dehydrogenation was observed in 1898 for an iron α,α'-dipiperidyl complex by Blau, the outcome was not understood until the investigative work of Krumholz in 1953. Since then, oxidative dehydrogenations have been described for macrocyclic amines, ethylenediamine derivatives, monodentate ligands and coordinated alcohols (Scheme 7).

![Scheme 7: Ruthenium(II) promoted oxidative dehydrogenation of ethylenediamine and an alcohol ligand.](image)

Ruthenium, osmium, iron and nickel complexes are particularly effective at mediating the oxidative dehydrogenation, whereas only one example for an iridium-promoted dehydrogenation has been reported so far. Despite an increasing number of publications, in particular by Keene et al., the mechanism of the oxidative dehydrogenation is far from being fully understood. Initial mechanistic studies of macrocyclic amine complexes by Busch et al. showed that the oxidative dehydrogenation involves the oxidation of the metal centre at the outset, followed by intramolecular redox processes in which the ligand is oxidized and the metal reduced (Scheme 8).
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In contrast to the dehydrogenation of monodentate primary amines, which leads to nitriles, the oxidation of ethylenediamine based bidentate ligands never progresses further than the α,α’-diimine stage.

3 Diazadiene Complexes

The α,α’-diimine entity RN=C(R’)-C(R’)=NR, also referred to as diazadiene² (DAD), has attracted much attention as a building block for ligands, due its versatile coordination modes and remarkable σ-donor and π-acceptor properties. Since the preparation of the first aliphatic diazadiene complex in 1953 by Krumholz,² since the preparation of the first aliphatic diazadiene complex in 1953 by Krumholz,⁹² numerous transition metal complexes have been synthesized.⁹⁶ Due to its strong π-acceptor properties, the diazadiene ligand is able to contribute actively to the redox state of the metal centre.⁹⁷ This non-innocent behaviour of the diazadiene ligand may lead to the formation of redox isomers, whose structures A, B and C are displayed in Scheme 9.

Scheme 9: Isomeric structures of metal complex with a non-innocent diazadiene ligand: A) diazadiene complex, B) diazadiene-radical complex, C) enediamido complex.

In structure A, the neutral diazadiene ligand is structurally unchanged. Transfer of one electron from the metal to the ligand leads to B, a ligand centred radical complex. In contrast, the transfer of a second electron results in the formation of an enediamido complex C.

Structural, spectroscopic and theoretical studies of diazadiene complexes have provided insight into the unique interaction between diazadiene ligands and transition metals, thus facilitating

² Most known 1,4-diaza-1,3-butadienes (DAD) have the general formula RN=C(R’)-C(R’)=NR and herein will be denoted as R⁰DAD. An important subgroup is RN=CH-CH=NR (R⁴DAD). If R’ is not specifically stated, the abbreviation R⁰DAD is used, implying proton substitution at the α,α’-diimine carbon atoms.
unambiguous assignment.\textsuperscript{[119]} Due to their non-innocent behaviour, diazadienes can relieve the metal of excess electron density or supply it when required and can thus act as “electronic buffers” in redox reactions. A side effect of these strong $\sigma$-donor and $\pi$-acceptor properties is that the ligand itself is susceptible to electrophilic and nucleophilic attack.\textsuperscript{[116, 120]} The degree of activation is controlled by electronic and steric properties, which can be tuned by the substituents at the diazadiene ligand. The correlation between the reactivity of the complex and the substituents at the diazadiene has been demonstrated by Kaim and et al.\textsuperscript{[121]} Depending on the reaction conditions and the substituents in 1,4-position at the diazadiene, the iridium(III) complex 10 reacts in a different manner with sodium cyanotrihydroborate (Scheme 10).

\begin{center}
\includegraphics[width=\textwidth]{Scheme_10.png}
\end{center}

\textbf{Scheme 10:} Different reactivity of sodium cyanotrihydroborate towards diazadiene iridium(III) complexes 10: i) chloride/hydride exchange, ii) reduction in non-protic solvents, iii) partial or full hydrogenation in protic solvents.

A simple chloride/hydride exchange occurs when the diazadiene ligand is not easily reduced or hydrogenated, e.g. when $R = o$-tolyl (11). Under non-protic conditions, the non-aromatic diazadiene complex 10 ($R = c$-hexyl) can undergo a reduction to an enediamido iridium(III) complex 12. In contrast, under protic conditions, the partially (mono)imino(mono)amino complex or fully hydrogenated ethylenediamine complex 13 were obtained. The latter reaction can simply be considered to be the reverse process of the oxidative dehydrogenation of coordinated amines and will be referred to as reductive hydrogenation.

Zelewsky et al. studied the stereochemistry of the reductive hydrogenation of a diazadiene ruthenium(II) complex.\textsuperscript{[122]} They demonstrated that the formed ethylenediamine ligand of the ruthenium(II) complex can adapt all possible configurations, but with a strong preference for the $\Lambda\cdot R,R/\Delta\cdot S,S$ pair. Although the intermediate of the hydrogenation reaction, the partially hydrogenated
(mono)imino(mono)amino complex, was detected in low concentration by $^1$H NMR spectroscopy, it could not be isolated.

The hydrogenation of binuclear diazadiene complexes with molecular hydrogen has been studied by Vrieze et al. (Scheme 11).\textsuperscript{123-126}

![Scheme 11: Hydrogenation of dinuclear complex 14 with molecular deuterium, giving 15.][125]

The binuclear [FeRu(CO)$_6$((iPr)$_2$DAD)] complex 14 reacts with molecular hydrogen or deuterium exclusively to the trans substituted ethylenediamine complex 15.\textsuperscript{125} Hydrogenation of mononuclear diazadiene complexes with molecular hydrogen has yet to be demonstrated.

In contrast to numerous well-studied transition metal diazadiene complexes, the chemistry of diazadiene iridium complexes remained largely unexplored.\textsuperscript{116} The main contribution in this field has been made by Garralda et al., who prepared iridium(I) diazadiene olefin complexes\textsuperscript{127-129} and Kaim whose work largely focused on iridium(III) diazadiene complexes (vide supra).\textsuperscript{121, 130, 131}

Recently, redox-active olefin rhodium(I) and iridium(I) diazadiene complexes [M(trop$_2$DAD)]OTf 18\textsubscript{a,b} and [M(trop$_2$MeDAD)]OTf 19\textsubscript{a,b} have been synthesized by our group.\textsuperscript{132} Due to their non-innocent behaviour, the reduction occurs at the ligand rather than at the metal centre (Scheme 12).

![Scheme 12: Synthesis of the diazadiene-olefin rhodium(I) and iridium(I) complexes 18\textsubscript{a,b} and 19\textsubscript{a,b} and the radical complexes 20\textsubscript{a,b}.][132]

Structural analysis by X-ray diffraction has shown that 18\textsubscript{a,b} are best described as rhodium(I) and iridium(I) diazadiene complexes (Scheme 9A). Both complexes can be reduced quantitatively to the neutral complexes [M(trop2DAD)] 20\textsubscript{a,b} at the lowest potentials reported to date for any 16-electron rhodium and iridium complex.\textsuperscript{132} Wave and pulse EPR spectroscopy in combination with DFT calculations have shown that the unpaired electron is predominantly located on the diazadiene entity.
in accordance with structure B (Scheme 9). In contrast to iridium(I) amine complexes 6b-9b, a wide range of ligands can coordinate to the iridium(I) diazadiene complex 18b, forming square pyramidal complexes (Scheme 13).[89]

Scheme 13: Possible structures for the pentacoordinated complexes which form upon reaction of 18b with different nucleophiles. The benzo groups of the trop unit have been omitted for clarity.

Noteworthy is the differing reactivity of the rhodium(I) and iridium(I) diazadiene complexes towards nucleophiles. In contrast to 18b, the rhodium(I) diazadiene complex 18a does not react with a fifth ligand. In this example, the redox-active diazadiene ligand might act as an “electronic buffer”, accepting electron density from the metal, shifting it into the backbone of the ligand. To which degree the electron shift occurs and which of the resonance structures D, E and F best describes this phenomenon has yet to be investigated.

Despite their interesting properties and reactivity, diazadiene complexes have found only moderate attention as catalysts. They have been used as “spectator” ligands in catalysis, e.g. as catalysts for C-H activation,[133-138] olefin polymerization,[139-141] hydrogenation[142] and hydrogen transfer reactions.[128, 129, 143] A cooperative behaviour of these ligands in catalysis has yet to be reported.

4 Oxygen Donor Olefin Complexes in Catalysis

Few late transition metal alkoxides and amides have been isolated, compared to numerous early transition metal complexes and until recently their chemistry remained relatively unexplored.[144] The most widely accepted explanation for the relative shortage of alkoxide and amide derivatives is that their bonds are characteristically weak as a result of the mismatch between the hard ligands and the soft late transition metal centres.[145] As a result, late transition metal complexes containing metal-nitrogen and metal-oxygen bonds have been proposed as intermediates for a wide range of catalytic industrial[83] and biological processes[20, 146]. Prominent examples for catalytic reactions are the Wacker process[147], hydroamination[148, 149], transfer hydrogenation[150-153] and Oppeauer-type oxidations[154, 155].
New synthetic strategies have made the isolation of complexes with late transition metal-oxygen and nitrogen bonds possible and the number of well-characterized compounds has increased significantly. The oxygen-donor is frequently incorporated into the chelating ligands, which improves the stability of the oxygen-metal bonds in late transition metal complexes. Numerous cationic rhodium(I) and iridium(I) olefin complexes with nitrogen- or phosphorous donor ligands have been described. However, few related stable olefin complexes with oxygen-donor ligands have been reported (Figure 2).

![Diagram of complexes]

Figure 2: Examples of isolated olefin rhodium(I) and iridium(I) complexes with oxygen-donor ligands.

Stable rhodium(I) olefin complexes are obtained with acetylacetone 21, dihydroxy-naphthalene 22a, amine N-oxides 23, acetone 24, phosphine oxides 25 and sulphoxides 26, whereas only two iridium(I) complexes 22b and 27 are presently known. To date, no stable complexes with bidentate oxygen-donor olefin ligands have been reported.

The primary interest in this class of compounds arises from their interesting reactivity and properties, e.g. nitrogen and oxygen based ligands are less sensitive to oxygen than phosphanes. In particular, tri- and tetradeutate amino-olefin ligands form stable complexes with extraordinary catalytic properties. In this context, and with regard to the planned modification of the established [Ir(trop,DACH)]OTf 6b catalyst for the alcohol oxidation, the synthesis of oxygen-donor olefin ligands is of interest.
5 Thesis Objective and Outline

Homogeneous catalysis is a research area that has grown enormously in recent years and plays a significant role today in both bulk and fine chemical production. The ideal homogeneous catalyst is facile and cheap in synthesis, stable (with sufficiently long life time with respect to deactivation) and active (in a very selective manner, with a high functional group tolerance). Apart from the metal employed, the ligand synthesis adds enormously to the cost of a catalytic system. In light of this consideration, the ligand’s structure should be simple and easy to modify.

Modification of the existing catalytic system [Ir(tropolDACH)]OTf 6b, to improve the yield and scope of the alcohol oxidation, will form a focal point of this work. In general, there are two approaches to the modification of a catalytic system: the first focuses on modifying the catalytic system by trial and error, the second on obtaining a full understanding of the catalytic cycle. Although trial and error modification can give important hints at the role of the metal, the ligand and other additives in the reaction mechanism, only the second approach will make the development of tailor-made catalysts with customized properties possible. Both approaches were used in this work to develop a 2nd generation catalyst for the oxidation of alcohols.

The first part of this work will focus primarily on the modification of the backbone of the ligand framework of 6b. Due to the fact that no chiral induction was observed with the enantiomerically pure ligand, future ligand syntheses will focus on the use of achiral building blocks for economic reasons. Figure 3 displays possible new frameworks for the 2nd generation catalyst.

Figure 3: New frameworks (type I and II) of possible catalysts for the dehydrogenation of alcohols.\(^3\)

The electronic and steric properties of the framework will change dramatically due to the nature of the donor atoms (either oxygen or nitrogen) and the substituents on the backbone of the ligand. Ligand-type I is a bidentate ligand whereas ligand-type II has a tetridentate framework similar to 6b but its backbone will be non-substituted. In addition to the syntheses of these ligands and their complexes, their catalytic activity will be assessed in the dehydrogenation of alcohols.

\(^3\) E is used to denote a donor atom, in this case an oxygen or a nitrogen atom.
We are convinced that a complete understanding of the mechanism of the [Ir(trop$_2$DACH)]OTf 6b catalyzed oxidation will pave the way for the development of a more efficient and selective 2$^\text{nd}$ generation catalyst. Encouraged by the excellent results with 6b, we set out to explore and understand the fundamental role of its ligand and the other reagents added in the catalytic cycle. Based on the working hypothesis that the assignments of the aminyl radical complexes [Ir(trop$_2$DACH-2H)] 8a,b are wrong, the second part will focus on the correct assignment of the observed paramagnetic species. As the absence of the chiral induction of 6b could be explained by the loss of chirality through oxidative dehydrogenation of the amine ligand, the ability to promote the oxidative dehydrogenation of 6a,b and the type II complexes will be intensively studied by means of NMR and EPR spectroscopy (Scheme 14).

Scheme 14: Possible oxidative dehydrogenation of [M(trop$_2$DACH)]OTf 6a,b and related complexes of type II.

The oxidative dehydrogenation should lead to the formation of coordinated (mono)imines or diazadienes, similar to [M(trop$_2$DAD)]OTf 18a,b that have been recently synthesized by our group.

Based on the results from part one and two, a 2$^\text{nd}$ generation catalyst will be designed in the last part of this thesis. In this context, its catalytic activity and chemoselectivity will be investigated, as well as the scope and the versatility of the new catalytic system. Emphasis will be placed on the oxidation of polyols in order to move closer to the main goal: the selective oxidation of carbohydrates. In addition, the electronic properties and the reaction mechanism of the 2$^\text{nd}$ generation catalyst will be studied in more detail.
II. Stable Alcohol- and Ether-Olefin Rhodium(I) Complexes
Stable Alcohol- and Ether-Olefin Complexes

Numerous cationic rhodium(I) and iridium(I) olefin complexes with nitrogen- and phosphorus-donor ligands have been described. However, few examples of stable olefin complexes with oxygen-donor ligands have been prepared so far (see Introduction). The primary interest in this class of compounds arises from their interesting electronic properties and reactivity; like nitrogen-based ligands, oxygen donors are less sensitive to oxygen than phosphanes. Inspired by the excellent results with the amino-olefin catalyst [Ir(trop$_2$DACH)]OTf 6b in the field of alcohol oxidation, we hope to enhance the catalytic activity by modifying the framework of the established trop$_2$DACH ligand 28. At the same time, one of the main challenges will be to find a balance between the stability of the catalyst (and its insensitivity to impurities) and its high catalytic activity.

In this chapter, the synthesis of bidentate oxygen-donor olefin ligands and their coordination to rhodium(I) will be described. Furthermore, their catalytic activity in the alcohol oxidation will be assessed.

1 Syntheses of Alcohol- and Ether-Olefin Ligands

The straightforward syntheses of the alcohol- and ether-olefin ligands tropOH 30 and tropOEt 32 are outlined in Scheme 15. The reaction conditions for each step are given in the scheme caption.

Scheme 15: Synthesis of the bidentate ligands tropOH 30 and tropOEt 32. Reaction conditions: i) NaBH$_4$, MeOH, 15 h, rt; ii) SO$_2$Cl$_2$, dichloromethane, 12 h, rt; iii) K$_2$CO$_3$, EtOH, 6 h, reflux.

Commercially available dibenzotropolone 29 was used as the starting material for the syntheses of ligands 30 and 32. Sodium tetrahydroborate in methanol was used to reduce 29 to corresponding alcohol 30 in 90% yield. For the synthesis of the ether-olefin ligand 32, thionyl chloride was used to transform 30 into the corresponding chloride 31. Subsequently, 31 was reacted with ethanol in the presence of potassium carbonate, yielding the desired ether-olefin ligand 32. This three-stage synthesis produced 32 with an overall yield of 52%.

---

$^{4}$ In order to distinguish between metal complexes with the same ligand, we use the following letters: a for rhodium and b for the iridium complexes, e.g. [Rh(trop$_2$DACH)]OTf will be referred to as 6a and [Ir(trop$_2$DACH)]OTf as 6b.
At room temperature, only exchange-broadened NMR resonances of 30 and 32 were observable on the NMR timescale. Low temperature NMR spectroscopy of 32 confirmed the formation of endo- and exo-isomers in a 1:4 ratio, a distribution that arises from inversion at the 5-position of the seven-membered ring. In the boat conformation adopted by the dibenzocycloheptatrienyl moiety, the substituent can be in either the equatorial or the axial position. The prefix endo refers to the isomer with the substituent in the axial position, i.e. endo with respect to the carbon-carbon double bond. Conversely, the exo prefix refers to the isomer with the substituent in the equatorial position.

Recrystallization of tropOEt 32 from n-hexane gave colourless crystals suitable for structural analysis using X-ray diffraction methods (Figure 4). Selected bond lengths and angles are given in the figure caption.

![ORTEP plot of exo-tropOEt 32](image)

Figure 4: ORTEP plot of exo-tropOEt 32. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): O1-C1 = 1.422(7), O1-C9 = 1.274(7), C9-C10 = 1.471(8), C4-C4' = 1.321(7), C1-O1-C0 = 118.70(5).

Figure 4 displays the crystal structure of the major isomer exo-32, in which the ether substituent is orientated away from the seven-membered ring. This ring adopts a boat-conformation, giving the ligand mirror symmetry. Crystals of the endo-isomer were not obtained.
2 Syntheses of Rhodium(I) Complexes

The simple synthesis of $[\text{Rh(tropOH)}_2]\text{OTf}$ 33 and $[\text{Rh(tropOEt)}_2]\text{PF}_6$ 34 is outlined in Scheme 16.

Scheme 16: Synthesis of the rhodium(I) complexes $[\text{Rh(tropOH)}_2]\text{OTf}$ 33 and $[\text{Rh(tropOEt)}_2]\text{PF}_6$ 34.

Both rhodium(I) complexes were obtained by reacting four equivalents of the ligand with the rhodium precursor $[\text{Rh}_2(\mu-\text{Cl})_2(\text{C}_2\text{H}_4)_4]$ in the presence of thallium(I) triflate or hexafluorophosphate. While the synthesis of 33 (carried out in THF) took only 1 h at room temperature, 16 h of refluxing in dichloromethane were required for the synthesis of 34. Recrystallization by slow diffusion of n-hexane into a concentrated dichloromethane solution of 33 gave yellow crystals in 90% yield. The same approach was used for obtaining red crystals of 34 in 94% yield.

2.1 Molecular Structures of the Complexes

The slow diffusion of n-hexane into a solution of $[\text{Rh(trop}_2\text{OH})]\text{OTf}$ 33 or $[\text{Rh(trop}_2\text{OEt})]\text{PF}_6$ 34 in dichloromethane yielded crystals suitable for X-ray diffraction analysis. The molecular structures of the cationic 16-electron complexes 33 and 34 are shown in Figure 5 and Figure 6. Selected bond length, bond angles are given in the figure captions.
Figure 5: ORTEP plot of \([\text{Rh(tropOH)}_2]\text{OTf}^3\). Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms (apart from the hydroxyl protons) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh-O1 = 2.109(2), Rh-O2 = 2.117(2), Rh-C4 = 2.127(2), Rh-C5 = 2.128(2), Rh-C19 = 2.118(2), Rh-C20 = 2.122(2), Rh-ct1 = 2.002, Rh-ct2 = 2.008, C4-C5 = 1.406(3), C19-C20 = 1.398(3), O1-Rh-O2 = 86.3(7), ct1-Rh-ct2 = 96.3, O1-Rh-ct1 = 88.8, O2-Rh-ct2 = 88.6, O3-H31 = 1.817, O5-H32 = 1.858, \(\varphi\) = 1.6.

Figure 6: ORTEP plot of \([\text{Rh(tropOEt)}_2]\text{PF}_6^3\). Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms and the counter ion (PF\(_6^\text{−}\)) are omitted for clarity. Selected bond length [Å] and angles [°]: Rh-O1 = 2.169(3), Rh-O2 = 2.128(3), Rh-C4 = 2.141(4), Rh-C5 = 2.107(4), Rh-C19 = 2.124(4), Rh-C20 = 2.102(4), Rh-ct1 = 2.005, Rh-ct2 = 1.989, C4-C5 = 1.401(6), C19-C20 = 1.428(6), O1-C31 = 1.453(5), O2-C33 = 1.474(6), O1-Rh-O2 = 91.1(1), ct1-Rh-ct2 = 95.9, O1-Rh-ct1 = 91.1, O2-Rh-ct2 = 90.6, \(\varphi\) = 15.8.
Stable Alcohol- and Ether-Olefin Complexes

In both complexes, two bidentate ligands coordinate to the rhodium atom in a chelating fashion, in which the olefins are cis to each other. At 91.1°, the O1-Rh-O2 bond angle of 34 is slightly wider than the 86.3° angle of 33. Hydrogen bonding between the hydroxyl protons and the oxygen atoms of the triflate counter ion can be observed in 33, which is consistent with the findings for the corresponding amino-olefin complex cis-[Rh(tropNH₂)₂]OTf 9a. The degree of distortion can be expressed by the intersection angle φ, which is defined by the planes running through the rhodium atom, the donor atom E and the olefin centroid of each bidentate ligand. The coordination sphere around the rhodium atom is almost perfectly pseudo-planar⁵ for [Rh(tropOH)₂]OTf 33 (φ = 1.6°). In contrast, the steric hindrance of the ethyl groups in [Rh(tropOEt)₂]PF₆ 34 prohibits a pseudo-planar geometry: the ethyl groups face opposite sides of the complex, leading to a distorted coordination sphere around the rhodium centre (φ = 15.8°). The Rh-C₅ bond lengths are different in rhodium(I) complex 34, as the coordination sphere is distorted around the rhodium atom. As a result of unequal metal-to-olefin backdonation, the Rh-C₅ and Rh-C₂0 bonds are shorter than those of Rh-C₄ and Rh-19; the C₅-M-C₅ triangle is best described as scalene (vide infra Figure 7). Furthermore, metal-to-ligand backdonation in complex 34 leads to an elongation of the coordinated olefins from 1.32 Å in the free ligand to 1.41 Å. Selected bond lengths [Å] and angles [°] of the rhodium(I) complexes 33 and 34 are compared to those of cis-[Rh(tropNH₂)₂]OTf 9a and trans-[Rh(tropOEt)₂]PF₆ 35a⁶ in Table 1.

Table 1: Selected bond lengths [Å] and angles [°] of cis-[Rh(tropOH)₂]OTf cis-33, cis-[Rh(tropOEt)₂]PF₆ cis-34, cis-[Rh(tropNH₂)₂]OTf cis-9a and trans-[Rh(tropOEt)₂]PF₆ trans-35a.

<table>
<thead>
<tr>
<th></th>
<th>M-E⁷</th>
<th>M-ct</th>
<th>C=C₅</th>
<th>φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[Rh(tropOH)₂]OTf cis-33</td>
<td>2.109(2), 2.117(2)</td>
<td>2.002, 2.008</td>
<td>1.406(3), 1.398(3)</td>
<td>1.6</td>
</tr>
<tr>
<td>cis-[Rh(tropOEt)₂]PF₆ cis-34</td>
<td>2.169(3), 2.128(3)</td>
<td>2.005, 1.989</td>
<td>1.401(6), 1.428(6)</td>
<td>15.8</td>
</tr>
<tr>
<td>cis-[Rh(tropNH₂)₂]OTf cis-9a</td>
<td>2.093(7), 2.109(7)</td>
<td>2.051, 2.061</td>
<td>1.414(12), 1.363(12)</td>
<td>2.4</td>
</tr>
<tr>
<td>trans-[Rh(tropp⁶)₂]PF₆ trans-35a</td>
<td>2.298(14)</td>
<td>2.150</td>
<td>1.398(5)</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The Rh-ct distance of 33 and 34 (average 2.00 Å) is similar to comparable rhodium(I) olefin complexes 21 with coordinated acetylacetone ligands.⁵⁶ Although the Rh-O (average 2.13 Å) bond length is slightly longer than for these complexes (average 2.06 Å), the overall bond lengths are comparable to

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⁵ To simplify the description of the structure of the olefin complexes, the expression pseudo-planar will be used to refer to the geometrical arrangement in which the metal, the two donor atoms and the two olefin centroids lie on a plane.

⁶ trop⁶ = (S)-dibenzo[a,d]cyclo-heptene-5-syl)diphenylphosphane

⁷ E is used to denote a donor atom, in this case an oxygen, nitrogen or phosphorus atom.
the Rh-ct and Rh-N distances of 9a. In contrast, the Rh-P and Rh-ct bond lengths of trans-[Rh(tropp$^{\text{Rh}}$)$_2$]PF$_6$ 35a differ significantly from the structurally related complexes 33, 34 and 9a, a result which is consistent with the NMR data. The elongation of these bonds can be attributed to the competition of the phosphorus and the olefin for the same metal orbital, which results in reduced metal-to-olefin back-donation.

2.2 NMR Spectroscopy of Rhodium(I) and Iridium(I) Olefin Complexes

NMR spectroscopy can give insight into the structure of the trop-type olefin complexes and in particular, as the rotation of the coordinated olefins is blocked, valuable information about bond strength and geometry can be obtained. The value of the coordination shift approximately corresponds to the strength of the metal-olefin interaction.$^{[170]}$ To facilitate future analyses of rhodium(I) and iridium(I) olefin complexes, the correlation between their symmetry and the resulting NMR spectroscopic and crystallographic data will now be discussed. The interactions observed can be applied to the majority of complexes described in this work. The olefinic $^1$H NMR resonances can be used to distinguish between organometallic species with mirror symmetry and those with reduced symmetry. Consideration of the molecular symmetry can predict or explain the observed olefinic proton resonances in the $^1$H NMR spectrum, as well as the M-C$_{\text{ol}}$ and M-ct bond distances determined by single crystal X-ray diffraction analysis. Figure 7 displays the most common symmetry elements found in rhodium(I) and iridium(I) complexes with trop-type olefin ligands: either two bidentate or a tetradentate ligand.
Complex A has two perpendicular planes of mirror symmetry, $\sigma_v$ and $\sigma_h$, which both intersect the metal centre. The horizontal plane of symmetry, $\sigma_h$, passes through the olefin centroids, the donor atoms and the metal centre. In this arrangement, since the olefinic carbons are all equidistant from the metal centre, the four M-C$_{\text{ol}}$ bonds are of equal length. This equivalence results in a singlet for the olefinic protons in the $^1$H NMR spectra. In contrast, in complex B the two donor atoms coordinated to the metal centre are different ($A \neq B$) which leads to a reduction in symmetry: the loss of the mirror plane $\sigma_v$ perpendicular to plane $\sigma_h$ ($A$, Ct1, M, Ct2, B). As a result, two distinct singlets can be observed for the olefinic protons $H_a$ and $H_b$ in the $^1$H NMR spectra. Furthermore, the bond distances M-C$_{\text{ol}}^a$ differ from those of M-C$_{\text{ol}}^b$ and consequently, the metal-centroid distances of the olefins will be different (M-ct1 $\neq$ M-ct2).

Further reduction in symmetry, resulting from the distortion of the pseudo-planar ligand geometry of the coordination sphere, leads to more complex $^1$H NMR spectra. The degree of distortion is expressed by the intersection angle $\phi$, defined by the planes running through the metal centre, the donor atom (either A or B) and the olefin centroid of each side of the complex. In complexes C and D, the olefin centroids and donor atoms A and B are twisted out of plane, resulting in a further reduction of symmetry. Due to its identical donor atoms, complex C possesses $C_2$ symmetry, leading to two distinct doublets in the $^1$H NMR spectrum for the olefinic protons and to two pairs of M-C$_{\text{ol}}$ bonds of differing bond length (M-C$_{\text{ol}}^a \neq$ M-C$_{\text{ol}}^b$). The C$_{\text{ol}}^a$-M-C$_{\text{ol}}^b$ triangles are best described as scalene. However, both M-ct bonds are of equal length. In contrast, due to the non-identical donor moieties A and B, no

Figure 7: Schematic representation of the symmetry operations in rhodium(I) and iridium(I) complexes with bidentate or tetradentate trop-type olefin ligands. The symmetry of the complexes decreases stepwise from A to D.
symmetry elements are present in complex D, resulting in four distinct doublets for each olefinic proton in the $^1$H NMR spectra and four different M-C$_a$ bond lengths.

### 2.2.1 NMR Spectroscopy of the Rhodium(I) Alcohol- and Ether-Olefin Complexes

Theoretically, the formation of cis- and trans-isomers is possible upon coordination of two bidentate ligands to the rhodium atom. Nevertheless, spectroscopic characterization of [Rh(tropOH)$_2$]OTf 33 and [Rh(tropOEt)$_2$]PF$_6$ 34 in solution indicated that one isomer was formed exclusively, i.e. only a single data set was observed in the $^1$H and $^{13}$C NMR spectra. The olefinic protons give only a singlet in 33, indicating a symmetric structure. At room temperature, the rhodium(I) complex 34 gave exchange-broadened proton signals for the olefinic and benzylic protons; sharp NMR signals were only obtained for measurements taken at low temperatures. In comparison to 33, two doublets were observed for the olefinic protons of the ether-olefin complex 34, suggesting a distorted coordination sphere around the rhodium(I) centre (vide supra). Selected $^1$H and $^{13}$C chemical shifts of 33 and 34 are compared with the structural related complexes cis-[Rh(tropNH)$_2$]OTf 9a$^{[89]}$ and cis-[Rh(tropp$^{\text{ph}}$)$_2$]PF$_6$ 35a$^{[171]}$ in Table 2.

Table 2: Selected $^1$H and $^{13}$C chemical shifts of [Rh(tropOEt)$_2$]PF$_6$ 34, [Rh(tropOH)$_2$]OTf 33, cis-[Rh(tropNH)$_2$]OTf cis-9a and cis-[Rh(tropp$^{\text{ph}}$)$_2$]PF$_6$ cis-35a measured in CD$_2$Cl$_2$. Chemical shifts given on the δ scale are expressed in ppm. The coordination shifts $\Delta$δ$_\text{coord} = \delta_{\text{complex}} - \delta_{\text{ligand}}$ calculated with respect to the major conformer of the free ligand, are given in brackets.

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ $^1$H$_{\text{rot}}$</th>
<th>$\delta$ $^1$H$_{\text{NH/ OH}}$</th>
<th>$\delta$ $^{13}$C$_{\text{C}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[Rh(tropOEt)$_2$]PF$_6$ 34</td>
<td>3.84 (-3.34)</td>
<td>4.83 (-2.35)</td>
<td>67.0 (-64.5)</td>
</tr>
<tr>
<td>cis-[Rh(tropOH)$_2$]OTf 33</td>
<td>4.30 (-2.87)</td>
<td>8.64 (6.08)</td>
<td>72.3 (-58.6)</td>
</tr>
<tr>
<td>cis-[Rh(tropNH)$_2$]OTf cis-9a</td>
<td>4.55 (-2.50)</td>
<td>3.74 (1.69)</td>
<td>78.5 (-52.6)</td>
</tr>
<tr>
<td>cis-[Rh(tropp$^{\text{ph}}$)$_2$]PF$_6$ cis-35a</td>
<td>6.50 (-0.25)</td>
<td>106.1 (-25.0)</td>
<td></td>
</tr>
</tbody>
</table>

The low frequency shift of the olefinic protons and carbons of the complexes 33, 34 and cis-9a upon coordination indicates strong metal-to-ligand back-donation. In comparison, the back-donation to the olefins of cis-35a is rather weak (see coordination shifts in brackets in Table 2). A plausible explanation is that the phosphorus atom, as a good σ-donor and π-acceptor, competes with the olefins for the same metal orbitals, leading to less back-donation from the metal to the olefins. The proton resonance of the alcohol function of complex 33 is shifted to higher frequencies upon coordination to the rhodium atom, which is consistent with the observed acidification of coordinated amines.$^{[1]}$ Compared to the amine group of 9a, the resonance of the hydroxyl group of 33 is shifted to substantially higher
Stable Alcohol- and Ether-Olefin Complexes

frequencies; this implied stronger acidity of the coordinated alcohol could potentially allow deprotonation (*vide infra*).

In recent times, transition metal NMR spectroscopy (TM NMR) has become an important tool in organometallic chemistry as it provides valuable information on the electronic structure around the metal centre generated by the ligands in the first coordination sphere.\[^{172, 173}\] The sensitivity of the transition metal resonance to small steric and electronic changes in the coordination sphere is high. To a large extent, the donor atom in the first coordination sphere of the rhodium atom determines the \(^{103}\)Rh chemical shift, as demonstrated by complexes \(\text{33, cis-9a and cis-35a}\) (Table 3).

Table 3: \(^{103}\)Rh chemical shift of rhodium(I) complexes \(\text{34, 33, cis-9a, cis-35a and trans-35a}\) measured in CD\(_2\)Cl\(_2\). Chemical shifts given on the \(\delta\) scale are expressed in ppm.

<table>
<thead>
<tr>
<th></th>
<th>(\delta) (^{103})Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{cis-[Rh(tropOEt)}_2]\text{PF}_6\text{cis-34)}</td>
<td>1411</td>
</tr>
<tr>
<td>(\text{cis-[Rh(tropOH)}_2]\text{OTf cis-33)}</td>
<td>1315</td>
</tr>
<tr>
<td>(\text{cis-[Rh(tropNH)}_2]\text{OTf cis-9a)}</td>
<td>957</td>
</tr>
<tr>
<td>(\text{cis-[Rh(tropp}^\text{Ph})_2]\text{PF}_6\text{cis-35a)}</td>
<td>-253</td>
</tr>
<tr>
<td>(\text{trans-[Rh(tropp}^\text{Ph})_2]\text{PF}_6\text{trans-35a)}</td>
<td>210</td>
</tr>
</tbody>
</table>

As the complexes \(\text{cis-33, cis-9a and cis-35a}\) all exist as \(\text{cis}\) isomers with an almost pseudo-planar structure, the influence of the complex’s geometry is negligible. This allows the electronic influences of the donor atoms O, N and P on the \(^{103}\)Rh chemical shift to be studied. The shielding of the rhodium atom is largely determined by the HOMO-LUMO separation, this energy difference follows the spectrochemical series: strong field ligands, such as tropp\(^\text{Ph}\), shield the rhodium atom effectively, resulting in a lower \(^{103}\)Rh chemical shift.\[^{172}\] Compared to tropNH\(_2\), the tropOH ligand \(\text{30}\) is a weaker ligand field; the rhodium atom in \(\text{33}\) is less shielded than in \(\text{9a}\), which results in a higher \(^{103}\)Rh chemical shift for \(\text{33}\).

The observed \(^{103}\)Rh chemical shifts of \(\text{33}\) and \(\text{9a}\) are in the typical range for complexes with oxygen \((\delta\) \(^{103}\)Rh = 1287 - 1372) and nitrogen ligands \((\delta\) \(^{103}\)Rh = 751 - 1035).\[^{173}\] The small deviation from this range for complex \(\text{34}\) might be a result of geometric changes: \(^1\)H and \(^{13}\)C NMR data indicate that the geometry around the metal center is distorted. Furthermore, the geometric influence of \(\text{cis-}\) and \(\text{trans-}\) isomers causes a substantial difference in the \(^{103}\)Rh chemical shift of several hundred ppm, as observed for \(\text{cis-35a}\) and \(\text{trans-35a}\).
Stable Alcohol- and Ether-Olefin Complexes

For complexes 33 and 34, spectroscopic characterization in solution and solid-state characterization proved that only the isomer in which the olefins are located in the mutual cis position was formed. The exclusive formation of the rhodium(I) complexes 33 and 34 as cis-isomers can be attributed to the anti-symbiotic behaviour of the rhodium atom and the trans-influence of the olefin ligands.\(^{[174, 175]}\) The coordination of a soft base to a soft acid, in particular platin group metals, lowers the affinity of the trans site to the soft base for another soft base.\(^{[85]}\) When coordinated to the soft transition metal, two olefins in a mutually trans position have a destabilizing effect, since they compete for the same metal orbital. Replacing the oxygen atom for a softer donor, such as nitrogen or phosphorus, increases the likelihood of trans isomer formation. In fact, the formation of both isomers has been observed for the complexes \([\text{Rh(tropNH}_{2}\text{)O}]\text{OTf}\) and \([\text{Rh(tropp}^\text{P}^\text{H})_{2}]\text{PF}_6\) 35a. In contrast to the oxygen atom, as the phosphorus and the olefin are both soft donor atoms with strong trans-influences, the formation of the cis isomer is no longer favoured and the formation of both isomers becomes possible.

### 3 Synthesis of a Rhodium(I) Alkoxide-Olefin Complex

In general, late transition metal alkoxide complexes are synthesized by metathesis of metal chloride or triflate complexes or by oxidative addition reactions.\(^{[83]}\) In the case of amino-olefin complexes, the di(amido) complexes can be obtained by deprotonation of the corresponding amine complexes.\(^{[1, 87, 176]}\)

The following di(alkoxide) complex \(\text{Na[Rh(tropO)_{2}]}\) 36 was prepared in this manner (Scheme 17).

\[
\begin{align*}
\text{Na}\quad\text{OTf} \\
\text{THF, rt} \\
\end{align*}
\]

Scheme 17: Deprotonation of the rhodium(I) complex 33 to the di(alkoxide)-olefin complex \(\text{Na[Rh(tropO)_{2}]}\) 36.

As indicated by the chemical shift of the alcohol function, the hydroxyl groups of \([\text{Rh(tropOH)}_{2}]\text{OTf}\) 33 were highly acidic and could be deprotonated by two equivalents of sodium tert-butoxide, forming the di(alkoxide) complex 36 within five minutes. A colour change from yellow to orange was observed upon deprotonation. The resulting deprotonated complex was then characterized in situ by NMR spectroscopy. Selected \(^1\text{H}, \quad^{13}\text{C}\) and \(^{103}\text{Rh}\) chemical shifts of 33 and 36 are shown in Table 4.
Table 4: Selected $^1$H, $^{13}$C and $^{103}$Rh shifts of [Rh(trop$_2$OH)]OTf 33 and the corresponding deprotonated complexes Na[Rh(trop$_2$O)] 36 measured in [D$_8$]-THF. Chemical shifts are given on the $\delta$ scale in ppm. The coordination shifts $\Delta\delta_{\text{coord}} = \delta_{\text{complex}} - \delta_{\text{ligand}}$, calculated with respect to the major conformer of the free ligand, are given in brackets.

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ $^1$H$_{\text{ol}}$</th>
<th>$\delta$ $^1$H$_{\text{OH}}$</th>
<th>$\delta$ $^{13}$C$_{\text{ol}}$</th>
<th>$\delta$ $^{103}$Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[Rh(tropOH)$_2$]OTf 33</td>
<td>4.64 (-2.53)</td>
<td>8.64 (6.08)</td>
<td>72.6 (-58.3)</td>
<td>1297</td>
</tr>
<tr>
<td>cis-Na[Rh(tropO)$_2$] 36</td>
<td>3.73 (-3.44)</td>
<td>-</td>
<td>71.2 (-59.7)</td>
<td>1065</td>
</tr>
</tbody>
</table>

The $^1$H NMR spectrum of the double deprotonated di(alkoxide) complex Na[Rh(trop$_2$O)] 36 showed only a singlet for the olefinic protons, implying a symmetric coordination sphere around the metal centre. Upon deprotonation, the $^1$H resonances of the olefins trans to the alkoxide groups are shifted to lower frequencies, as they accept the increased electron density of the metal centre. In contrast, the $^{13}$C resonances are shifted only marginally upon deprotonation. It has previously been shown that the deprotonation of coordinated amino-olefin ligands leads to shorter Rh-N bond distances, shifting the $^{103}$Rh signal to lower frequencies. The same observation was made for the alcohol-olefin complex: double deprotonation of 33 resulted in a $^{103}$Rh chemical shift from 1297 to 1065 ppm for the di(alkoxide) complex 36, implying a shorter Rh-O bond length.

4  Reactivity Studies

4.1  Redox Chemistry - Electrochemical Investigations

Previously, we showed that phosphano- and amino-olefin ligands are suitable for stabilizing low oxidation states at transition metal centres.\cite{1, 171, 177-180} Given that the redox waves are at least quasi-reversible, cyclic voltammograms can provide valuable information on the relative stability of the redox-active species. Using this technique, the stability and the reactivity of the rhodium(I) complexes [Rh(tropOH)$_2$]OTf 33 and [Rh(tropOEt)$_2$]PF$_6$ 34 was assessed. Figure 8 shows the resulting cyclic voltammogram of 34 in THF.
The rhodium(I) complex 34 can be electrochemically reduced in two reversible one-electron transfer steps. This electron transfer initially generated the paramagnetic complex [Rh(tropOEt)₂] 37 (E₁½ = -1.56 V) before finally producing the [Rh(tropOEt)₂]⁻ 38 (E₂½ = -2.14 V). The two (quasi)-reversible redox waves of 34 demonstrate the stabilizing properties of the ether-olefin ligand. At present, no attempts have been made to synthesize and isolate the neutral paramagnetic species 37 or the rhodate 38. In contrast to 34, the electrochemical reduction of 33 and [Rh(tropNH₂)₂]OTf 9a gave only non-reversible redox waves and led to decomposition in the case of 33. As a result, only the half-wave redox potentials of 34 and trans-[Rh(tropp₃Ph)₂]PF₆ 35a are compared in Table 5.

Table 5: Half-wave redox potentials E₁½ and E₂½ [V] and potential difference ΔE = E₁½ - E₂½ of 34 and the reference complex.

<table>
<thead>
<tr>
<th></th>
<th>E₁½ [V]</th>
<th>E₂½ [V]</th>
<th>ΔE [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[Rh(tropOEt)₂]PF₆ 34</td>
<td>-1.56</td>
<td>-2.14</td>
<td>0.58</td>
</tr>
<tr>
<td>trans-[Rh(tropp₃Ph)₂]PF₆ 35a</td>
<td>-1.00</td>
<td>-1.19</td>
<td>0.19</td>
</tr>
</tbody>
</table>

The redox potentials of [Rh(tropOEt)₂]PF₆ 34 are cathodically shifted when compared to 35a. The influence of the donor/acceptor properties of the donor atoms on the complexes’ redox potential cannot be assessed due to the different geometry of the rhodium(I) complexes. No attempt was made to synthesize and isolate the neutral paramagnetic species 37 or the [Rh(tropOEt)₂]⁻ 38.
4.2 Reaction with Nucleophiles

A key intermediate in the catalytic cycle of alcohol oxidation is assumed to be the formation of a pentacoordinated complex with the substrate (see Introduction). As a result, the ability of [Rh(tropOH)$_2$]OTf 33 and [Rh(tropOEt)$_2$]PF$_6$ 34 to form pentacoordinated complexes with different nucleophiles was investigated. For the cationic 16-electron complexes [M(tropp$^{ph}$)$_2$]PF$_6$ 35a,b, it has been shown that they exist as cis- and trans-isomers, which interconvert in coordinating solvents via a pentacoordinated intermediate (Scheme 18).[^181]

![Scheme 18: Cis/trans-isomerisation of 16-electron [M(tropp$^{ph}$)]$^+$ complexes 35a,b through a pentacoordinated intermediate (ML(tropp$^{ph}$))$^+$ (L = acetonitrile, n = +1; L = Cl, n = 0).](image)

The amino-olefin rhodium(I) complex trans-9a is able to form trigonal-bipyramidal adducts with acetonitrile and chloride, but does not undergo cis/trans-isomerisation through a pentacoordinated complex. In contrast, no pentacoordinated species can be detected for the corresponding cis-9a by NMR spectroscopy.[^89]

Similar to the behaviour of cis-9a (vide supra), cis-[Rh(tropOH)$_2$]OTf 33 did not form a stable pentacoordinated species or the trans-isomer. In the presence of acetonitrile, the slow formation of the free ligand and an unidentified black precipitate was observed. In contrast, upon the addition of lithium chloride (or acetonitrile) to cis-[Rh(tropOEt)$_2$]OTf 34, the trans-isomer of 34 could be observed by NMR spectroscopy. Unfortunately, the conversion of 34 to a black precipitate and free ligand was too fast to make the characterization of trans-34 possible and as a result, the cis/trans-isomerisation via a pentacoordinated species cannot be ruled out. In all likelihood, the release of the free ligands tropOH 30 and tropOEt 32 upon addition of a strongly coordinating fifth ligand to 33 and 34 is a result of both the oxygen-donor and the olefins being weak ligands.

[^181]: Scheme 18: Cis/trans-isomerisation of 16-electron [M(tropp$^{ph}$)]$^+$ complexes 35a,b through a pentacoordinated intermediate (ML(tropp$^{ph}$))$^+$ (L = acetonitrile, n = +1; L = Cl, n = 0).
[^89]: Similar to the behaviour of cis-9a (vide supra), cis-[Rh(tropOH)$_2$]OTf 33 did not form a stable pentacoordinated species or the trans-isomer. In the presence of acetonitrile, the slow formation of the free ligand and an unidentified black precipitate was observed. In contrast, upon the addition of lithium chloride (or acetonitrile) to cis-[Rh(tropOEt)$_2$]OTf 34, the trans-isomer of 34 could be observed by NMR spectroscopy. Unfortunately, the conversion of 34 to a black precipitate and free ligand was too fast to make the characterization of trans-34 possible and as a result, the cis/trans-isomerisation via a pentacoordinated species cannot be ruled out. In all likelihood, the release of the free ligands tropOH 30 and tropOEt 32 upon addition of a strongly coordinating fifth ligand to 33 and 34 is a result of both the oxygen-donor and the olefins being weak ligands.
4.3 Catalytic Activity

The catalytic activity of [Rh(tropOH)$_2$]OTf 33 and [Rh(tropOEt)$_2$]PF$_6$ 34 was determined for the oxidation of the inactivated alcohol 1-octanol (Scheme 19).

![Scheme 19: Oxidation of 1-octanol in THF with 0.1 mol% of complex 33 or 34 with p-benzoquinone as co-oxidant.](image)

Both complexes 33 and 34 showed no catalytic activity for the oxidation of 1-octanol. The instability of these complexes in presence of a large excess of a coordinating substrate, such as 1-octanol, might explain this inactivity.

5 Conclusion and Outlook

In this chapter, we presented the first synthesis of stable rhodium(I) complexes with bidentate oxygen-donor olefin ligands. By means of NMR spectroscopic and structural analysis, we showed that the resulting complexes, Rh(tropOH)$_2$]OTf 33 and [Rh(tropOEt)$_2$]OTf 34, are structurally related to the amino-olefin rhodium(I) complex 9a. We also demonstrated that 33 can be doubly deprotonated, yielding the di(alkoxide) complex [Rh(tropO)$_2$]Na 36. Cyclic voltammetric study of the rhodium(I) complexes 33 and 34 revealed that only the ether-olefin ligand 32 was able to stabilize the rhodium atom in low oxidation states.

Even though rhodium(I) complexes 33 and 34 exist as stable cis-isomers in weakly coordinating solvents such as THF, they decompose upon the addition of acetonitrile or lithium chloride. As expected, given their instability toward coordinating ligands, none of the rhodium(I) complexes catalyzed the alcohol oxidation.

Overall, these results highlight the influence of the complex’s stability in the presence of a coordinating substrate on its catalytic activity. The advantage of the established catalyst [Ir(trop$_2$DACH)]OTf 6b in catalysis seems to be its tetradeinate ligand framework with two strongly binding nitrogen donor atoms. In order to improve this established catalytic system, the synthesis of a
tetradentate ether-amino olefin ligand was targeted, which is expected to combine the stability of amino-olefin complexes, with respect to nucleophiles, with the electronic properties of the oxygen donor. In addition, the focus will turn to the synthesis of a tetradentate amino-olefin ligand of type II (see Introduction Figure 3) to study the catalytic behaviour of its complexes.
III. Design of New Tetradsentate Amino-Olefin Ligands
Design of New Tetradeinate Amino-Olefin Ligands

The modification of the [Ir(trop$_2$DACH)]OTf 6b$^8$ system, in particular the ligand framework, will now take centre stage. Despite the use of this enantiomerically pure catalyst, no chiral induction during the alcohol oxidation was observed (see Introduction). Consequently, our focus will turn to the synthesis of achiral ligands for the design of a 2$^{nd}$ generation catalyst. Previous results revealed that complexes with bidentate ether- and alcohol-olefin ligands of type I (see Introduction Figure 3) were not catalytically active in the oxidation of alcohols, largely due to their instability in the presence of a coordinating substrate. In an attempt to resolve this problem, new tetradeinate ethylenediamine- and aminoethanol-based olefin ligands will be synthesized and then coordinated to rhodium(I) and iridium(I) metal centres. The resulting complexes are expected to combine the catalytic activity and stability of 6b with the new electronic and steric properties of the modified framework.

1 Ethylenediamine as Building Block for Amino-Olefin Ligands

1.1 Synthesis of the Tetradeinate Amino-Olefin Ligand

Ethylenediamine based ligands with sterically demanding substituents at the nitrogen atoms are commonly synthesized in two stages: the diazadiene is formed first by reacting an amine with a 1,2-dicarbonyl compound, e.g. glyoxal, and then it is reduced to the corresponding ethylenediamine derivative.$^{[182]}$ Unfortunately, as trop$_2$DAD cannot be reduced, this approach could not be used to synthesize a trop-substituted ethylenediamine ligand. In response to this limitation, a new synthesis strategy was developed to synthesize $N,N'$-bis(5H-dibenzo[a,d]cyclohepten-5-yl)-1,2-diaminoethane (trop$_2$DAE) 39 in a single step (Scheme 20).

![Scheme 20: Synthesis of the tetradeinate amino-olefin ligand trop$_2$DAE 39. Reaction conditions: i) toluene, 2h, reflux.](image)

Under inert conditions, the reaction of tropCl with $N,N'$-bis(trimethylsilyl)ethylenediamin gave the tetradeinate ligand trop$_2$DAE 39 in 75% yield. The absence of sterically demanding substituents at the backbone of the ligand resulted in a fast interconversion of the ligand on the $^1$H NMR timescale at

---

$^8$ In order to distinguish between metal complexes with the same ligand, the following letters were used: a for rhodium and b for the iridium complexes, e.g. [Rh(trop$_2$DACH)]OTf will be referred to as 6a and [Ir(trop$_2$DACH)]OTf as 6b.
room temperature and as a result, only exchange-broadened proton signals could be observed in the $^1$H NMR spectrum. At lower temperatures, the proton signals sharpened sufficiently enough to distinguish three sets of signals in the $^1$H NMR spectrum with a ratio of 1 : 1 : 2. This distribution might arise from inversion at the 5-position of the seven-membered ring. As each trop unit can assume either an endo or exo conformation, the ligand can adopt either an endo-endo, exo-endo or exo-exo conformation. Furthermore, rapid inversion at the nitrogen atoms could give rise to different diastereomers. While the diastereomers of bis(trop$^\text{ph}$)ethane$^{178}$ could be separated by fractional crystallisation, all attempts to separate the isomers of the nitrogen-analogue remained unsuccessful.

1.2 Synthesis of the Complexes

The reaction of the ligand trop$_2$DAE 39 with organometallic precursors of rhodium(I) and iridium(I) in the presence of thallium(I) hexafluorophosphate gave the corresponding complexes [M(trop$_2$DAE)]PF$_6$ 40a,b in excellent yields (Scheme 21).

\[
\text{[Rh}_2(\mu_2-\text{Cl})_2(\text{C}_2\text{H}_4)_4] \text{ or [Ir}_2(\mu_2-\text{Cl})_2(\text{coe})_4]}
\]
TIPF$_6$, THF, rt
- 2 TICI

\[
\text{PF}_6
\]

\[
rac-40a,b
\]

\[
meso-40a,b
\]

\[
dr = 62 : 38 \ rac-40a : meso-40a
\]

\[
dr = 90 : 10 \ rac-40b : meso-40b
\]

Scheme 21: Diastereoselective synthesis of the rhodium(I) and iridium(I) complexes [M(trop$_2$DAE)]PF$_6$ rac-40a,b and meso-40a,b.

Two stereogenic centres result, in addition to those created by coordination of the olefins to the metal centre, once the ligand coordinates to a metal centre in a tetradentate fashion: as the two nitrogen atoms in the complex bind to four different substituents, they can have SS or RR (rac-40a,b) and SR or
Design of New Tetradeionate Amino-Olefin Ligands

RS (meso-40a,b) configurations. Furthermore, the conformation of the non-planar five-membered metallocycle can either form a puckered ring or a symmetric envelope (Scheme 22).

\[
\text{puckered-ring } \delta \quad \text{symmetric envelope} \quad \text{puckered-ring } \lambda.
\]

Scheme 22: Main conformations for five-membered metallocycles.

The envelope conformation constrains the protons at the nitrogen atoms to the same side of the complex. The resulting meso-40a,b has mirror symmetry \( \sigma \), and is hence achiral. Pairwise inequivalent olefinic protons are expected: the olefinic protons above the pseudo-planar geometry (ct1, N, M, N, ct2) experience a slightly different chemical environment than the olefinic protons orientated towards the opposite site of the complex. In contrast to the meso-complex, the protons on the nitrogen atoms of the puckered ring formation are on opposite sides of the complex, resulting in a \( C_2 \)-symmetry. This compound, referred to as rac-40a,b, is chiral and can form \( \delta \)- and \( \lambda \)-enantiomers. As a result of the puckered-ring conformation of the backbone of the ligand, a significant twist of the olefin centroids and the nitrogen atoms out of the pseudo-planar plane can be assumed (see Figure 7C). Unequal backdonation of the metal to the twisted olefins is expected to produce a shorter and a longer \( M-C \) bond, resulting in a scalene \( C_{\text{sc}}=M-C_{\text{ol}} \) triangle. As a result of the \( C_2 \)-symmetry in this arrangement, pairwise inequivalent olefinic protons resonances are expected. As the coordination sphere around the metal centre in the rac-complexes is expected to deviate more from planarity, a larger difference between the \(^1\)H chemical shifts can be expected for the two inequivalent olefinic protons compared the meso-complexes.

The energy barrier for the \( \delta-/\lambda \)-conversion is within the range 2 - 4 kcal/mol and as a result, rapid interchange between the two enantiomers cannot be stopped. Although facile inversion at the amine nitrogen atoms precluded separation of the different conformers of the ligand, the coordination to a transition metal precursor was diastereoselective, forming rac- and meso-complexes 40a,b.

1.2.1 NMR Spectroscopy of the Complexes

As expected, two diastereomers meso-40a,b and rac-40a,b were formed, as indicated by two sets of proton signals in the \(^1\)H NMR spectra. The rhodium(I) complexes rac-40a and meso-40a showed broad signals at room temperature, suggesting that the coordinated ligand interconverts between the \( \delta \) and \( \lambda \) conformation over the envelope form as an intermediate. Low temperature NMR spectroscopy at
268 K gave sharp NMR spectra. In contrast, rac-40b and meso-40b complexes gave sharp NMR signals at room temperature (Figure 9).

![NMR spectrum](image)

**Figure 9:** Section of the $^1$H NMR of [Ir(tropol2DAE)]PF$_6$ 40b, measured in [D$_8$]-THF at room temperature.

Based on these structural considerations (see Chapter II, Figure 7) and 2D NMR spectroscopic studies, the doublets of the olefinic protons at 3.95 and 4.72 ppm were assigned to rac-40b and those at 4.29 and 4.43 ppm to meso-40b (marked with X). This assignment is in agreement with the analogue rac- and meso-phosphano-olefin complexes previously synthesized.$^{[178, 180]}$ The diastereomeric ratio (dr) is used to measure the degree of diastereoselectivity. It was calculated by integrating the olefinic proton peaks of the $^1$H NMR spectrum. The reaction of ligand 39 with [Ir$_2$(μ-Cl)$_2$(CO)$_4$] was more diastereoselective, $\text{dr} = 90 : 10$ (rac- : meso-40b), than with the rhodium precursor, $\text{dr} = 62 : 38$ (rac- : meso-40a). In both cases the formation of the rac-40a,b was favoured, as the steric hindrance is reduced when the protons of the nitrogen atoms point in opposite directions. Selected $^1$H and $^{13}$C NMR spectroscopic data of the complexes rac-40a,b and meso-40a,b are listed in Table 6.
Table 6: Selected $^1$H- and $^{13}$C- chemical shifts of trop$_2$DAE 39 and its complexes [M(trop$_2$DAE)]PF$_6$ 40a,b, measured in [D$_6$]-THF. Chemical shifts given on the $\delta$ scale are expressed in ppm.

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ $^1$H$_{ol}$</th>
<th>$\delta$ $^{13}$C$_{ol}$</th>
<th>$\delta$ $^1$H$_{cri}$</th>
<th>$\delta$ $^{13}$C$_{cri}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>39$^{[a]}$</td>
<td>7.23</td>
<td>131.6</td>
<td>2.92</td>
<td>48.0</td>
</tr>
<tr>
<td>rac-40a</td>
<td>4.30</td>
<td>71.4</td>
<td>2.37</td>
<td>50.6</td>
</tr>
<tr>
<td></td>
<td>5.40</td>
<td>84.0</td>
<td>3.08</td>
<td></td>
</tr>
<tr>
<td>meso-40a</td>
<td>4.91</td>
<td>77.1</td>
<td>2.31</td>
<td>45.7</td>
</tr>
<tr>
<td></td>
<td>81.7</td>
<td>3.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>rac-40b</td>
<td>3.95</td>
<td>54.6</td>
<td>2.50</td>
<td>52.2</td>
</tr>
<tr>
<td></td>
<td>4.71</td>
<td>69.3</td>
<td>3.52</td>
<td></td>
</tr>
<tr>
<td>meso-40b</td>
<td>4.29</td>
<td>61.4</td>
<td>2.33</td>
<td>46.7</td>
</tr>
<tr>
<td></td>
<td>4.43</td>
<td>66.9</td>
<td>3.24</td>
<td></td>
</tr>
</tbody>
</table>

$^{[a]}$ Only chemical shifts of the major conformer are given.

NMR data of olefin transition metal complexes can give valuable insight into their structure, in particular, their bond strength and geometry. The low-frequency shift of the olefinic $^1$H and $^{13}$C NMR signals upon coordination highlights a significant metallacyclopropane character for the olefins metal bond, which results from strong metal-to-ligand back-donation. Compared to the corresponding rhodium complexes, the olefinic $^1$H and $^{13}$C signals of meso-40b and rac-40b were shifted to lower frequencies, indicating a higher degree of back donation for the iridium complexes. The significantly different chemical shifts of the olefinic protons of the rac-complexes 40a,b imply a strongly distorted coordination sphere around the metal centre. In contrast, the olefinic proton resonances of the meso-complexes 40a,b were nearly equivalent, suggesting that the complexes have an almost pseudo-planar structure. The protons at the backbone are diastereotopic, which results in distinct sets of signals, as one pair of the diastereotopic protons is shifted to higher frequencies compared to the free ligand 39 (Table 6).

1.2.2 Molecular Structures of the Complexes

The molecular structure of the cationic tetracoordinated 16-electron [M(trop$_2$DAE)]PF$_6$ complexes rac-40a and meso-40a,b was determined by X-ray diffraction analysis. Suitable crystals of 40a were grown by diffusion of n-hexane into a concentrated THF solution. The disorder observed in the crystal structure of 40a can be attributed to the presence of both diastereomers, i.e. a mixture of rac-40a and meso-40a. Both diastereomers of 40a are displayed in Figure 10: the solid bonds in the backbone of the ligand refer to meso-40a and the dashed bonds to rac-40a. Selected bond length and angles are given in the figure caption.
The structure of rac-40a and meso-40a confirmed that ligand 39 binds to the metal centre in a tetradeinate fashion. The structure of rac-40a showed that the five-membered RhN₂C₂ chelate has a puckered ring conformation: the N1a-Rh-N2 bite angle (82.1 °) is in the typical range of 81 – 83 °. In comparison, the five-membered metallocycle of meso-40a has a bite angle of 75.6 ° and the ethyl backbone is folded by 42.0 ° along the N-N vector. The Rh-N (average 2.09 Å) and Rh-ct (average 2.03 Å) distances of 40a are typical for amino-olefin rhodium(I) complexes, such as [Rh(trop₂DACH)]OTf 6a. As expected given the ¹H NMR data, the geometry of rac-40a around the rhodium atom is distorted (φ = 22.1 °), whereas the envelope conformation of meso-40a allowed for a coordination sphere closer to pseudo-planar (φ = 9.3 °).

Crystallization of 40b by slow diffusion of n-hexane into a concentrated dichloromethane solution gave exclusively crystals of the meso-40b isomer (Figure 11). Selected bond length and angles are given in the figure caption.
Design of New Tetradeinate Amino-Olefin Ligands

Figure 11: ORTEP plot of meso-[Ir(trop₂DAE)]OTf meso-40b. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms (apart from the amine protons) and the counter ion (PF₆) are omitted for clarity. Selected bond length [Å] and angles [°]: Ir-N1 = 2.088(2), Ir-N2 = 2.085(2), Ir-C4 = 2.147(2), Ir-C5 = 2.147(2), Ir-C19 = 2.141(2), Ir-C20 = 2.124(2), Ir-ct1 = 2.009, Ir-ct2 = 2.026, C4-C5 = 1.422(4), C19-C20 = 1.429(3), C31-N1 = 1.495(3), C32-N2 = 1.500(3), C31-C32 = 1.544(4), N1-Ir-N2 = 76.9(1), N1-Ir-ct1 = 92.8, N2-Ir-ct2 = 92.5, ct1-Ir-ct2 = 97.8, φ = 2.7.

The steric stress imposed by the ligand conformation was clearly reflected in the structure of meso-40b. Compared to meso-40a, the corresponding iridium complex had an almost perfect pseudo-planar geometry (φ = 2.7 °), with a comparable N-M-N bite angle of 76.9 °. The ethyl backbone of meso-40b was folded more than meso-40a, with 48.4 ° along the N-N vector. Selected structural data of rac-40a and meso-40a,b are compared in Table 7.

Table 7: Selected bond length [Å] and angles [°] for [M(trop₂DAE)]PF₆ 40a,b complexes.

<table>
<thead>
<tr>
<th></th>
<th>M-N</th>
<th>M-ct</th>
<th>C=C_C₄</th>
<th>N-M-N</th>
<th>N-M-Ct</th>
<th>Ct-M-Ct</th>
<th>φ</th>
</tr>
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<tbody>
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<td>rac-40a</td>
<td>2.130(4)</td>
<td>2.019</td>
<td>1.404(6)</td>
<td>82.1(2)</td>
<td>90.9</td>
<td>98.5</td>
<td>22.1</td>
</tr>
<tr>
<td></td>
<td>2.072(3)</td>
<td>2.033</td>
<td>1.402(4)</td>
<td></td>
<td>92.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>meso-40a</td>
<td>2.074(6)</td>
<td>2.019</td>
<td>1.404(6)</td>
<td>75.6(2)</td>
<td>93.2</td>
<td>98.5</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td>2.072(3)</td>
<td>2.033</td>
<td>1.402(4)</td>
<td></td>
<td>92.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>meso-40b</td>
<td>2.088(2)</td>
<td>2.009</td>
<td>1.422(4)</td>
<td>76.9(1)</td>
<td>92.8</td>
<td>97.8</td>
<td>2.7</td>
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<tr>
<td></td>
<td>2.085(2)</td>
<td>2.026</td>
<td>1.429(3)</td>
<td></td>
<td>92.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As expected from the NMR spectra, the elongation of the olefins from 1.34 Å in the free ligand to 1.42 Å upon coordination to iridium is greater than the corresponding rhodium complex 40a. Furthermore, the M-C₄ bond lengths in rac-40a differ significantly: Rh-C4 and Rh-C19 bonds are significantly shorter
than those of Rh-C5 and Rh-C20. This difference in bond strength is a result of unequal backdonation
due to the distorted geometry around the rhodium atom (Figure 7C). In contrast, the bond lengths of
meso-40b are almost identical.

1.3 Reaction with Base – Deprotonation of Amine Complexes

The deprotonation reactions of the amino-olefin complexes 40a,b are of interest as the deprotonation
of [Ir(trop2DACH)]OTf 6b to the di(amido) complex K[Ir(trop2DACH)-2H] 7b was thought to be the first
step of the catalytic cycle, which enables the oxidation to the aminyl radical complex
[Ir(trop2DACH)-2H] 8b (see Introduction).[2, 3] The deprotonation of the cationic complexes 40a,b with
one equivalent of NaO^tBu in THF cleanly yielded the neutral amino-amido complexes
[M(trop2DAE-1H)] 41a,b. Double deprotonation with two equivalents of NaO^tBu in THF gave the
di(amido) complexes Na[M(trop2DAE-2H)] 42a,b (Scheme 23).

![Scheme 23. Deprotonation reaction of [M(trop2DAE)]PF_6 40a,b with NaO^tBu in THF. The benzo groups at the trop unit were omitted for clarity.](image)

The deprotonated complexes were not isolated but characterized in situ by NMR spectroscopy. In
addition to selected ^1H and ^13C NMR data of 41a,b and 42a,b, the ^103Rh chemical shifts are listed in
Table 8.
The spectroscopic data of 41a,b and 42a,b has a high degree of similarity to the data of the [M(trop_2DACH-1H)] 43a,b and K[M(trop_2DACH-2H)] 7a,b complexes.\[1,3, 87\] Single deprotonation of 40a,b destroys the C_2-symmetry of the rac-40a,b and the C_2-symmetry of the meso-40a,b complexes. As the amine nitrogen atom is bound to four different substituents in the resulting complex, (R)- or (S)- configurations at the stereogenic centre are possible. Evidently, the two enantiomers of 41a,b cannot be distinguished by NMR spectroscopy. However, broad proton signals at room temperature indicate rapid proton exchange between the two nitrogen atoms, which precludes separation of the enantiomers. Furthermore, as the complex has a reduced symmetry, a double set of patterns was obtained in the NMR spectra. Upon deprotonation, the ¹H and ¹³C resonances of the olefins in trans position to the amide are shifted to lower frequencies as they accept the increasing electron density of the metal centre. The hydrogen atoms at the CH₂ groups are diastereotopic and yield four multiplets in the ¹H-NMR spectrum. In this conformation, each hydrogen atom is expected to have larger couplings constants (> 8 Hz) due to vicinal trans (dihedral angle ≈ 180 °) and geminal couplings and one small coupling constant (< 5 Hz) due to vicinal cis (dihedral angle ≈ 60 °) coupling. In accordance to previous findings, the resonance of the remaining NH proton is shifted to lower frequencies upon deprotonation, implying that the second hydrogen is less acidic and the abstraction requires a stronger base.\[87\]
In comparison, the $^1$H NMR spectra of the di(amido) complex Na[M(trop$_2$DAE-2H)]$_{42a,b}$ show singlets for the olefinic and benzylic protons and a broad signal for the four protons at the CH$_2$ group. The singlet set of peaks observed in the $^1$H NMR spectra is a direct result of rapid inversion at the deprotonated nitrogen atoms on the NMR timescale.

The $^{103}$Rh chemical shift was 862 ppm for rac-40a and 773 ppm for meso-40a, which both lie in the typical range of 750-1060 ppm for cationic 16-electron amino-olefin complexes of type [Rh(COD)(NR$_3$)$_2$]X. According to model calculations by Elsevier and Bühl, the Rh-N distance has the most significant influence on the $^{103}$Rh chemical shift. Increasing the Brønsted basicity of the nitrogen atoms by deprotonation results in shorter Rh-N bond distances, better shielding and a low frequency shift of the $^{103}$Rh resonance.$^{[173]}$ Accordingly, a $^{103}$Rh chemical shift of 656 ppm was observed for the amido-amino complex [M(trop$_2$DAE-1H)]$_{41a}$ and 523 ppm for the di(amido) complex Na[M(trop$_2$DAE-2H)]$_{42a}$.

2 Aminoethanol as a Building Block for a New Tetradentate Olefin Ligand

An ether-amino olefin ligand was designed for reactivity studies. This ligand was intended to combine the features of the ligand systems presented so far: the bidentate ether-olefin ligand tropOEt$_{32}$ and the tetradentate amino-olefin ligands trop$_2$DAE$_{39}$ and trop$_2$DACH$_{28}$.

2.1 Synthesis of the Ether-Amino-Olefin Ligand

The straightforward synthesis of the ether-amino-olefin ligand trop$_2$EAA$_{46}$ is outlined in Scheme 24. The reaction conditions of each step are given in the scheme caption.

Under inert conditions, ethylchloroacetate was reacted with tropNH$_2$ in the presence of a base to give 44 in 81% yield. In the second step, the carboxylic ester was reduced by lithium aluminiumhydride to give the corresponding alcohol 45 in average yield. In the last step, 45 was reacted with trop$_2$Cl under
basic conditions to give the tetradeutate ether-amino olefin ligand trop₂EEA 46 in 84% yield. As the synthesis of trop₂EEA 46 is composed of three reaction steps, it is more complex than the synthesis of trop₂DAE 39; the overall yield for the three steps is 45%. The flux of the ligand was fast on the NMR timescale at room temperature. Low temperature NMR at 233 K showed the co-existence of three distinct conformations in a 1.8 : 4.5 : 1 ratio.

2.2 Syntheses of the Rhodium(I) and Iridium(I) Complexes

Reacting trop₂EEA with organometallic precursors of rhodium(I) and iridium(I) in THF and thallium(I) hexafluorophosphate produced the [M(trop₂EEA)]PF₆ 47a,b complexes in excellent yields (Scheme 25).

Scheme 25: Synthesis of the [M(trop₂EEA)]PF₆ complexes (R)-47a,b and their enantiomeric complexes (S)-47a,b.

Once the ligand coordinates to the metal atom in a chelating fashion, the formation of diastereomeric complexes is possible. The complex’s chirality arises from the nitrogen atom, which binds to four different substituents and the coordinated olefins. The complex can therefore have either a (S)- or (R)-configuration at the nitrogen atom. By referring to this stereogenic centre, it is possible to distinguish two enantiomers: (S)-47a,b and (R)-47a,b.

2.2.1 Conformational Analysis of the Complexes by NMR Spectroscopy

The NMR data of the [M(trop₂EEA)]PF₆ 47a,b complexes gave valuable insight into the structure of the complex. Using NMR spectroscopy and the chemical shift of the olefinic protons, CH₂ and NH groups, it was determined that the ligand 46 coordinates to the rhodium or iridium atom in a tetradeutate fashion. Four distinct doublets for the olefinic protons were observed in the ¹H NMR spectra. In accordance with the structural considerations of the complexes 40a,b (Figure 7 and Scheme 22), this result implies that the complex has neither C₂ nor C₃ symmetry and that the coordination sphere around the metal atom is distorted; as a result, a puckered ring conformation for the five-membered metallocycle is assumed. Although the envelope conformation is not observable by NMR spectroscopy, its existence as an intermediate in the exchange between λ and δ conformation cannot be ruled out. Selected ¹H and ¹³C NMR data of the complexes 47a,b are listed in Table 9.
Design of New Tetradentate Amino-Olefin Ligands

Table 9: Selected $^1$H and $^{13}$C chemical shifts of trop$_2$EEA 46 and its complexes [M(trop$_2$EEA)]PF$_6$ 47a,b, measured in [D$_8$]-THF. Chemical shifts given on the $\delta$ scale are expressed in ppm.

<table>
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<th>$\delta$ $^1$H$_{NH}$</th>
<th>$\delta$ $^1$H$_{CH2N}$</th>
<th>$\delta$ $^1$H$_{OH2}$</th>
<th>$\delta$ $^1$H$_{OH}$N</th>
<th>$\delta$ $^{13}$C$_{OH}$N</th>
<th>$\delta$ $^1$H$_{OH}$O</th>
<th>$\delta$ $^{13}$C$_{OH}$O</th>
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<td>46$^{[a]}$</td>
<td>2.92</td>
<td>3.05</td>
<td>3.91</td>
<td>7.22</td>
<td>131.4</td>
<td>7.25</td>
<td>131.4</td>
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<td>47a</td>
<td>5.89</td>
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<td>3.88</td>
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<td>75.2</td>
<td>4.58</td>
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<td>4.01</td>
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<td>65.0</td>
<td>5.29</td>
<td>83.1</td>
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<tr>
<td>47b</td>
<td>6.64</td>
<td>2.59</td>
<td>4.28</td>
<td>4.07</td>
<td>49.1</td>
<td>4.28</td>
<td>62.7</td>
</tr>
<tr>
<td></td>
<td>3.17</td>
<td>4.34</td>
<td>4.34</td>
<td>59.4</td>
<td>4.68</td>
<td>67.4</td>
<td></td>
</tr>
</tbody>
</table>

$^{[a]}$ Only the chemical shifts of the major conformer are given.

Upon coordination, the NH proton resonance is shifted to higher frequencies, which is consistent with the acidification of this group. The proton and carbon signals for the olefinic unit of 47b are shifted to lower frequencies compared to 47a. This observation confirms the expected increase in metal-to-ligand back-donation.

As four different substituents are bound to the nitrogen atom, the adjacent CH$_2$ group is diastereotop, resulting in two distinct multiplets in the $^1$H NMR spectrum, as one hydrogen atom is shifted significantly to lower frequencies compared to the free ligand. Although the CH$_2$O group is also diastereotop, the effect is diminished, as it is farther away from the chiral centre. In the spectrum of 47b, the coupling constants cannot be estimated as the CH$_2$O multiplets overlap. Figure 12 displays a section of the $^1$H, $^1$H COSY of 47a, recorded at room temperature in [D$_8$]-THF.
Figure 12: Section of the $^1$H, $^1$H COSY NMR spectrum of 47a, measured in [D$_8$]-THF at room temperature and the conformation of the backbone of the ligand.

In this section of the $^1$H, $^1$H COSY spectrum, as the splitting patterns of the diasterotop hydrogens at the ethyl bridge are well resolved, an exact assignment of each hydrogen is possible. The hydrogens, $H_A$ and $H_B$, couple with each other, with the NH group and with adjacent hydrogens at the CH$_2$O group. In this conformation, each hydrogen is expected to have a larger coupling constant (> 8 Hz) due to a large geminal and vicinal trans coupling (dihedral angle $\approx$ 180 °) and a smaller coupling constant ($\leq$ 5 Hz) due to a vicinal cis coupling (dihedral angle $\approx$ 60 °). However, when the dihedral angle between two vicinal protons is 90 °, it is possible for the coupling constant to be zero (Karplus equation). The hydrogen atom $H_A$ splits up as $dq$, due to the three equally large couplings ($^2J_{HH} = 12.0$ Hz) to $H_B$, $H_C$ and NH and a small coupling to $H_D$ ($^3J_{HH} = 5.5$ Hz). In contrast, $H_B$ gives a $dt$, resulting from two strong couplings to $H_A$ and NH ($^2J_{HH} = 12.0$ Hz) and a small coupling constant to $H_C$ ($^3J_{HH} = 3.0$ Hz). Similarly, the alkyllic hydrogens next to the oxygen split up; the geminal coupling constant ($^2J_{HH} = 9.0$ Hz) for $H_C$ and $H_D$ is smaller than the one between $H_A$ and $H_B$, implying that the influence of the chiral nitrogen diminishes. No coupling between $H_A$ and $H_B$ can be observed, implying that the dihedral angle between them is almost 90 °. The conformation at the backbone of the ligand was determined by using the coupling constants (Figure 12).
2.2.2 Molecular Structures of the Complexes

Single crystals of the 16-electron complexes 47a,b were grown by slow diffusion of n-hexane into a concentrated solution of the complex in THF. The molecular structures are displayed in Figure 13 and Figure 14. Selected bond length and angles are given in the figure caption.

![Molecular Structure Diagram](image)

Figure 13: ORTEP plot of (R){Rh(trop$_2$EEA)}PF$_6$ 47a. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms (apart of the amine hydrogen) and the counter ion (PF$_6$) are omitted for clarity. Selected bond length [Å] and angles [°]:

- Rh-N = 2.081(3), Rh-O = 2.073(2), Rh-C4 = 2.140(3), Rh-C5 = 2.104(2), Rh-C19 = 2.146(2), Rh-C20 = 2.127(2), Rh-ct1 = 2.001, Rh-ct2 = 2.017, C4-C5 = 1.411(5), C19-C20 = 1.408(4), C31-N = 1.420(4), C32-O = 1.459(3), C31-C32 = 1.505(4), O-Rh-N = 80.3(1), N-Rh-ct1 = 91.1, O-Rh-ct2 = 91.1, ct1-Rh-ct2 = 99.0, \(\varphi\) = 13.2.
Design of New Tetradeutate Amino-Olefin Ligands

Figure 14: ORTEP plot of \((\text{R})-[\text{Ir(trop}_2\text{EEA)]PF}_6\) \(47\text{b}\). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms (apart of the amine hydrogen), three THF solvent molecules and the counter ion (\(\text{PF}_6\)) are omitted for clarity. Selected bond length [\(\text{Å}\)] and angles ['']: \(\text{Ir}-\text{N} = 2.065(4)\), \(\text{Ir}-\text{O} = 2.054(3)\), \(\text{Ir}-\text{C}4 = 2.124(4)\), \(\text{Ir}-\text{C}5 = 2.093(5)\), \(\text{Ir}-\text{C}19 = 2.128(4)\), \(\text{Ir}-\text{C}20 = 2.116(4)\), \(\text{Ir}-\text{ct}1 = 1.985\), \(\text{Ir}-\text{ct}2 = 2.000\), \(\text{C}4-\text{C}5 = 1.427(7)\), \(\text{C}19-\text{C}20 = 1.419(7)\), \(\text{C}31-\text{N} = 1.407(7)\), \(\text{C}32-\text{O} = 1.452(6)\), \(\text{C}31-\text{C}32 = 1.512(7)\), \(\text{O}-\text{Ir}-\text{N} = 79.9(1)\), \(\text{N}-\text{Ir}-\text{ct}1 = 91.1\), \(\text{O}-\text{Ir}-\text{ct}2 = 91.4\), \(\text{ct}1-\text{Ir}-\text{ct}2 = 98.5\), \(\phi = 10.3\).

The crystal structures of \(47\text{a,b}\) confirmed that the ligand \(46\) coordinates in a tetradeutate fashion to the metal atom, resulting in a five-membered metallocycle with a puckered ring conformation \(\phi = 13.2^\circ\), \(47\text{b} \phi = 10.3^\circ\). Whereas the enantiomers (\(S\))- \(47\text{a,b}\) and (\(R\))-\(47\text{a,b}\) are not distinguishable by NMR spectroscopy, X-ray diffraction analysis allows the determination of the absolute configuration at the nitrogen atom. Only the crystal structure of (\(R\))-\(47\text{a,b}\) could be obtained. Selected bond lengths and angles of the complexes \(47\text{a,b}\) are compared in Table 10 with related complexes \(34\) and \(40\text{a,b}\).
Design of New Tetradentate Amino-Olefin Ligands

Table 10: Selected bond lengths [Å] and angles [°] of [M(trop₂EEA)]PF₆ 47a,b, [Rh(tropOEt)₂]PF₆ 34 and [M(trop₂DEA)]PF₆ 40a,b.

<table>
<thead>
<tr>
<th></th>
<th>M-E¹</th>
<th>M-ct</th>
<th>C=Col</th>
<th>E-M-E</th>
<th>φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>rac-[Rh(trop₂DEA)]PF₆ rac-40a</td>
<td>2.133(4)</td>
<td>2.019</td>
<td>1.402(6)</td>
<td>81.9(2)</td>
<td>22.1</td>
</tr>
<tr>
<td></td>
<td>2.072(3)</td>
<td>2.032</td>
<td>1.401(5)</td>
<td></td>
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</tr>
<tr>
<td>meso-[Ir(trop₂DEA)]PF₆ meso-40b</td>
<td>2.088(2)</td>
<td>2.009</td>
<td>1.422(4)</td>
<td>76.9(1)</td>
<td>2.7</td>
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<tr>
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<td>2.085(2)</td>
<td>2.026</td>
<td>1.429(3)</td>
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<tr>
<td>(R)-[Rh(trop₂EEA)]PF₆ (R)-47a</td>
<td>2.081(3)</td>
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<td>(R)-[Ir(trop₂EEA)]PF₆ (R)-47b</td>
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<td>1.985</td>
<td>1.427(7)</td>
<td>79.9(1)</td>
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<tr>
<td></td>
<td>2.054(3)</td>
<td>2.000</td>
<td>1.419(7)</td>
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<tr>
<td>cis-[Rh(tropOEt)₂]PF₆ 34</td>
<td>2.169(3)</td>
<td>2.005</td>
<td>1.401(6)</td>
<td>91.1(1)</td>
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</tr>
<tr>
<td></td>
<td>2.128(3)</td>
<td>1.989</td>
<td>1.428(6)</td>
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</tr>
</tbody>
</table>

As expected from the NMR data, the puckered-ring conformation imposes a distorted geometry around the metal centre, similar to those of rac-40a. The M-N and M-O bond lengths in 47a,b are in the same range. When the Rh-O bond length of 47a is compared to those of 34 (Table 10), a substantial shortening is observed, from an average of 2.15 Å in the bidentate ligands to 2.07 Å in the tetradentate ligand. Since all M-Col bond lengths differ significantly, with each coordinated olefin possessing a shorter and a longer M-Col bond, the complexes do not have C₂ symmetry. Furthermore, the M-ct bond distance differs depending on whether the oxygen or nitrogen atom resides trans to the olefin; M-ct1 (trans to the oxygen atom) is about 0.015 Å shorter than M-ct2 (trans to the nitrogen atom). Comparison with the structurally related [M(trop₂DEA)]PF₆ 40a,b complexes does not reveal significant changes in the structure, implying that substituting a nitrogen atom for an oxygen atom has no significant influence on the structure. In contrast, changing from bidentate to tetradentate ligands hugely impacts the structure of the rhodium(I) and iridium(I) complexes, especially the E-M-E bite angle.

¹ E is used to denote a donor atom, in this case an oxygen or a nitrogen atom.
2.3 Deprotonation of the Complexes

The deprotonation of the cationic complexes 47a,b in THF with one equivalent of sodium tert-butoxide quantitatively yielded the neutral amido complex \([\text{M(trop}_2\text{EEA})-\text{1H}] 48a,b\) within a few minutes (Scheme 26).

![Scheme 26: Deprotonation of the amino complexes 47a,b to the corresponding amido complexes 48a,b.]

The deprotonated complexes 48a,b were not isolated but characterized in situ by NMR spectroscopy. The NH signal in the \(^1\text{H}\) NMR vanished upon deprotonation of the coordinated amine. Only a singlet set of peaks can be observed in the \(^1\text{H}\) NMR spectra, due to rapid inversion at the deprotonated nitrogen atom on the NMR timescale. As a result, averaged chemical shifts are obtained, in which the CH\(_2\) groups appear to be no longer diasterotopic, giving a triplet for each CH\(_2\) group (\(^3\)J\(_{\text{HH}}\) \approx 5.0 Hz). Two singlets are observed for the olefinic protons on both sides of complex 48b, pointing to a pseudo-planar coordination sphere around the iridium atom. The chemical shifts of 48a,b show significant similarity to the Na[\text{M(trop}_2\text{DAE})-\text{2H}] 42a,b and Na[\text{M(trop}_2\text{DACH})-\text{2H}] 7a,b complexes (vide supra).

Table 11 lists selected spectroscopic data of the amido complexes 48a,b and compares them to the corresponding cationic complexes 47a,b.

Table 11: Selected \(^1\text{H}, \ ^{13}\text{C}\) and \(^{103}\text{Rh}\) chemical shifts of \([\text{M(trop}_2\text{EEA})]\text{PF}_6\) 47a,b and its deprotonated complexes \([\text{M(trop}_2\text{EEA})-\text{1H}]\) 48a,b, measured in \([\text{D}_8]\)-THF at room temperature. Chemical shifts given on the \(\delta\) scale are expressed in ppm.

<table>
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<th>(\delta^{1}\text{H}_{\text{ol-N}})</th>
<th>(\delta^{13}\text{C}_{\text{ol-N}})</th>
<th>(\delta^{1}\text{H}_{\text{ol-O}})</th>
<th>(\delta^{13}\text{C}_{\text{ol-O}})</th>
<th>(\delta^{103}\text{Rh})</th>
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<td>62.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.17</td>
<td>4.34</td>
<td>4.34</td>
<td>59.4</td>
<td>4.68</td>
<td>67.4</td>
<td></td>
</tr>
<tr>
<td>48b</td>
<td>3.54</td>
<td>3.83</td>
<td>3.78</td>
<td>52.3</td>
<td>3.18</td>
<td>51.2</td>
<td></td>
</tr>
</tbody>
</table>
The electron density at the metal centre increases upon deprotonation because the amide is a more effective \( \sigma \)-donor than the amine. As a result, more electron density is shifted from the metal to the olefin in the trans position of the amide and thus, the chemical shifts of the olefinic protons on the oxygen moiety are shifted to significantly lower frequencies. A similar phenomenon is observed for the \( ^{103}\)Rh chemical shift upon deprotonation: the increased Brønsted basicity of the nitrogen atoms leads to shorter Rh-N bond length and consequently produces a lower frequency of chemical shift.\[^{1}\] The \( ^{103}\)Rh chemical shift changes from 1001 ppm for the amine complex 47a to 839 ppm for the neutral amido complex 48a. Note that the \( ^{103}\)Rh resonance is shifted to higher frequencies upon substitution of a nitrogen for a oxygen atom: [Rh(trop$_2$DAE)]PF$_6$ has a \( ^{103}\)Rh chemical shift of 862 for rac-40a and 773 ppm for the meso-40a. This observation is in agreement with the results of the bidentate amino-olefin and oxygen-donor olefin complexes (Chapter II).

3 Reactivity Studies

3.1 Redox Chemistry - Electrochemical Investigations

The effect of the structure of the meso-40a,b and rac-40a,b on the redox potential is of particular interest. Understanding the factors that influence the redox potential of transition metal complexes is fundamental for the design of customized properties. It has been shown that the structure of copper(II) and nickel(II) complexes\[^{183, 184}\] influences their redox potential.\[^{185, 186}\] By enforcing tetrahedral structures on these usually planar metal(II) complexes, their redox potentials are shifted significantly to less negative values (\( |E_A^0| < |E^0| \)) (Figure 15).

![Figure 15: Schematic representation of the stereochemical influence on the redox potential of transition metal complexes. Left: destabilization of the oxidized form \( |E_A^0| < |E^0| \). Right: destabilization of the reduced form \( |E_A^0| > |E^0| \).](image)

The reason for the anodic shift of the redox potential is that the electronically preferred tetrahedral geometry of the reduced metal(I) complex is more easily obtained when the metal(II) complexes are pre-orientated. This concept has recently been extended to transition metal complexes of the fifth and
Design of New Tetradentate Amino-Olefin Ligands

sixth period by studying the rac- and meso-diastereomers of [Rh(bis(tropp^Ph)propane)]OTf 49.\[178-180\] By using diastereomers, the influence of the complex’s structure on the redox potential can be studied directly because electronic influences such as different donor/acceptor properties are negligible. It has been shown that the enforcement of an unfavourable, almost planar coordination sphere around the metal results in a destabilization of the reduced species by the energy $E_{\text{t red}}$ and leads to a cathodic shift of the reduction potential $|E^0_a| > |E^0|$ (Figure 15).

This concept can be transferred to other transition metal complexes such as [Rh(trop_2DAE)]PF_6 40a. The stacked cyclic voltammograms of 40a and 40b, measured in THF at 233 K, are displayed in Figure 16.

Figure 16: Cyclic voltammogram of a mixture of 40a (solid line) and 40b (dotted line) recorded in THF at 233 K at a scan rate of 100 mV/s with 0.1 M [nBu_4N]PF_6 as electrolyte, referenced versus Fc/Fc^+.

The cyclic voltammogram of [Rh(trop_2DAE)]PF_6 rac/meso-40a shows three (quasi) reversible redox waves with an approximate intensity ratio of 3 : 2 : 1. Due to the known ratio of rac-40a to meso-40a (2 : 1) and previous results for [Rh(bis(tropp^Ph)propane)]OTf, the two waves with higher intensity are assigned to rac-40a and the wave with the more negative potential to meso-40a. The first redox wave of meso-40a is not observed, a result of superposition. In contrast, the cyclic voltammogram of rac/meso-40b showed irreversible redox waves; the same observation was made for [M(trop_2EEA)]PF_6 47 complexes (cyclic voltammograms are not displayed).
The redox potential of 40a and the electrochemical data of the rac-[Rh(trop,DPEN)]OTf 6a,[1] rac-[Rh(trop,DPEN)]OTf 50,[1] [Rh(trop,DAD)]OTf 18a[132] and the phosphorus analogues meso- and rac-[Rh(bis(tropp\(\text{Ph}\))ethane)]OTf 51[178] and [Rh(bis(tropp\(\text{Ph}\))propane)]OTf 49[179] are listed in Table 12.

Table 12: Half-wave redox potentials \(E^\text{1/2}\) and \(E^\text{2/2}\) [V] and potential difference \(\Delta E = E^\text{1/2} - E^\text{2/2}\) of [Rh(trop,DAE)]PF\(_6\) 40a and reference complexes, versus Fc/Fc\(^+\).

<table>
<thead>
<tr>
<th>Donor atom</th>
<th>(E^\text{1/2}) [V]</th>
<th>(E^\text{2/2}) [V]</th>
<th>(\Delta E) [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>rac-[Rh(trop,DAE)]OTf 40a</td>
<td>N</td>
<td>-1.85</td>
<td>-2.23</td>
</tr>
<tr>
<td>meso-[Rh(trop,DAE)]OTf 40a</td>
<td>N</td>
<td>(\sim) -1.9</td>
<td>-2.64</td>
</tr>
<tr>
<td>rac-[Rh(trop,DACH)]OTf 6a</td>
<td>N</td>
<td>-1.83</td>
<td>-2.27</td>
</tr>
<tr>
<td>rac-[Rh(trop,DPEN)]OTf 50a</td>
<td>N</td>
<td>-1.78</td>
<td>-2.24</td>
</tr>
<tr>
<td>rac-[Rh(bis(tropp(\text{Ph}))ethane)]OTf 51a</td>
<td>P</td>
<td>-1.30</td>
<td>-1.68</td>
</tr>
<tr>
<td>meso-[Rh(bis(tropp(\text{Ph}))ethane)]OTf 51a</td>
<td>P</td>
<td>-1.60</td>
<td>-2.00</td>
</tr>
<tr>
<td>rac-[Rh(bis(tropp(\text{Ph}))propane)]OTf 49a</td>
<td>P</td>
<td>-1.46</td>
<td>-1.77</td>
</tr>
<tr>
<td>meso-[Rh(bis(tropp(\text{Ph}))propane)]OTf 49a</td>
<td>P</td>
<td>-1.71</td>
<td>-2.07</td>
</tr>
<tr>
<td>[Rh(trop,DAD)]OTf 18a</td>
<td>DAD</td>
<td>-0.92</td>
<td>-1.65</td>
</tr>
<tr>
<td>[Ir(trop,DAD)]OTf 18b</td>
<td>DAD</td>
<td>-0.70</td>
<td>-1.45</td>
</tr>
</tbody>
</table>

Comparison of the redox potentials of rac- and meso-40a with their phosphorus analogous rac- and meso-[Rh(bis(tropp\(\text{Ph}\))ethane)]OTf 51a shows that the exchange of the donor group from tertiary phosphane to a secondary amine leads to a cathodic shift of approximately 300-400 mV. A plausible explanation for this observation is that the amines in the reduced species are depleting less of the surplus electron density via metal-to-ligand back bonding. As a result, the neutral complex [Rh(trop,DAE)] is stabilized less in comparison to the analogous complexes with phosphorus donor atoms, which are better \(\pi\)-acceptors. In contrast, the redox potential of [Rh(trop,DAD)]OTf 18a with a strong \(\pi\)-acceptor diazadiene ligand is significantly anodically shifted.

The introduction of substituents at the backbone of the ligand has no influence on the redox potential. However, the enlargement of the metallacycles from five- to six-membered in rac/meso-[Rh(bis(tropp\(\text{Ph}\))ethane)]\(^+\) 51a to rac/meso-[Rh(bis(tropp\(\text{Ph}\))propane)]\(^+\) 49a results in a cathodic shift of around 150 mV.
Straightforward explanations for these trends can be given as follows: the cathodic shift of the redox potentials of meso-40a,b shows that more energy is needed for the reduction as the ligand, with its envelope conformation, cannot easily adapt to the electronically preferred tetrahedral geometry of the 17-electron species. In contrast, the puckered ring conformation of the rac-isomers is already pre-orientated, therefore allowing the coordination sphere to adapt more easily to the favourable tetrahedral geometry of the reduced complex. Similar arguments can be used to explain the cathodic shift of the redox potential upon chelate ring enlargement, as five-membered ring are more flexible than six-membered chelate rings.

### 3.2 Catalytic Activity

The catalytic activity of [M(trop₂DAE)]PF₆ 40a,b and [M(trop₂EEA)]PF₆ 47a,b was determined for the oxidation of alcohols, e.g. benzylic alcohol (Scheme 27).

![Scheme 27: Oxidation of benzylic alcohol with 0.1mol% of the complexes 6a,b, 40a,b or 47a,b, 2 mol% NaO'Bu and p-benzoquinone as co-oxidant.](image)

In order to compare the catalytic activity of the different complexes, the oxidation of benzylic alcohol was stopped after 5 min and the conversion was compared to those of the 1st generation catalyst [Ir(trop₂DACH)]OTf 6b. The conversions to the aldehyde for the complexes were determined by gas chromatography and are listed in Table 13.
Design of New Tetradentate Amino-Olefin Ligands

Table 13: Catalytic oxidation of benzylic alcohol by [M(trop₂DAE)]PF₆₄₀a,b and [M(trop₂EEA)]PF₆₄₇a,b in comparison to [M(trop₂DACH)]OTf₆₆a,b. The conversion to benzoic acid is given in percent and was determined by GC.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh(trop₂DACH)]OTf₆₆a</td>
<td>0</td>
</tr>
<tr>
<td>[Ir(trop₂DACH)]OTf₆₆b</td>
<td>92</td>
</tr>
<tr>
<td>[Rh(trop₂DAE)]PF₆₄₀a</td>
<td>0</td>
</tr>
<tr>
<td>[Ir(trop₂DAE)]PF₆₄₀b</td>
<td>&gt; 98</td>
</tr>
<tr>
<td>[Rh(trop₂EEA)]PF₆₄₇a</td>
<td>0</td>
</tr>
<tr>
<td>[Ir(trop₂EEA)]PF₆₄₇b</td>
<td>0</td>
</tr>
</tbody>
</table>

The oxidation of benzylic alcohol with the iridium(I) complex ₄₀b gave complete conversion to the corresponding aldehyde, with no further oxidation to the carboxylic acid or side-product formation. The reaction rate of [Ir(trop₂DAE)]PF₆₄₀b was marginally higher than that of [Ir(trop₂DACH)]OTf₆₆b. It is possible that the absence of the substituents at the backbone in complex ₄₀b facilitates the interaction with the substrate or the formation of the corresponding diazadiene complex by oxidative dehydrogenation (see Introduction). However, the difference between both catalysts is not significant enough to support such an assumption, as it lies within the experimental error of the GC measurement. Overall, it can be concluded that ₄₀b is at least as good a catalyst as ₆b for the dehydrogenation of benzylic alcohol. In contrast, ₄₇b did not catalyze primary alcohol oxidation, even under long reaction times. Similar to the behaviour of [Rh(trop₂DACH)]OTf₆₆a, the rhodium(I) complexes ₄₀a and ₄₇a did not show any catalytic activity.

4 Conclusion

In the first two parts of this chapter, we described an efficient method for synthesizing the ethylenediamine derivative trop₂DAE ₃₉ in a single step and the ether-amino olefin ligand trop₂EEA ₄₆. The coordination of ₃₉ gave rise to diastereomeric complexes rac- and meso-[M(trop₂DAE)]PF₆₄₀a,b and, in the case of ₄₆, to the chiral complexes (S)- and (R)-[M(trop₂EEA)]PF₆₄₇a,b.

In the final part, the reactivity, stability and catalytic activity of the amino-olefin complexes were assessed. The iridium(I) complex ₄₀b showed tremendous catalytic activity in the alcohol oxidation, whereas the related complexes ₄₀a and ₄₇a,b did not catalyze the oxidation of alcohols at all. This result shows how easily catalytic activity can be influenced by changing the electronic properties of the complex by substituting one donor atom for another.
In summery, although the design of a new catalyst was achieved, important questions still remain unanswered: the reason why rhodium(I) complexes do not catalyze alcohol oxidation and whether the drastic drop of catalytic activity can be attributed to differing electronic properties. With regard to the [Ir(trop$_2$DACH)]OTf $6b$ system and the postulated aminyl radical intermediate $8b$ in the catalytic cycle, these issues will be addressed by studying in detail the behaviour of the complexes $6a,b$, $40a,b$ and $47a,b$ under catalysis reaction conditions.
IV. Transition Metal Promoted Oxidative Dehydrogenation of Coordinated Amines
The syntheses of the amino-olefin complexes [M(trop₂DAE)]PF₆ 40a,b and [M(trop₂EEA)]PF₆ 47a,b was described in the preceding chapter. Catalytic studies of these complexes have shown that 40b is at least as good a catalyst as [Ir(trop₂DACH)]OTf 6b for the alcohol oxidation (see Chapter III). In comparison, the corresponding rhodium complexes 40a and 47a,b were not catalytically active. Furthermore, it is significant that no chiral induction could be observed for the oxidation of racemic alcohols, despite the enantiomerically pure catalyst 6b. In this chapter, mechanistic studies were used to determine whether the ligand of 6b undergoes an irreversible transformation prior to catalysis. A plausible explanation is that the chiral information of the ligand backbone is lost during the oxidative dehydrogenation of the di(amine) complex 6b to the diazadiene complex [Ir(trop₂DICH)]OTf 52b, which is assumed to be the “true” catalyst.

The oxidative dehydrogenation of coordinated amines has been reported for a wide range of different transition metal complexes since the 1950s (see Introduction). So far no example of a rhodium(I) mediated and only one iridium(I) promoted oxidative dehydrogenation has been reported. The ability of [M(trop₂DACH)]OTf 6a,b and the structurally related complexes 40a,b and 47a,b to undergo oxidative dehydrogenation of the coordinated amino-olefin ligands was studied in this chapter by NMR and EPR spectroscopy.

1 NMR Spectroscopic Studies

The behaviour of the amino-olefin complexes [M(trop₂DAE)]PF₆ 40a,b, [M(trop₂DACH)]OTf 6a,b and [M(trop₂EEA)]PF₆ 47a,b under catalytic conditions was studied by NMR spectroscopy. The stepwise oxidative dehydrogenation of the non-substituted backbone of 40a,b should give rise to coordinated bis(aldimines) which have a ¹H chemical shift between 8 and 10 ppm for the imine proton HC=N. As their formation is easily identified by NMR spectroscopy, the oxidation of 40a,b was investigated first. Furthermore, the corresponding diazadiene complexes [M(trop₂DAD)]OTf 18a,b are known and have been already fully characterized (see Introduction).

Indeed, the oxidation of [M(trop₂DAE)]PF₆ 40a,b with four equivalents of silver(I) triflate and four equivalents of base led to the formation of [M(trop₂DAD)]OTf 18a,b (Scheme 28).

---

10 In order to distinguish between metal complexes with the same ligand, we use following letters: a for rhodium and b for the iridium complexes, e.g. [Rh(trop₂DAE)]PF₆ will be referred to as 40a and [Ir(trop₂DAE)]PF₆ as 40b.

11 DICH = 1,2-Diamo-cyclohexane
Mechanistic Investigations of the Oxidative Dehydrogenation

In order to verify this conjecture, the specific reaction conditions for the oxidative dehydrogenation were investigated in detail. It was found that 40a,b were not formed if either the oxidizing reagent or
base was added on its own to the amino-olefin complexes 40a,b. The addition of an excess of NaO\textsuperscript{t}Bu produced only the di(amido) complex Na[M(trop\textsubscript{2}DAE-2H)] 42a,b (Scheme 23). Furthermore, when four equivalents of silver(I) triflate and one equivalent of base were added to 40b, only 25% conversion to 18b was observed by NMR spectroscopy. It can therefore be concluded that the oxidation of amino-olefin complexes 40a,b to the corresponding diazadiene complexes 18a,b only takes place if the di(amido) complex 42a,b is formed in situ by deprotonation. These results are in accordance with the findings of Garcia-Herbosa et al.\textsuperscript{[100]} and refute the assumption that spontaneous dihydrogen evolvement occurs under oxidative conditions.

For the reverse process, the reductive hydrogenation of diazadiene complexes, the formation of a mono(imino)mono(amine) complex has been reported (see Introduction).\textsuperscript{[121, 122]} To determine whether the oxidative dehydrogenation immediately produces the diazadiene or if an mono(imino)mono(amine) complex is observable as the intermediate, half the amount of oxidant and base were added to 40b (Scheme 29).

![Scheme 29: Oxidative dehydrogenation of [Ir(trop\textsubscript{2}DAE)]PF\textsubscript{6} 40b to the mono(imino)mono(amine) complex [Ir(trop\textsubscript{2}MIMA)]OTf 53b.](image)

The oxidation of 40b with two equivalents of silver(I) triflate in the presence of two equivalents of NaO\textsuperscript{t}Bu gave [Ir(trop\textsubscript{2}MIMA)]OTf 53b\textsuperscript{12}, which was isolated in quantitative yield. The nitrogen atom is bound to four different substituents and is therefore a stereogenic centre, giving rise to enantiomeric complexes of either (R) or (S) conformation at the nitrogen atom. Instead of silver(I) triflate and base, \(p\)-benzoquinone was also suitable for use as the oxidizing reagent. Under these reaction conditions, the formation of the corresponding [Rh(trop\textsubscript{2}MIMA)]OTf 53a was observed only in low concentration by NMR spectroscopy and could therefore not be isolated.

### 1.1.1 Conformational Analysis of [Ir(trop\textsubscript{2}MIMA)]OTf by NMR Spectroscopy

In accordance with the structural geometry of five-membered metallocycles (Scheme 22), the four olefinic protons of [Ir(trop\textsubscript{2}MIMA)]OTf 53b are inequivalent, resulting in four distinct doublets in the

\textsuperscript{12} MIMA = mono(imino)mono(amine)
Rhodium(I) and Iridium(I) Promoted Oxidative Dehydrogenation of Coordinated Amines

$^1$H spectrum. Based on this NMR data, a puckered ring conformation with a distorted geometry around the iridium atom is assumed. Although, the envelope configuration was not observed by NMR spectroscopy, its existence as an intermediate cannot be ruled out. Selected $^1$H and $^{13}$C NMR data of $53b$ are compared with those of [Ir(trop$_2$DAE)]PF$_6$ $40b$ and [Ir(trop$_2$DAD)]OTf $18b$ in Table 14.

Table 14: Selected $^1$H and $^{13}$C chemical shifts of [Ir(trop$_2$MIMA)]OTf $53b$ in comparison to [Ir(trop$_2$DAE)]PF$_6$ $40b$ and [Ir(trop$_2$DAD)]OTf $18b$, measured in [D$_8$]-THF. Chemical shifts are given on the δ scale are expressed in ppm.

<table>
<thead>
<tr>
<th></th>
<th>$\delta^1$H$_{CH_2}$</th>
<th>$\delta^{13}$C$_{CH_2}$</th>
<th>$\delta^1$H$_{ol}$</th>
<th>$\delta^{13}$C$_{ol}$</th>
<th>$\delta^1$H$_{ol'}$</th>
<th>$\delta^{13}$C$_{ol'}$</th>
<th>$\delta^1$H$_{NH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(trop$_2$DAE)]PF$_6$ $40b$</td>
<td>2.33 3.24</td>
<td>46.7 4.29</td>
<td>61.3 4.43</td>
<td>66.9 6.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ir(trop$_2$MIMA)]OTf $53b$</td>
<td>3.33 4.72</td>
<td>58.4 4.16</td>
<td>62.8 4.43</td>
<td>60.9 7.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ir(trop$_2$DAD)]OTf $18b$</td>
<td></td>
<td>5.64 74.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Upon oxidative dehydrogenation, the $^1$H resonance of NH group was shifted to higher frequencies compared to [Ir(trop$_2$DAE)]PF$_6$ $40b$, implying an acidification of the amine.$^{[1]}$ Furthermore, the $^1$H and $^{13}$C chemical shift of the CH$_2$ group was substantially shifted to higher frequencies due the adjacent imine group. Compared to the diazadiene complex $18b$, the olefinic protons of $53b$ are at lower frequencies. Conformational analysis of the ligand backbone was performed by two-dimensional NMR spectroscopy. Figure 17 displays a section of the $^1$H,$^1$H COSY of $53b$, recorded in [D$_8$]-THF at room temperature.
Rhodium(I) and Iridium(I) Promoted Oxidative Dehydrogenation of Coordinated Amines

Due to the stereogenic nitrogen atom, the adjacent CH$_2$ group is diastereotopic, resulting in two distinct multiplets for each hydrogen atom H$_{A/B}$. Geminal coupling results in a large coupling constant ($^{3}J_{HH} = 18.0$ Hz). Furthermore, H$_{A}$ has a large vicinal “trans” coupling constant to the adjacent NH group ($^{3}J_{HH} = 9.0$ Hz) and H$_{B}$ has a smaller vicinal “cis” coupling constant to the NH group ($^{3}J_{HH} = 4.5$ Hz) and to H$_{C}$ ($^{3}J_{HH} = 1.5$ Hz). Accordingly, the hydrogen atom H$_{A}$ at 3.33 ppm splits up as a doublet of doublets, H$_{B}$ has an eight line splitting pattern and a doublet of doublets is observed for the NH group. Even though the hydrogen atom H$_{C}$ shows only a broadened singlet, it is obvious from the cross peak in the $^{1}$H, $^{1}$H COSY NMR spectrum of 53b that H$_{C}$ and H$_{B}$ undergo coupling (Figure 17). Based on the NMR spectra, it can be concluded that the small coupling constant for the coupling between H$_{C}$ and H$_{B}$ results from a small dihedral angle and that the absence of coupling between H$_{C}$ and H$_{A}$ is due to a dihedral angle of almost 90 ° (Karplus equation). The schematic representation of the conformation at the backbone of the ligand is displayed in Figure 17.

Figure 17: Section of the $^{1}$H, $^{1}$H COSY NMR spectrum of 53b in [D$_{8}$]-THF at room temperature.
1.1.2 Molecular Structure of the Intermediate

Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of $n$-hexane into a concentrated solution of $[\text{Ir(trop}_2\text{MIMA}])\text{OTf 53b}$ in dichloromethane (Figure 18).

![Figure 18: ORTEP plot of $[\text{Ir(trop}_2\text{MIMA}])\text{OTf 53b}$](image)

Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms (apart from those at the backbone and the amine), the counter ion (OTf) and solvent molecules are omitted for clarity. Selected bond length [Å] and angles [°]: Ir-N1 = 2.069(4), Ir-N2 = 2.018(4), Ir-C4 = 2.119(6), Ir-C5 = 2.162(6), Ir-C19 = 2.127(5), Ir-C20 = 2.139(5), Ir-ct1 = 2.009, Ir-ct2 = 2.019, C4-C5 = 1.420(9), C19-C20 = 1.435(8), C31-N1 = 1.457(7), C32-N2 = 1.289(7), C31-C32 = 1.499(7), N1-Ir-N2 = 78.6(2), N1-Ir-ct1 = 92.4, N2-Ir-ct2 = 91.1, ct1-Ir-ct2 = 98.6, $\phi = 11.0$.

In the solid state, 53b has a slightly distorted pseudo-planar geometry around the iridium atom ($\phi = 11.0 \, ^\circ$) and the five-membered metallocycle has an envelope conformation, which is folded 29.9 ° along the N-N vector. As the bond lengths determined by the X-ray diffraction analysis of $[\text{Ir(trop}_2\text{MIMA}])\text{OTf 53b}$ are subject to only small levels of experimental error, the trends in the structural changes for the oxidative dehydrogenation from $[\text{Ir(trop}_2\text{DAE}])\text{OTf 40b}$ to $[\text{Ir(trop}_2\text{DAD}])\text{OTf 18b}$ can be discussed. Scheme 30 compares the crystallographic data of 53b with those of $[\text{Ir(trop}_2\text{DAE}])\text{OTf 40b}$ and $[\text{Ir(trop}_2\text{DAD}])\text{OTf 18b}$. 
Rhodium(I) and Iridium(I) Promoted Oxidative Dehydrogenation of Coordinated Amines

Scheme 30: Schematic representation of the bond length in the backbone upon oxidative dehydrogenation of [Ir(trop₂DAE)]OTf 40b to [Ir(trop₂MIMA)]OTf 53b and [Ir(trop₂DAD)]OTf 18b. The characteristic bond distances are given in Å.

The crystal structure of [Ir(trop₂MIMA)]OTf 53b confirmed that a C=N double bond has been formed in the backbone of the ligand. The bond distances of N1-C31 and C31-C32 lie in the typical range of a single bond and the N2-C32 in the typical range of a double bond. As the diazadiene is a much better π-acceptor than an amine group, the Ir-N bond length shortens significantly upon oxidative dehydrogenation from the amino-olefin complex 40b to the diazadiene complex 18b.

1.1.3 Redox Chemistry - Electrochemical Investigations

Previously, we showed that trop-type diazadiene-olefin and amino-olefin ligands (see Chapter III.3.1) stabilize formally low oxidation states at the metal centre. The ability of the mono(imino)mono(amino)-olefin ligand to stabilize the iridium centre in low oxidation states was investigated by cyclic voltammetry (Figure 19).

Figure 19: Cyclic voltammogram of [Ir(trop₂MIMA)]OTf 53b, recorded in THF at 298 K at a scan rate of 100 mV/s with 0.1 M [nBu₄N]PF₆ as electrolyte, referenced versus Fc/Fc⁺.
The cyclic voltammogram of [Ir(trop₂MIMA)]OTf 53b showed irreversible redox waves, a result consistent with the observations made for [Ir(trop₂DEA)]PF₆ 40b.

2 EPR Spectroscopy

Despite an increasing number of publications, in particular by the groups of Keene,¹⁰⁷,¹¹⁴ Busch¹⁰⁸,¹⁸⁷ and Curtis⁹³,¹⁰⁹,¹¹⁰, the mechanism of the oxidative dehydrogenation is far from being fully understood.⁹⁰ In general, the oxidation of a coordinated amine to an imine can be either regarded as (i) a concerted two-electron transfer or as (ii) a two successive one-electron transfers via radical species, coupled with two deprotonations. Evidence for both pathways has been presented in the literature and there might not be an exclusive path for these reactions.⁹⁰ EPR spectroscopy studies have been performed to obtain an insight into the oxidative dehydrogenation of the amino-olefin complexes to the diazadiene complexes and to observe possible radical intermediates. Subsequently, the electronic structure of observed paramagnetic compounds was investigated by CW at various microwave frequencies (X- and Q-band) and pulse ENDOR and HYSCORE EPR spectroscopy. In combination with DFT calculations, performed by Bas de Bruin¹³, reliable statements as to the radical’s structure and electron density distribution could be made. The following EPR spectroscopic studies were performed in cooperation with Dr. Jeffrey Harmer¹⁴.

Finally, the oxidative dehydrogenation of [M(trop₂DAE)]PF₆ 40a,b was investigated by EPR spectroscopy, as the formation of [M(trop₂DAD)]OTf 18a,b has been already proved by NMR spectroscopy and the candidate radical intermediates [M(trop₂DAD)] 20a,b are known and have been fully characterized.¹³² Following this, [M(trop₂DACH)]OTf 6a,b was studied; the isolation of the corresponding diazadiene complexes [M(trop₂DICH)]OTf 52a,b was unsuccessful.

2.1 EPR Spectroscopic Studies of the Oxidation of [M(trop₂DAE)]PF₆

The oxidation of [M(trop₂DAE)]PF₆ 40a,b with one equivalent FcOTf in the presence of two equivalents of KO’Bu led to the formation of the diazadiene radical complex [M(trop₂DAD)] 20a,b. Figure 20 displays the well-resolved EPR spectrum of 20a and Figure 21 the spectrum of 20b.

¹³ Dr. Bas de Bruin, University of Amsterdam, NL.
¹⁴ Dr. Jeffrey Harmer, University of Oxford, UK.
Rhodium(I) and Iridium(I) Promoted Oxidative Dehydrogenation of Coordinated Amines

Figure 20: X-band CW EPR spectra of 20a measured at room temperature. A) Reduction of [Rh(trop₂DAD)]OTf with activated zinc powder in THF (unbroken line), B) Oxidation of [Rh(trop₂DAE)]PF₆ with 2 eq. KOtBu and 1 eq. FcOTf in THF (dashed line) and C) simulation (dotted line) with a spin Hamiltonian comprising $g_{iso} = 2.0022$, $2 \times A^{(14N)} = 11.9$ MHz, $2 \times A^{(1H)} = 14.3$ MHz and $A^{(103Rh)} = 5.3$ MHz.

Figure 21: Q-band FID detected EPR spectrum of the radical complex [Ir(trop₂DAD)] 20b, obtained by oxidation of [Ir(trop₂DAE)]PF₆ (A; unbroken line) or by reduction of [Ir(trop₂DAD)]OTf 18b (B; dashed line) and the simulation (C; dotted line).

Both spectra are identical to those obtained from the reduction of [M(trop₂DAD)]OTf 18a,b with activated zinc powder, implying that the [M(trop₂DAD)] 20a,b was formed upon oxidation of 40a,b.
Rhodium(I) and Iridium(I) Promoted Oxidative Dehydrogenation of Coordinated Amines

Furthermore, the oxidative dehydrogenation of the isolated intermediate [Ir(trop₂MIMA)]OTF 53b with one equivalent of ferrocenium triflate and one equivalent base was investigated by EPR spectroscopy. As expected, the formation of the diazadiene radical complex 20b was observed. Experimentally derived EPR parameters are listed in Table 15 and are identical within the experimental limits to the published EPR parameters of 20a,b, which are given in brackets.

Table 15: EPR parameters of the [M(trop₂DAD)] radical complex 20a,b obtained by oxidative dehydrogenation of [M(trop₂DAE)]PF₆ 40a,b in comparison to those obtained by reduction of [M(trop₂DAD)]OTf 18a,b[132] which are given in brackets.

<table>
<thead>
<tr>
<th></th>
<th>EPR data of 20a[a]</th>
<th>EPR data of 20b[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A₁₁₁ [MHz][c]</td>
<td>A₁, A₂, A₃ [MHz][c]</td>
</tr>
<tr>
<td>¹⁴N × 2</td>
<td>11.9 (11.9)</td>
<td>3.0, 36.0, 3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.9, 34.0, 0.9)</td>
</tr>
<tr>
<td>¹H × 2</td>
<td>14.1 (14.3)</td>
<td>22.5, 15.3, 5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(22.5, 15.3, 5.0)</td>
</tr>
<tr>
<td>¹⁰³Rh</td>
<td>-5.3 (-5.3)</td>
<td>-</td>
</tr>
</tbody>
</table>

[a] g₁₁₁ = 2.0022 (2.0022), [b] g₁₁₁ = 2.006, g₁ = 1.9825, g₂ = 1.9889, g₃ = 2.0302 (g₁₁₁ =2.0024, g₁ = 1.9870, g₂ = 1.9870, g₃ = 2.0332). [c] Estimated error of about ± 1 MHz.

The spin Hamiltonian parameters are identical to those of 20a,b, which were obtained by reduction of [M(trop₂DAD)]OTf 18a,b with activated zinc powder.[132] This data, in combination with NMR spectroscopic studies of the oxidation of [M(trop₂DAE)]PF₆ 40a,b under basic conditions, is clear proof for the oxidative dehydrogenation of the ligand trop₂DAE 39 to trop₂DAD 16.

Depending on the base to oxidant ratio, the formation of a second paramagnetic species can be observed by EPR spectroscopy for the oxidation of 40a. The stacked X-band CW EPR spectra of both radical complexes measured in THF at 298 K are shown in Figure 22A.
Figure 22: A) Stacked X-band CW EPR spectra of the oxidation of 40a, measured in THF at room temperature with different amounts of KOtBu (denoted as B) and silver(I) triflate (denoted as Ox); and B) Amplified EPR spectra of [Rh(trop₂DAD)] 20a and the unidentified radical complex 54, taken from figure 22A.

The spectrum of 20a was obtained upon addition of base and oxidant in a 2:1 ratio. In comparison, oxidation with a 4:3 ratio gave a broad EPR signal of low intensity with two resolved equivalent nitrogen hyperfine couplings. The amplified spectra of both paramagnetic species are displayed in Figure 22B. The unknown radical complex was simulated with $g_{\text{iso}} = 2.012$ and isotropic hyperfine couplings from two identical nitrogen nuclei, $A_{\text{iso}}(^{14}\text{N}) = 11.9$ MHz. This unidentified paramagnetic species, denoted as 54, was stable at room temperature for 3 h.

Unfortunately, the second paramagnetic species 54 could not be identified. For the corresponding iridium complex, the formation of a second paramagnetic species was not observed and the only species detected under all conditions was the diazadiene radical complex [Ir(trop₂DAD)] 20b.
Rhodium(I) and Iridium(I) Promoted Oxidative Dehydrogenation of Coordinated Amines

2.2 EPR Spectroscopic Studies of the Oxidation of [M(trop₂DACH)]OTf

Analogous to [M(trop₂DAE)]PF₆ 40a,b, the oxidation of [M(trop₂DACH)]OTf 6a,b under basic conditions was investigated by EPR spectroscopy.

2.2.1 EPR Spectroscopic Studies of the Oxidation of [Rh(trop₂DACH)]OTf

In accordance with the results of the [Rh(trop₂DAE)]PF₆ 40a, the formation of two different paramagnetic species has been observed for the oxidation of [Rh(trop₂DACH)]OTf 6a, depending on the amount of base and oxidant added. Figure 23 displays the stacked X-band CW EPR spectra obtained by oxidation of [Rh(trop₂DACH)-1H] 43a with FcOTf in the presence of different amounts of KOtBu.

![Figure 23: X-band CW spectrum of 43a, measured in THF at room temperature with A) 1 eq. oxidant, B) 1 eq. base and 1 eq. oxidant and C) 2 eq. base and 1 eq. oxidant.](image)

Two different paramagnetic species were detectable by EPR spectroscopy. The addition of one equivalent of oxidant gave a broad signal with two resolved equivalent nitrogen hyperfine couplings $A_{iso}^{(14}N) = 13.4$ MHz; this unidentified paramagnetic species will be denoted as 55. Addition of one equivalent of base decreased the signal intensity of 55. Subsequent addition of a second equivalent of base resulted in a well-resolved spectrum. Previously this spectrum has been assigned erroneously to the aminyl radical complex [Rh(trop₂DACH-2H)] 8a. However, in combination with DFT calculations, this paramagnetic species could now be identified as the radical complex [Rh(trop₂DICH)] 56a. Experimentally derived parameters of 56a are given in Table 16, along with the data calculated by DFT methods.
Rhodium(I) and Iridium(I) Promoted Oxidative Dehydrogenation of Coordinated Amines

Table 16: EPR parameters and spin populations ρ of [Rh(trop₂DICH)] 56a and calculated values of [Rh(cht₂DICH)] 56a′ given in brackets. The signs of the experimental hyperfine interactions were assigned according to the DFT results.

<table>
<thead>
<tr>
<th>EPR Data of [Rh(trop₂DICH)] 56a[a]</th>
<th>ρ [%]</th>
<th>A₁, A₂, A₃ [MHz]</th>
<th>Aiso [MHz][b]</th>
<th>T₁, T₂, T₃ [MHz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹⁰³Rh</td>
<td></td>
<td>6.0, 4.6, -13.3 [d]</td>
<td>-0.7</td>
<td>6.9, 5.5, -12.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(8.1, 6.3, -4.9)</td>
<td>(-56.8)</td>
<td>(11.9, 7.2, -19.1)</td>
</tr>
<tr>
<td>¹⁴N[b]</td>
<td>24%× 2</td>
<td>-1.9, 37.0, -1.9 [e]</td>
<td>11.1</td>
<td>-12.9, 25.9, -12.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-1.5, -1.8, 32.2)</td>
<td>(12.1)</td>
<td>(-14.0, 27.5, -13.0)</td>
</tr>
<tr>
<td>²⁴H₀</td>
<td>2.3% × 2</td>
<td>27.1, 29.3, 34.5 [e]</td>
<td>32.6</td>
<td>-3.2, -1.0, 3.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(25.8, 26.1, 31.5)</td>
<td>(55.9)</td>
<td>(-2.9, -1.0, 3.9)</td>
</tr>
<tr>
<td>²⁴H₄</td>
<td>1% × 2</td>
<td>11.5, 14.5, 19.0 [d]</td>
<td>14.3</td>
<td>-3.5, -0.5, 4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(12.0, -1.3, 17.7)</td>
<td>(6.6)</td>
<td>(-2.6, -2.0, 4.7)</td>
</tr>
</tbody>
</table>

[a] Biso = 1.996 ± 3, g₁ = 2.005 ± 1, g₂ = 1.992 ± 1, g₃ = 1.991 ± 1 (Biso = 1.996, g₁ = 2.010, g₂ = 1.994, g₃ = 1.983). [b] The nuclear quadrupole parameters are κ = e₂qQ/h = 2.2 MHz and η = 1. DFT gives κ = 2.7 MHz, η = 0.9. [c] Isotropic part of the hyperfine interaction, Aiso = (A₁ + A₂ + A₃)/3, dipolar part of the hyperfine interaction, (T₁, T₂, T₃) = (A₁ - Aiso, A₂ - Aiso, A₃ - Aiso). [d] Estimated errors ± 0.5 MHz. [e] Estimated errors ± 1.0 MHz.

In contrast to the EPR parameters calculated for [Rh(cht₂DACH)-2H] 8a, the experimental data of 56a is in good agreement to the calculated data of [Rh(cht₂DICH)] 56a′.

In the assignment of 8a, the hydrogen atoms H₄ at the cyclo-hexyl ring were incorrectly assigned as the protons at the α-carbon atom and H₃ as the benzylic protons (Figure 24 8a,b).

Figure 24: Structures of the proposed aminyl radical complexes [M(trop₂DACH)-2H] 8a,b and the [16 + 1] diazadiene radical complexes [M(trop₂DICH)] 56a,b.

The assumption that H₄ is located at the C₆ of the cyclo-hexyl ring makes sense considering the small dipolar part of the hyperfine interaction T, which indicates that the spin density of C₆ is negligible. The distribution of the spin density is centered mainly on the diazadiene moiety (Figure 24 56a,b).

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¹⁵ For the DFT calculations the trop ligand was simplified by omitting the benzo groups: cht = cycloheptatrienyl. These model complexes are denoted using an apostrophe e.g. [Ir(trop₂DAD)]OTf 18b and [Ir(cht₂DAD)]OTf 18b′.
A slow conversion of the unidentified radical complex 55 into the highly resolved spectrum of [Rh(trop₂DICH)] 56a was observed upon addition of two equivalents of base and one equivalent of oxidant to the amino-olefin complex [Rh(trop₂DACH)]OTf 6a in THF (Figure 25).

![X-band CW EPR spectra](image)

Figure 25: X-band CW EPR spectra of the oxidation of 6a with 2 eq. base and 1 eq. FcOTf, measured versus time at room temperature in THF. Stacked plot of the EPR spectra versus time with the first spectrum at the bottom and the last recorded after 40 min.

The stacked EPR spectra displayed in Figure 25 reveal that the unidentified radical complex 55 is only a transient intermediate, which converts to the diazadiene radical complex [Rh(trop₂DICH)] 56a. A vital insight into the progress of the reaction can be obtained by studying the variation in intensity with time for the two paramagnetic species 55 and 56a (Figure 26).
Rhodium(I) and Iridium(I) Promoted Oxidative Dehydrogenation of Coordinated Amines

The concentration of the unidentified radical complex 55 is at a maximum at t = 0, after which it steadily decreases with time. After approximately 8 minutes, although the concentration of 55 has almost reached zero, the concentration of [Rh(trop$_2$DICH)] 56a still remains low. From this point of time onwards, the concentration of 56a rapidly increases. This result implies that the radical complex 55 is transient and is converting to 56a through a diamagnetic intermediate. Furthermore, Figure 26 reveals that the maximum concentration of 55, at t = 0, is less than the final concentration of 56a. For this reason, it can be assumed that only a fraction of [Rh(trop$_2$DACH)]OTf 6a is converted into the paramagnetic species 55 under these conditions.

For the detailed characterization of the unidentified paramagnetic species 55, CW and pulse EPR spectroscopy measurements were performed. The X-band EPR spectra, measured at room temperature, could be simulated with an isotropic g-value, $g_{iso} = 2.006$, and two equivalent nitrogen hyperfine couplings, $A_{iso}(^{14}\text{N}) = 13.4 \text{ MHz}$. The measurement was repeated in frozen solution (70K) (Figure 27).
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Figure 27: X-band CW EPR spectra (1st (A) and 2nd harmonic (B)) of the unidentified paramagnetic species 55, measured at 70K; (unbroken line experimental data, dotted line simulation).

At 70K, an axial spectrum with resolved hyperfine splittings along $g_3$ (≡ $g_4$) was obtained which could be simulated by two equivalent nitrogen hyperfine couplings, $A_3(^{14}N) = 35.8$ MHz. Along $g_{1,2}$ (≡ $g_1$) no resolved hyperfine splittings were observed, indicating that the nitrogen interactions are comparably small and that the nitrogen hyperfine interactions have a large anisotropy.

2.2.2 EPR Spectroscopic Studies of the Oxidation of [Ir(trop$_2$DACH)]OTf

In accordance to [Rh(trop$_2$DACH)]OTf 6a, the oxidation of [Ir(trop$_2$DACH)]OTf 6b led to the formation of two paramagnetic species that interconvert over time. Figure 28 displays the stacked X-band CW EPR spectra, measured at 115K in THF versus time.
Upon addition of two equivalents of KO\textsuperscript{t}Bu and one equivalent of FcOTf to [Ir(trop\textsubscript{2}DACH)]OTf 6b, a slow conversion of the initial unidentified paramagnetic species 57 (g-value order of \( g_{\parallel} < g_{\perp} \)) to the diazadiene radical complex [Ir(trop\textsubscript{2}DICH)] 56b (g-value order of \( g_{\parallel} > g_{\perp} \)) was observed. Overall, the conversion of 57 to 56b takes longer than the conversion of the unidentified rhodium radical complex 55 to [Rh(trop\textsubscript{2}DICH)] 56a. Pulse EPR measurements were used to confirm the EPR spin Hamiltonian model from the X-band CW EPR data and to investigate the range of proton hyperfine couplings for 56b and 57. The EPR parameters and hyperfine couplings for the nuclei found for 57 and 56b are listed in Table 17.

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Figure 28: X-band CW EPR spectra of the reaction mixture obtained from 6b with 2 eq. KO\textsuperscript{t}Bu and 1 eq. FcOTf, recorded in THF at 115K versus time [h]. The samples were stored at room temperature between the measurements.
Rhodium(I) and Iridium(I) Promoted Oxidative Dehydrogenation of Coordinated Amines

Table 17: EPR parameters of the unidentified radical complex 57 and [Ir(trop2DICH)] 56b; calculated values of [Ir(cht2DIC)] 56b' are given in brackets.

<table>
<thead>
<tr>
<th></th>
<th>EPR Data of [Ir(trop2DICH)] 56b[a]</th>
<th>EPR Data of 57[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>p [%]</td>
<td>A1, A2, A3 [MHz]</td>
</tr>
<tr>
<td>14N</td>
<td>28 × 2</td>
<td>-2, 37, -2</td>
</tr>
<tr>
<td>1H</td>
<td>1 × 2</td>
<td>20, 14, 15</td>
</tr>
<tr>
<td>1H</td>
<td>2.3 × 2</td>
<td>29, 38, 31</td>
</tr>
</tbody>
</table>

[a] $g_{iso} = 1.998, g_1 = 1.974, g_2 = 1.993, g_3 = 2.028 \quad g_{iso} = 2.009, g_1 = 2.029, g_2 = 2.012, g_3 = 1.988$, $g_1 = 2.011, g_2 = 2.031, g_3 = 2.031, g_5 = 1.972$. [b] Isotropic part of the hyperfine interaction, $A_{iso} = (A_1 + A_2 + A_3)/3$, dipolar part of the hyperfine interaction, $(T_1, T_2, T_3) = (A_1 - A_{iso}, A_2 - A_{iso}, A_3 - A_{iso})$. [c] The nuclear quadrupole parameters are $\kappa = eQ/Q/h = 2.2$ MHz and $\eta = (Q_x - Q_y)/Q_z$ with $Q_x = Q_y = -\frac{1}{2} \kappa (1 - \eta)$ and $Q_z = \frac{3}{2} \kappa$. [d] Estimated errors $\pm 1.0$ MHz. [e] Euler angles define a rotation of the hyperfine or nuclear quadrupole principal axis system in the g-matrix principal axis system, e.g. $A = R(\alpha, \beta, \lambda) A_{diagonal} R^T(\alpha, \beta, \lambda)$. Estimated errors in the experimental Euler angles are $\pm 10^\circ$. [g] Estimated errors $\pm 0.4$ MHz. [h] Estimated errors $\pm 0.2$ MHz.

The EPR parameter of 56b match perfectly with the DFT calculated data of [Ir(cht2DIC)] 56b'. In contrast to the calculated data of [Ir(trop2DACH)-2H] 8b, the dipolar part of the hyperfine interaction and the isotropic component are in agreement with the calculated values.

To conclude, it can be stated that the existence of the diazadiene radical complexes [M(trop2DAD)] 20a,b and [M(trop2DIC)] 56a,b has been proven by EPR spectroscopy. As a result, the oxidation of the amino-olefin ligands over a successive one-electron transfer via radical species is presumed.

3 Mechanism of the Oxidative Dehydrogenation

The oxidative dehydrogenation of ethylenediamine based ligands, such as trop2DACH 28 and trop2DAE 39, to the corresponding diazadiene formally requires the removal of four protons and four electrons. Keene et al. proposed that the initial step of the mechanism is an one-electron oxidation of the metal centre, followed by consecutive deprotonation reactions and intramolecular redox processes, in which the ligand is oxidized and the metal reduced (see Introduction).
Based on the NMR and EPR spectroscopic studies, the following mechanism is proposed for the oxidative dehydrogenation of the amino-olefin complexes [M(trop$_2$DACH)]OTf 6a,b and [M(trop$_2$DAE)]PF$_6$ 40a,b. The mechanism involves the deprotonation of the saturated amino-olefin complexes followed by redox processes which leads to radical intermediates. Further consecutive one-electron oxidations coupled with deprotonation reactions and rearrangements give the unsaturated diazadiene complexes as final products (Scheme 31).

Scheme 31. Proposed mechanism for the oxidative dehydrogenation of amino-olefin rhodium(I) and iridium(I) complexes; R = H, -(CH$_2$)$_4$- and M = Rh, Ir.

Deprotonation of the amino-olefin complex I gives the di(amido) complex II, which is then oxidized to the aminyl radical complex III, in which the radical is delocalized over the two nitrogen atoms and the metal centre. Complex IV is formed by a 1,2-H-shift from the α-carbon to the nitrogen atom. In the next step, the oxidation of IV leads to the formation of the mono(imino)mono(amine) complex V, which can then be isolated (see Section IV.1.1). The double deprotonation of V gives VI, which was proved experimentally by deprotonation of the isolated complex [Ir(trop$_2$MIMA)]OTf with two
Rhodium(I) and Iridium(I) Promoted Oxidative Dehydrogenation of Coordinated Amines

equivalents of NaO\(^{18}\)Bu (see Section VI.3.3). Oxidation of VI produces the highly persistent diazadiene radical complex VII which was observed and fully characterised by EPR spectroscopy for 20a,b and 56a,b. Further oxidation gives the diazadiene complex VIII as the final product. The diazadiene complexes could be isolated as products for the oxidative dehydrogenation of [M(trop\(_2\)DAE)]PF\(_6\) 40a,b but not of [M(trop\(_2\)DACH)]OTf 6a,b (see Section IV.1). In summary, this proposal is based upon a series of complexes as intermediates, which could be fully characterized by either NMR or EPR spectroscopy apart from the radical complexes III and IV.

4 Conclusion

We were able to demonstrate that the amino-olefin ligands of [M(trop\(_2\)DACH)]OTf 6a,b and [M(trop\(_2\)DAE)]PF\(_6\) 40a,b undergo oxidative dehydrogenation to the corresponding diazadiene complexes. Even though the corresponding [M(trop\(_2\)DICH)]OTf 52a,b could not be prepared from the amino-olefin complexes 6a,b by the addition of four equivalents of silver(I) triflate and base, EPR spectroscopic studies in combination with DFT calculations have proved that the corresponding diazadiene radical complexes 56a,b were formed.

Based on EPR and NMR spectroscopic studies, a mechanism for the oxidative dehydrogenation has been proposed which involves the formation of radical complexes by consecutive one-electron oxidation steps in combination with deprotonation reactions. In contrast to the findings of Keene and others, the oxidation of the metal centre as an initial step could not be confirmed. Moreover, it was found that the oxidative dehydrogenation only takes place if \textit{in situ} deprotonation has taken place first. It might be possible, however, that different mechanistic pathways exist for the oxidative dehydrogenation, depending on the ligand system and the transition metal centre. In general, it can be stated that the amino-olefin ligands trop\(_2\)DACH and trop\(_2\)DAE belong to the class of redox-active ligands, meaning that the ligand is oxidized instead of the transition metal.

The ability of the amino-olefin complexes to undergo oxidative dehydrogenation is assumed to be linked to its catalytic activity and that the “true” catalyst is either a diazadiene radical or a cationic diazadiene complex. This assumption is supported by the results obtained by [M(trop\(_2\)EEA)]PF\(_6\) 47a,b, which do not undergo oxidative dehydrogenation and are not catalytically active. However, this assumption is refuted by the catalytically inactive rhodium(I) complexes [Rh(trop\(_2\)DAE)]PF\(_6\) 6a and [Rh(trop\(_2\)DACH)]OTf 40a, which still promote the oxidative dehydrogenation. This clearly demonstrates that additional factors determine the catalytic activity once the diazadiene complexes are formed and if so, the diazadiene complexes [Ir(trop\(_2\)DAD)]OTf 18b will be an effective catalysts for the oxidation of alcohol, whereas 18a will not be catalytically active.
V. Catalytic Dehydrogenation of Alcohols
The oxidation of alcohols is a fundamental transformation in organic chemistry. Key compounds, such as aldehydes and ketones, are important starting materials and intermediates in large-scale industrial processes and fine chemical synthesis. The world production of carbonyl compounds is in the region of $10^7$ tones per year.\(^{[188]}\) A significant amount is obtained by oxidation of the corresponding alcohol, e.g. half the annual methanol production is oxidized to formaldehyde. Aldehydes are of particular industrial significance: they are mainly used as solvents, flavouring agents and perfumes, as well as intermediates in the manufacture of food additives for animals, plastics, dyes, pharmaceuticals and pesticides. The increasing demand for carbonyl compounds has heightened the intensity of the search for efficient alcohol oxidation catalysts. In particular, there is a significant need for highly selective catalysts with a high functional group tolerance (see Introduction).

Excellent results were obtained with the [Ir(trop$_2$DACH)]OTf $\text{6b}^{16}$ system for the oxidation of primary alcohols with even secondary unprotected hydroxyl groups in the substrate (see Introduction). Unfortunately, in spite of the enantiomerically pure complex $\text{6b}$, no chiral induction was observed for the oxidation of racemic alcohols.\(^{[88]}\) Mechanistic NMR and EPR spectroscopic studies of [M(trop$_2$DACH)]OTf $\text{6a,b}$ and [M(trop$_2$DAE)]OTf $\text{40a,b}$ revealed that the chiral information of $\text{6a,b}$ is lost under catalytic conditions due to formation of the corresponding diazadiene complexes by oxidative dehydrogenation (see Chapter IV). As a result, it is assumed that these diazadiene complexes, [M(trop$_2$DICH)]OTf $\text{52a,b}$ and [M(trop$_2$DAD)]OTf $\text{18a,b}$, or their corresponding diazadiene radical complexes are the catalytically active complexes in the oxidation of alcohols. The confirmation of this assumption will open a unique strategy for the development of a 2nd generation catalyst, as the steric hindrance and electronic properties of the diazadienes are strongly influenced by the substituents in the 1,4- and 2,3-position. In the following chapter, the catalytic activity of previously synthesized [M(trop$_4$DAD)]OTf $\text{18a,b}^{[132]}$ and $\text{19a,b}^{[89]}$ complexes in the oxidation of alcohols is studied. Furthermore, the extent to which diazadienes, in combination with olefins, can be used as a general building block in the framework of an effective catalyst will be investigated.

\(^{16}\) In order to distinguish between metal complexes with the same ligand, we use following letters: $\text{a}$ for rhodium and $\text{b}$ for the iridium complexes; e.g. [Rh(trop$_2$DACH)]OTf will be referred to as $\text{6a}$ and [Ir(trop$_2$DACH)]OTf as $\text{6b}$. 

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Catalytic Dehydrogenation of Alcohols
1 Optimization of the Catalytic System – Finding the Winning Team

1.1 Synthesis of Rhodium(I) and Iridium(I) Diazadiene-Olefin Complexes

The diazadiene-olefin complexes \([\text{M}(\text{trop}_2^8\text{DAD})]\text{OTf} \ \text{18a,b and 19a,b}\) have been synthesized and analyzed before in our group.\(^{[89, 132]}\) The improved synthesis of these diazadiene complexes is displayed in Scheme 32.

\[ \text{[M]} \quad \text{AgOTf} \quad \text{THF, 2 h, rt} \quad \text{M = Rh, Ir} \]

Scheme 32: Improved synthesis of rhodium(I) and iridium(I) diazadiene complexes \([\text{M}(\text{trop}_2^8\text{DAD})]\text{OTf} \ \text{18a,b and 19a,b and the radical complexes [M(trop_2DAD)}] \ \text{20a,b}.\]

The diazadiene-olefin ligands trop_2DAD 16 and trop_2MeDAD 17 readily react with a rhodium(I) and iridium(I) precursor in the presence of silver(I) triflate to form the corresponding complexes in excellent yield. Reduction of 18a,b with activated zinc powder gave the corresponding radical complexes \([\text{M}(\text{trop}_2\text{DAD})] \ \text{20a,b in quantitative yield (Scheme 32). To complement previous work, crystals of [Ir(trop_2DAD)]OTf 18b suitable for X-ray diffraction analysis were grown by slow diffusion of n-hexane into a concentrated solution of 18b in a mixture of DME and benzene (ratio 1:1). The molecular structure of 18b is displayed in Figure 29; selected bond length and angles are given in the figure caption.}

17 Most known 1,4-diaza-1,3-butadienes (DAD) have the general formula RN=CR'(R')=NR and herein will be denoted as \(\text{R}^8\text{DAD}\). An important subgroup is RN=CH=CH=NR (\(\text{R}^9\text{DAD}\)). If \(\text{R}'\) is not specifically stated, the abbreviation \(\text{R}^9\text{DAD}\) is used, implying proton substitution at the \(\alpha,\alpha'-\text{diimine carbon atoms.}\)
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Figure 29: ORTEP plot of [Ir(trop₂DAD)]OTf 18b. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms (apart of the imino hydrogens) and the counter ion (OTf) are omitted for clarity. Selected bond length [Å] and angles [°]:

\[
\begin{align*}
\text{Ir-N1} & = 2.013(1), \quad \text{Ir-N2} = 2.011(1), \quad \text{Ir-C4} = 2.170(2), \quad \text{Ir-C5} = 2.177(2), \quad \text{Ir-C19} = 2.162(2), \\
\text{Ir-C20} & = 2.151(2), \quad \text{Ir-ct1} = 2.036, \quad \text{Ir-ct2} = 2.055, \\
\text{C4-C5} & = 1.415(4), \quad \text{C19-C20} = 1.418(3), \quad \text{C31-N1} = 1.295(2), \quad \text{C32-N2} = 1.297(2), \quad \text{C31-C32} = 1.457(3), \\
\text{N1-Ir-N2} & = 78.7(6), \quad \text{N1-Ir-ct1} = 90.9, \quad \text{N2-Ir-ct2} = 91.3, \quad \text{ct1-Ir-ct2} = 99.2, \quad \phi = 3.8.
\end{align*}
\]

The crystal structure of 18b demonstrates that trop₂DAD 16 acts as a tetradentate ligand, resulting in an almost perfect $C_{2v}$-symmetric structure (\(\phi = 3.8^\circ\)). Compared to the corresponding rhodium(I) complex 18a, the C=C bonds of 18b are slightly elongated by 0.03 Å, a result of higher metal-to-ligand back-donation. Apart from this, the bond distances and angles are almost identical.\(^{[132]}\)

### 1.2 Catalytic Activity of Diazadiene-Olefin Complexes

In preliminary studies, the catalytic activity of \([M(trop₂DAD)]OTf\) 18a,b, [Ir(trop₂MeDAD)]OTf 19b and \([M(trop₂DAD)]\) 20a,b in the alcohol oxidation was assessed. To determine whether diazadiene-olefin complexes are generally effective catalysts for this transformation, the activity of the known complex [Ir((c-hex)₂DAD)COD]PF₆ 58\(^{[129]}\) was studied.

The reaction conditions for the oxidation of alcohols were adapted from the [Ir(trop₂DACH)]OTf 6b system with $p$-benzoquinone as co-oxidant. The reactions were performed in THF instead of chlorobenzene and no base was added, if not otherwise noted. For practical reasons, 1-octanol was chosen as the test substrate. This substrate is an unactivated aliphatic alcohol, normally problematic to oxidize, and is not oxidized by the employed co-oxidant alone. Furthermore, the corresponding aldehyde is easily distinguishable from the unreacted educt by GC (Table 18).
Table 18: Oxidation of 1-octanol with different diazadiene-olefin catalysts. Reaction conditions: 0.1 mol% catalyst, 1.3 eq. BQ, 80 °C in THF if not noted otherwise.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time</th>
<th>Conversion [%]^[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Ir(trop₂DAD)]OTf 18b</td>
<td>10 min</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>[Rh(trop₂DAD)]OTf 18a</td>
<td>20 h</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>[Ir(trop₂DAD)] 20b</td>
<td>10 min</td>
<td>95</td>
</tr>
<tr>
<td>4</td>
<td>[Rh(trop₂DAD)] 20a</td>
<td>20 h</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>[M(trop₂MeDAD)]OTf 19b</td>
<td>3 h</td>
<td>93^[b]</td>
</tr>
<tr>
<td>6</td>
<td>[Ir((c-hex)₂DAD)COD]PF₆ 58</td>
<td>2 h</td>
<td>10</td>
</tr>
</tbody>
</table>

^[a] The conversion of the alcohol was determined by GC.^[b] NaO₄Bu (0.5 mol%) was added.

The results showed that the diazadiene complexes [Ir(trop₂DAD)]OTf 18b and [Ir(trop₂DAD)] 20b are both powerful catalysts for the oxidation of 1-octanol, whereas the corresponding rhodium complexes 18a and 20a do not catalyze the oxidation of 1-octanol. This result is in agreement with previous observations. In comparison, [Ir(trop₂MeDAD)]OTf 19b is a less active catalyst and the addition of 0.5 mol% NaO₄Bu and longer reaction times are needed to complete the oxidation (Entry 5). Apart from the methyl groups at the diazadiene unit, the complexes 18b and 19b have the same structure, suggesting that the increased steric hindrance at the backbone significantly decreases the reaction rate. Iridium(I) complex 58 showed the poorest catalytic activity, as the conversion to the aldehyde stopped after 10%. This result implies deactivation of the catalyst, probably due to the loss of the labile bound COD ligand. In conclusion, iridium complexes with tetradentate diazadiene-olefin ligands without sterically demanding substituents at the backbone give the best results for the oxidation of 1-octanol.

In contrast to the established [Ir(trop₂DACH)]OTf 6b system, no additional base is needed for the dehydrogenation of alcohols. However, decreasing the catalyst loading to 0.01 mol% requires the presence of 0.01 mol% of sodium tert-butoxide. Moreover, it has been shown that the addition of NaO₄Bu to [Ir(trop₂DAD)]OTf 18b gives a strong signal of the diazadiene radical complex [Ir(trop₂DAD)] 20b in the EPR spectrum. This observation implies that the diazadiene radical complex 20b might be the catalytically active species, which is formed by reaction with base under catalytic conditions when using 18b as catalyst precursor (see Chapter VI). Since the catalytic activity of 18b and
Catalytic Dehydrogenation of Alcohols

20b has been shown to be identical, the cationic complex 18b was used as catalyst in subsequent reactions as it is less sensitive than the paramagnetic complex 20b.

Furthermore, the ability of 18b to oxidize secondary alcohols was investigated (Table 19).

Table 19: Catalytic dehydrogenation of alcohols with p-benzoquinone as the hydrogen acceptor. The conversion was determined by GC. Reaction conditions: 0.1 mol% 18b, 1.3 equivalents BQ, 80 °C in THF.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Time</th>
<th>Conversion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>10 min</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>18 h</td>
<td>64</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>18 h</td>
<td>32</td>
</tr>
</tbody>
</table>

The results presented in Table 19 show that 1-octanol was oxidized within 10 min and that secondary alcohols were converted to ketones although at much slower reaction rates. The conversion of the activated alcohol, 1-phenylethanol, can be explained by the fact that BQ is able to oxidize activated alcohols to a certain degree in absence of a catalyst (Entry 2). In contrast, the slow conversion of the unactivated alcohol, 2-butanol, indicates that 18b is a poor catalyst for the oxidation of secondary alcohols: merely 32% 2-butanone was formed after 18 h (Entry 3). The chemoselectivity of this catalytic system will be discussed later in more detail (vide infra). Before the investigation of the scope of this method, the replacement of p-benzoquinone was targeted.

1.3 Replacement of p-Benzoinone as Co-Oxidant

p-Benzoinone is a well-known oxidant and electron carrier in catalysis and organic chemistry. Despite its popularity, p-benzoinone is toxic and harmful to the environment. Given the environmental restrictions on industrial oxidation technology, the replacement of p-benzoquinone with a benign co-oxidant is highly desirable. Employing [Ir(trop₂DAD)]OTf 18b directly as catalyst facilitates the substitution of p-benzoquinone, as it is not needed anymore for the oxidative dehydrogenation of the amino-olefin complexes prior to catalysis.

1.3.1 Replacement of p-Benzoinone by Different Quinones

The replacement of the co-oxidant was approached systematically by first substituting the p-benzoquinone for other quinones. This investigation allowed the electronic and steric properties
that define \( p \)-benzoquinone as an effective co-oxidant to be estimated. Table 20 displays the 1,2- and 1,4-quinones that were used as co-oxidants in the oxidation of 1-octanol, ordered by their redox potential.

Table 20: Iridium-catalyzed oxidation of 1-octanol with 1,2- and 1,4-quinones as co-oxidants. The conversion was determined by GC after 15 min reaction time. The \( \text{pK}_a \) values were calculated for the corresponding hydroquinones in aqueous solution with the programme ACD \( \text{pK}_a \) DB. The uncertainty of the program’s \( \text{pK}_a \) prediction is given as ±\( \Delta \text{pK}_a \) in brackets. The redox potentials were measured by Peover et al. in acetonitrile at 25 °C versus SCE. \(^{[189]} \). The converted redox potentials of the quinones versus Fc/Fc⁺ are given in brackets.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Co-Oxidant</th>
<th>Redox potential [V]</th>
<th>calc. ( \text{pK}_a ) values</th>
<th>Conversion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>-0.75; -1.25</td>
<td>10.85 (± 0.30)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-1.057; -1.557)</td>
<td>12.26 (± 0.30)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>-0.73; -1.24</td>
<td>11.89 (± 0.23)</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-1.037; -1.707)</td>
<td>13.43 (± 0.23)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>-0.66; -1.22</td>
<td>8.93 (± 0.30)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.967; -1.507)</td>
<td>12.27 (± 0.30)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>-0.58; -1.10</td>
<td>11.79 (± 0.18)</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.887; -1.407)</td>
<td>11.96 (± 0.18)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>-0.51; -1.14</td>
<td>10.33 (± 0.13)</td>
<td>&gt;98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.817; -1.447)</td>
<td>11.86 (± 0.13)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>+0.01; -0.73</td>
<td>5.53 (± 0.33)</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.297; -1.037)</td>
<td>7.08 (± 0.33)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>+0.51; -0.30</td>
<td>3.79 (± 0.33)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.203; -0.607)</td>
<td>5.33 (± 0.33)</td>
<td></td>
</tr>
</tbody>
</table>

Most quinones, especially very strong and weak oxidants such as 1,4-antraquinone, 9,10-phenantrenquinone and DDQ, did not act as co-oxidants in the dehydrogenation of 1-octanol (Entry 1, 3 and 7). The most likely explanation is that as oxidants, 1,4-antraquinone and 9,10-phenantrenquinone are too weak, whereas DDQ is too strong. On the other hand, DDQ might coordinate via the nitrile groups to the iridium atom and thus deactivate the catalyst. In order to verify whether the redox potential or the coordination of DDQ prohibits the oxidation of 1-octanol, \( p \)-chloranil was used as it possesses no coordinating groups but is a strong oxidant (Entry 6). Similar to
methyl-p-benzoquinone, the catalysis with p-chloranil gave 21 % conversion to the 1-octanal after 15 min. In contrast to methyl-p-benzoquinone, the reaction with p-chloranil did not proceed further, even after the addition of p-benzoquinone, indicating that the catalyst had decomposed. Conclusively, it was assumed that excessively strong oxidants deactivate the catalyst. Although the oxidation with methyl-p-benzoquinone gave complete conversion to the aldehyde, the reaction rate was comparatively low (Entry 4). The catalysis with 2,5-di-tert-butylquinone gave 3% conversion (Entry 2), even though it is a weaker oxidant than 9,10-phenantrenquinone. Based on these findings, it was considered that, aside from the redox potential of the co-oxidant, the acidity of the formed hydroquinone might be an important factor: the pKₐ value of 2,5-di-tert-butylhydroquinone is considerably higher than that of the catechol.

In conclusion, it was found that only methyl-p-benzoquinone could replace p-benzoquinone as co-oxidant but at the expense of much longer reaction times, despite the similar redox potentials and pKₐ value of the formed hydroquinones. The only difference between both quinones is their steric hindrance, a factor which might readily explain the deviation of the reaction rates, assuming that the co-oxidant approaches the metal centre during the re-oxidation process. Overall, three factors may determine the suitability of the co-oxidant: the redox potential, the steric hindrance and the acidity of the corresponding hydroquinone (see Chapter VI for detailed discussion).

1.3.2 Replacement of p-Benzoquinone by Inorganic Oxidants

Inorganic oxidants are widely used in organometallic chemistry and are usually regarded as outer sphere reagents such as ferrocenium triflate (FcOTf). Oxidation of 1-octanol with 1 mol% [Ir(trop,DAD)]OTf 18b in the presence of two equivalents of both FcOTf and NaO'Bu in THF gave the corresponding aldehyde after 30 min at reflux. Without the addition of two equivalents of base, no oxidation has been observed. This finding draws into question the hypothesis of a coordination-assisted re-oxidation of the catalyst by quinones and supports the assumption that p-benzoquinone has two roles in the oxidation of alcohols, acting as the oxidizing reagent and base. However, the possibility that, depending on the co-oxidant, the re-oxidation of the catalysts occurs via different pathways cannot be ruled out.

The disadvantages of ferrocenium salts are their relatively high costs and the need to synthesize them by the oxidation of ferrocene with p-benzoquinone. In addition, two equivalents of base are needed, which could lead to side reactions and group intolerance in more complex substrates than aliphatic alcohols without functional groups. Therefore, in the following section the focus centres on using p-benzoquinone in catalytic amounts.
1.3.3 Reoxidation of Hydroquinone by Inorganic Oxidants

Since the replacement of \( p \)-benzoquinone was not easily achieved, we decided to use it in catalytic amounts in combination with an external oxidant, capable of reoxidizing the formed hydroquinone. Activated manganese dioxide was used as an external oxidant for this purpose, as it has previously been reported in the literature (Table 21).\(^{[60,191,192]}\)

Table 21: Iridium-catalyzed (0.1 mol% 18b) oxidation of 1-octanol with activated manganese dioxide (1.1 eq) and catalytic amounts of \( p \)-benzoquinone and NaO\( ^{-} \)Bu in THF at 80 °C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>BQ [mol%]</th>
<th>NaO(^{-} )Bu [mol%]</th>
<th>BQ/NaO(^{-} )Bu ratio</th>
<th>Time [min]</th>
<th>Conversion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td></td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>2</td>
<td>10</td>
<td>90</td>
<td>32</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>1</td>
<td>20</td>
<td>90</td>
<td>97</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>0.5</td>
<td>40</td>
<td>120</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>0.5</td>
<td>20</td>
<td>90</td>
<td>88</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>0.25</td>
<td>20</td>
<td>90</td>
<td>82</td>
</tr>
</tbody>
</table>

Stoichiometric amounts of commercially available activated MnO\(_2\) were found to oxidize 1-octanol in combination with 0.1 mol% 18b in almost quantitative yield to 1-octanal, depending on the catalytic amount of \( p \)-benzoquinone and base added, whereas manganese dioxide itself (without addition of benzoquinone) gave no oxidation (Entry 1). Addition of 20 mol% of \( p \)-benzoquinone and 2 mol% base gave merely 32% conversion (Entry 2). It is assumed that the ratio of base to oxidant has a significant influence on the conversion, as it has been shown by EPR spectroscopy that \( p \)-benzoquinone can be reduced by NaO\(^{-} \)Bu to the semiquinone radical. In deed, decreasing the BQ/NaO\(^{-} \)Bu ratio to 20 gave complete conversion of 1-octanol; further decreasing of this ratio to 40 led to a slightly lower reaction rate (Entry 4). Even when the amount of \( p \)-benzoquinone was decreased further to 10 mol% and 5 mol%, with a constant BQ/NaO\(^{-} \)Bu ratio of 20, only a slight rate loss was observed (Entry 5 and 6).

These experiments show that although the substitution of \( p \)-benzoquinone with inorganic oxidants is possible and the formed hydroquinone can be reoxidized by an external inorganic oxidant, longer reaction times are needed to complete the reaction. In addition, large amounts of waste are generated, as the efficiency per weight of the inorganic co-oxidant is relatively low. As a result of these limitations, no further investigation was carried out into this approach.
1.3.4 Replacement of \( p \)-Benzoquinone by Molecular Oxygen and Peroxides

In comparison to inorganic oxidants, molecular oxygen and hydrogen peroxide have many advantages. On the one hand, they are environmental friendly, readily available, comparably inexpensive and show high atom efficiency. On the other hand, however, oxygen and hydrogen peroxide require severe safety handling for large-scale applications.

Investigation into the sensitivity of \([Ir(trop_2DAD)]OTf\ 18b\) towards oxygen confirmed the stability of the complex in the presence of oxygen: no decomposition was observed by NMR spectroscopy after one week’s worth of exposure. Even using water in combination with the oxygen did not decompose \(18b\), whereas the addition of an aqueous solution of sodium hydroxide in the presence of oxygen led to immediate decomposition.

Despite the insensitivity of \(18b\) to oxygen, the replacement of \( p \)-benzoquinone by oxygen or peroxides, such as hydrogen peroxide and benzoyl peroxide, gave no conversion of 1-octanol to the corresponding aldehyde or carboxylic acid. In all likelihood, the electron-transfer between the catalyst and oxygen or hydrogen peroxide is too slow, compared to the decomposition of the reduced metal complex.\(^{[62]}\)

1.3.5 Electron Transfer Mediators

In cases where the electron-transfer between the catalyst and oxygen or hydrogen peroxide is too slow, an electron-transfer mediator (ETM) can be inserted into the catalytic cycle, e.g. Bäckvall et al. have successfully applied metal salen complexes and related metal macrocycles as ETMs for the reoxidation of hydroquinones in the aerobic oxidation of alcohols (see Scheme 2).\(^{[61, 62]}\) For the oxidation of 1-octanol, the cobalt(II) salen complex \(59\) has been used as ETM in combination with \([Ir(trop_2DAD)]OTf\ 18b\) and \( p \)-benzoquinone (Scheme 33).

![Scheme 33: Three component catalytic system for the aerobic oxidation of primary alcohols. Reaction conditions: 0.1mol% \([Ir(trop_2DAD)]OTf\ 18b, 0.1 \text{ mol\% } [\text{Co(salen)}] 59, 5 \text{ mol\% } p \text{-benzoquinone, room temperature, THF.}]

The aerobic oxidation of 1-octanol catalyzed by \(18b\) resulted in only 11% conversion to the corresponding aldehyde. Careful reaction monitoring by GC showed that the conversion stopped after
24 h and did not proceed further with time. Altering the reaction conditions by increasing the amount of p-benzoquinone did not improve the performance and as a result, the investigation into aerobic oxidation was not continued.

Unfortunately replacing p-benzoquinone with a convenient, efficient and environmentally friendly co-oxidant was unsuccessful up to now. As a result, p-benzoquinone will be used as co-oxidant in the following reactions to investigate the scope of 18b in the catalytic oxidation of alcohols. Mechanistic studies are expected to give an insight into the role of p-benzoquinone in the catalytic cycle.

2 Catalytic Dehydrogenation of Alcohols

Although no base is needed for the oxidation of alcohols with 0.1 mol% [Ir(trop₂DAD)]OTf 18b, decreasing the catalyst loading to 0.01 mol% requires the presence of 0.01 mol% of sodium tert-butoxide (Scheme 34).

![Scheme 34: Oxidation of alcohols catalyzed by [Ir(trop₂DAD)]OTf 18b (0.01 mol%) with p-benzoquinone as co-oxidant.](image)

The catalyses were performed in THF at ambient temperature. The reaction was extremely exothermic, the severity varied according to the substrate, e.g. when 1-octanol was oxidized, the reaction vessel heated up to 90 °C during the course of the reaction. During the catalysis, the colour change of the reaction mixture from orange to black and the precipitation of hydroquinone were observed. Under the latter conditions, 18b oxidized a wide range of primary alcohols to the corresponding aldehydes.

2.1 Scope of the Catalytic Dehydrogenation

The scope of the method is illustrated by the wide range of primary allylic, benzylic and aliphatic alcohols that can be oxidized in high conversions and selectivity with low catalyst loadings (0.01 mol% 18b). Conversion rates and yields were both very high and the selectivity was excellent (Table 22).
Catalytic Dehydrogenation of Alcohols

Table 22: Catalytic dehydrogenation of primary alcohols with p-benzoquinone as the hydrogen acceptor. The conversions were determined by GC and $^1$H NMR. Yields of the isolated, pure products are given in brackets behind the conversions. Reaction conditions were as follows: 25 mmol substrate, 0.01 mol% 18b in THF at room temperature in the presence of 1.1 equivalents BQ and 0.01 mol% NaOTBu unless otherwise noted.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Time [min]</th>
<th>Conversion [%] (Yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>1.5</td>
<td>&gt; 98 (94)</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>2.5</td>
<td>96 (96)</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>2.5</td>
<td>&gt; 98 (97)</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>5.0</td>
<td>96 (96)</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>2.5</td>
<td>&gt; 98 (91)</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>2.5</td>
<td>&gt; 98 (89)</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>20.0</td>
<td>80 (72) $^{[a, b]}$</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td>5.0</td>
<td>&gt; 98 (73) $^{[a]}$</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td>10.0</td>
<td>85 (78) $^{[a, b, c]}$</td>
</tr>
</tbody>
</table>

$^{[a]}$ Aldehyde was isolated as corresponding 2,4-dinitrophenylhydrazone; $^{[b]}$ Reaction temperature 50 °C; $^{[c]}$ 1.3 Equivalents p-benzoquinone.

Aldehydes were formed exclusively under the catalytic conditions, without any observable overoxidation to the corresponding carboxylic acids. The selection of substrates was limited to synthetically relevant or challenging alcohols in order to demonstrate the versatility of the method. Similar to the results of the [Ir(trop$_2$DACH)]OTf 6b system, the oxidation of unactivated alcohols, such as 1-octanol, to the corresponding aldehyde was the fastest, completing within 90 s (Entry 1). However, the slightly more sterically hindered substrate 2-phenyl-1-propanol (Entry 2) was still converted with high activity.
Common problems presented by alcohols with double bonds were not encountered, as demonstrated by the oxidation of the naturally occurring alcohols lavandulol and geraniol (Entry 3 and 4). With the 1st generation catalyst 6b, the isomerisation of lavandulal to the higher substituted and thus thermodynamically more stable iso-lavandulal was observed.$^{[3]}$ However, under the almost base-free conditions of the $[\text{Ir(trop}_2\text{DAD})\text{OTf}]^{18b}$ system, no rearrangement of the double bond was observed. Compared to 6b, the S/C ratio could be enhanced from 1000 to 10000. The oxidation of geraniol with palladium catalyst normally suffers from a cis/trans isomerisation of the double bond.$^{[34]}$ This drawback was not encountered for this catalytic system: the oxidation of geraniol proceeded smoothly giving geranial in 97% yield without geometrical isomerisation of the double bond (Entry 4).

The catalytic system 18b also oxidized alcohols bearing a heteroatom such as oxygen and sulphur. The presence of a phenolic hydroxyl group (Entry 5) did not affect the catalyst’s efficiency and the phenolic hydroxyl group remained unaffected. The high chemoselectivity of this method is demonstrated by its tolerance towards even easily oxidizable functional groups such as thioethers (Entry 6 and 7). However, the reaction rate decreased substantially for the aliphatic alcohol 3-(methylthio)-1-propanol (Entry 7) and as a result, elevated temperatures were necessary. Note that the conversion of the glycerol derivative glycidol to glycidaldehyde (Entry 8) is very selective without any ring opening reaction of the epoxide being observed.

The most remarkable aspect of the catalytic system is its high chemoselectivity when polyols, such as 1,3-butandiol (Entry 9), were used as substrates. However, for the oxidation of polyols, slightly improved reaction conditions were necessary. Despite elevated reaction temperatures and the use of 1.3 equivalents of $p$-benzoquinone, only the primary alcohol was oxidized to give 3-hydroxybutanal exclusively within 10 min. The $[\text{Ir(trop}_2\text{DAD})\text{OTf}]^{18b}$ system is a very rare example of a catalytic oxidation method that does not require a protection group strategy for secondary alcohols.$^{[80, 81]}$

As the isolation of some aldehydes proved difficult, they were isolated as the corresponding 2,4-dinitrophenylhydrazones (Entry 7-9). The isolated yields given in Table 22 for those aldehydes are for the two-step reaction: oxidation of the alcohol and formation of the hydrazone. Given the difficulty of hydrazone formation for glycidaldehyde - to date its isolation has been described in literature with a 55% yield$^{[193]}$ - a yield of 73% can be considered excellent (Entry 8).

### 2.2 Monitoring the Conversion and Temperature versus Time

For the majority of substrates, the dehydrogenation reaction was started at ambient temperature. However, depending on the substrate, a rise of temperature was observed as the catalysis proceeded.
The conversion of 1-octanol to the corresponding aldehyde with was monitored with time; in addition, the change in temperature was measured (Figure 30).

![Figure 30: Conversion of 1-octanol to the corresponding aldehyde with time and the variation in temperature with time. Reaction conditions: 0.01 mol% [Ir(trop₂DAD)]OTf 18b, 0.01 mol% NaO₂Bu, 1.1 eq. p-benzoquinone, 25 mmol 1-octanol.

To determine the conversion, samples were taken from the reaction mixture and analyzed by GC and NMR spectroscopy. The observed differences between the measurements can be attributed to inaccuracies introduced by taking the samples every 10 s by hand. For clarity, a sigmoidal curve was fitted to the sampled data points.

The conversion of 1-octanol to the corresponding aldehyde was found to be slow at the beginning of the catalysis, which could be a result of the slow dilution of p-benzoquinone. The dehydrogenation of 1-octanol is exothermic; a rise in temperature of up to 90 °C during the course of reaction was observed. It can be assumed that the emission of heat accelerates the homogenisation of the reaction mixture and therefore the concentration of dissolved p-benzoquinone. Furthermore, it cannot be excluded that the slow reaction rate at the start of the reaction results from the formation of the catalytically active species from the precursor complex.
2.3 Oxidation of Carbohydrates

Carbohydrates provide complex, multifunctional and stereochemically pure compounds at moderate cost.\cite{194-196} In an environmental context they are currently of interest as alternative, renewable raw materials for the manufacture of fine chemicals.\cite{82} The selective oxidation of carbohydrates is considered to be one of the most challenging disciplines in oxidation chemistry. Certainly, it is an important chemical transformation and a convenient way to introduce new functionalities into the structure and to adjust their chemical and physical properties. Due to the thermal instability and high polarity of carbohydrates, mild reaction conditions in polar solvents, preferably water, are necessary. In the past decades considerable progress has been made in the field of mild oxidation reactions for carbohydrates. The Pfitzner-Moffat\cite{197} and related methyl sulfoxide based reagents\cite{198} have proved versatile. Furthermore, ruthenium tetroxide\cite{199} and chromium trioxide in pyridine\cite{200} have been found to be widely applicable.\cite{201} Even the aerobic oxidation of carbohydrates with heterogeneous palladium catalysts has been described.\cite{19,202} Since these oxidation methods do not discriminate between primary and secondary hydroxyl groups, a sophisticated group protection strategy is needed, which consequently results in moderate overall yields and considerable amounts of waste.

Given the success of the chemoselective oxidation of polyols, the focus was turned to the oxidation of carbohydrates. The first attempt centered on the oxidation of the partially protected carbohydrates; 1,2:3,4-di-O-isopropylidene-D-galactopyranose 60 was chosen as substrate due to its base resistant protecting groups (Scheme 35).

![Scheme 35: Oxidation of partially protected galactose catalyzed by [Ir(trop2DAD)]OTf 18b. Reaction conditions: i) 0.1 mol% [Ir(trop2DAD)]OTf 18b, 0.2 mol% NaO\text{t}Bu, 1.1 eq. BQ, THF, 2h, reflux; ii) 2,4-dinitrophenylhydrazine, THF, 15 min, reflux.](image)

The transformation of the primary alcohol at the carbohydrate to the aldehyde required improved reaction conditions: higher catalyst loading (0.1 mol% 18b), 0.2 mol% NaO\text{t}Bu and elevated temperatures. Under these conditions, the primary alcohol of the carbohydrate was converted to aldehyde 61 in 95% within 2 hours, which was then isolated as the corresponding
2,4-dinitrophenylhydrazone 62 in 84% yield. The hydrazone 62 was formed as (Z)- and (E)-isomers in a 1 : 3.7 ratio, which were then separated by flash chromatography and analyzed separately by NMR spectroscopy. Figure 31 displays a section of the $^1$H, $^1$H NOESY of (E)-62, measured in CDCl$_3$ at room temperature.

A $^1$H, $^1$H NOESY spectroscopy study was used to determine the structure of the major isomer. The cross peaks, indicated by the arrows, prove that the amine proton and the imine proton $H_E$ are located on the same side of the C=N double bond. From these studies it can be confirmed that the major isomer is the (E)-62, as the $^1$H, $^1$H NOESY of (Z)-62 did not show any contact between the amine and the imine proton. The absence of cross peaks for the contact between NH and $H_G$ and $H_G$ and $H_E$ implies that the aromatic ring is orientated perpendicularly to the C=N double bond when in solution.

Given the potential of the organocatalytic, highly selective oxidation of unprotected glycosides reported by Ramström et al.[82], we investigated the oxidation of methyl-α-D-glycopyranoside (Scheme 36).
Catalytic Dehydrogenation of Alcohols

Scheme 36: Oxidation of the unprotected glycoside, methyl-α-D-glycopyranoside.

Unfortunately, unprotected glycosides are highly polar and therefore only poorly soluble most organic solvents. Although complete conversion of 1-octanol is possible in DMSO with this catalytic system, the oxidation of methyl-α-D-glycopyranoside in DMSO, THF and/or DMSO does not convert the primary alcohol of the carbohydrate to the corresponding aldehyde. In fact, at room temperature, no reaction occurred and at elevated temperatures only the decomposition to unidentified products of this thermally unstable substrate was observed.

To the best of our knowledge, [Ir(trop$_2$DAD)]OTf 18b is the first homogeneous transition metal catalyst reported to oxidize a primary hydroxyl group of a carbohydrate to the corresponding aldehyde. Unfortunately, the substrate scope is limited to partially protected carbohydrates, as unprotected glycosides were not found to react.

3 Conclusion

The iridium(I) diazadiene complex 18b is an extremely efficient catalyst (0.01 mol% catalyst loading) for the oxidation of primary alcohols. In contrast to the in situ formation from the corresponding amino-olefin complexes [Ir(trop$_2$DAE)]PF$_6$ 40b and [Ir(trop$_2$DACH)]OTf 6b, milder reaction conditions are required when 18b is used directly as the catalyst and higher reaction rates were achieved. The selective oxidation of primary alcohols to aldehydes in the presence of unprotected secondary alcohols is an attractive preparative method in many respects, in particular because sophisticated group protection strategies are no longer required. In addition, this catalytic system has a high group tolerance and also oxidizes complex alcohols, such as partially protected carbohydrates.

The shortcomings of this system are the lack of reactivity of alcohols bearing nitrogen atoms and the use of p-benzoquinone as the co-oxidant. However, there is still potential for improvement with regard to the oxidation of unprotected glycosides, which require milder reaction conditions.

To obtain further insight into the catalytic cycle of the iridium-catalyzed oxidation, the properties of the diazadiene complexes 18a,b will be studied in more detail in the next chapter. A detailed knowledge of the mechanism is expected to help define the role of the ligand, the base and the
co-oxidant and may eventually facilitate the replacement of $p$-benzoquinone with an environmentally friendly co-oxidant.
VI. Mechanistic Insights – Reactivity of Diazadiene-Olefin Complexes
Mechanistic Insights – Further Reactivities of Diazadiene Complexes

Catalytic reactions offer many advantages, such as atom and process economy and the minimization of waste and pollution and they are widely used in industrial processes; more than half of the chemicals annually produced worldwide rely on the involvement of a catalyst.\textsuperscript{[203]} Unfortunately, the mechanistic study of these catalytic reactions can be difficult, as the amount of catalyst is normally insignificant compared to the amount of substrate. Besides, matters get complicated as the catalyst can interact with the substrate in various ways to form a range of catalytic intermediates. Furthermore, the catalytically active species regenerated at the end of each catalytic cycle may differ from the catalyst precursor. Since catalytic reactions normally proceed over an energetically favourable pathway, the reaction rate and selectivity of a reaction are genuinely affected. As a result, an understanding of the catalytic pathways can be used to enhance process efficiency and to develop selective catalysts.

The catalytic activity of the diazadiene complexes [M(trop\textsubscript{2}DAD)\textsuperscript{OTf} 18\textsubscript{a,b}]\textsuperscript{18} in alcohol oxidation and the scope of this method was investigated in the preceding chapter. As a result, this chapter will focus on the properties of the diazadiene complexes 18\textsubscript{a,b}. To increase our understanding of the catalytic cycle and the important features of efficient catalysts, a mechanistic study was carried out to determine the operating mechanism. This study primarily involved attempts to observe catalytic intermediates of the reaction cycle by means of NMR spectroscopy, isotopic exchange studies and DFT calculations. These results might enable us to understand why rhodium(I) diazadiene complexes are catalytically inactive.

1 Reduction of the Diazadiene-Olefin Complexes

As previously showed by cyclic voltammetry, both complexes [M(trop\textsubscript{2}DAD)\textsuperscript{OTf} 18\textsubscript{a,b}] can be (quasi) reversibly reduced, initially to the neutral complex [M(trop\textsubscript{2}DAD)]\textsuperscript{20a,b} and then to the enediamido complex [M(trop\textsubscript{2}DAD)]\textsuperscript{63a,b}. Chemically, the neutral paramagnetic compounds 20\textsubscript{a,b} were isolated by reduction of 18\textsubscript{a,b} with activated zinc powder and were characterized by continuous wave and pulse EPR spectroscopy (see Introduction). These results, in combination with DFT calculations, revealed that the paramagnetic complexes are best described as [16+1] electron complexes with the unpaired electron located predominately on the diazadiene unit (Scheme 37).\textsuperscript{[132]}

\textsuperscript{18} In order to distinguish between metal complexes with the same ligand, the following letters were used: \textit{a} for rhodium and \textit{b} for the iridium complexes; e.g. [Rh(trop\textsubscript{2}DAD)\textsuperscript{OTf} will be referred to as 18\textsubscript{a} and [Ir(trop\textsubscript{2}DAD)\textsuperscript{OTf} as 18\textsubscript{b}.}
To complement this previous work, we investigated the two-electron reduction of 18a,b with inorganic reducing agents. Preliminary investigations have shown that 18a can be reduced by two equivalents of decamethylcobaltocene, yielding the CoCp²⁺[Rh(trop₂DAD)][89] Herein we will apply the same strategy for the synthesis of the iridium complex 18b and investigate the role of the reducing agent.

1.1 Decamethylcobaltocene as Reducing Agent

The reduction of [Ir(trop₂DAD)]OTf 18b with two equivalents of decamethylcobaltocene in THF quantitatively yields the enediamido complex CoCp²⁺[Ir(trop₂DAD)] 63b (Scheme 37). Due to the insolubility of this salt in THF, red single crystals were obtained directly from the reaction mixture by slow diffusion of decamethylcobaltocene in THF into a concentrated solution of 18b in THF. The structure of the iridium containing anion of the salt 63b, determined by X-ray diffraction analysis, is displayed in Figure 32.

Scheme 37: Reduction of the 16-electron complexes 18a,b with activated zinc powder or two equivalents of decamethylcobaltocene.
Mechanistic Insights – Further Reactivities of Diazadiene Complexes

Figure 32: ORTEP plot of [CoCp₂][Ir(trop₂DAD)] 63b. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms (apart from those at the backbone) and the counter ion ([CoCp₂]⁺) are omitted for clarity. Selected bond length [Å] and angles [°]: Ir-N1 = 1.952(5), Ir-N2 = 1.943(5), Ir-C4 = 2.124(5), Ir-C5 = 2.122(5), Ir-C19 = 2.126(6), Ir-C20 = 2.115(5), Ir-ct1 = 1.993, Ir-ct2 = 1.997, C4-C5 = 1.441(7), C19-C20 = 1.443(8), C31-N1 = 1.379(8), C32-N2 = 1.377(8), C31-C32 = 1.343(8), N1-Ir-N2 = 80.2(2), N1-Ir-ct1 = 90.1, N2-Ir-ct2 = 89.6, ct1-Ir-ct2 = 100.3, \( \phi = 5.1 \).

The ligand is coordinated in a tetradentate fashion to the iridium atom and the complex has an almost pseudo-planar geometry (\( \phi = 5.1 \)). Diazadiene ligands are redox active (non-innocent) ligands and reduction can occur either at the metal centre or at the ligand (see Introduction).\(^{118}\)

In a solid state, the formed complexes can be distinguished from each other by means of the N-C\(_{DAD}\) and C-C\(_{DAD}\) bond lengths of the diazadiene ligand\(^{19}\), provided the crystallographic measurements are sufficiently accurate.\(^{204}\) Scheme 38 displays the redox processes of 18b and its characteristic bond patterns.

Scheme 38: Schematic representation of the redox processes of [Ir(trop₂DAD)]OTf 18b and its characteristic bond patterns as diazadiene complex 18b, radical complex 20b and enediamido complex 63b. Bond distances are given in Å, the radical complex’s bond length were calculated by DFT.

\(^{19}\) C-C\(_{DAD}\) denotes the C-C bond in the diazadiene moiety and C=C\(_{metal}\) denotes the metal-coordinated double bond.
Selected bond distances of 63a,b are compared in Table 23 with the corresponding diazadiene complexes 18a,b and the calculated bond lengths of the paramagnetic complexes [M(cht2DAD)] 20a,b.20

Table 23: Selected experimental bond lengths [Å] of [M(trop2DAD)]OTf 18a,b and CoCP₂⁺[M(trop2DAD)] 63a,b and calculated values (DFT) for [M(cht2DAD)] 20a,b'.

<table>
<thead>
<tr>
<th></th>
<th>M-N</th>
<th>N-C_DAD</th>
<th>C-C_DAD</th>
<th>C=C_DAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh(trop2DAD)]OTf 18a</td>
<td>2.025(5)</td>
<td>1.289(9)</td>
<td>1.460(1)</td>
<td>1.380(1)</td>
</tr>
<tr>
<td>[Ir(trop2DAD)]OTf 18b</td>
<td>2.013(1)</td>
<td>1.295(2)</td>
<td>1.457(3)</td>
<td>1.415(4)</td>
</tr>
<tr>
<td>[Rh(cht2DAD)] 20a</td>
<td>2.014</td>
<td>1.341</td>
<td>1.409</td>
<td>1.428</td>
</tr>
<tr>
<td>[Ir(cht2DAD)] 20b</td>
<td>2.004</td>
<td>1.345</td>
<td>1.407</td>
<td>1.442</td>
</tr>
<tr>
<td>CoCP₂⁺[Rh(trop2DAD)] 63a</td>
<td>1.957(3)</td>
<td>1.368(4)</td>
<td>1.355(5)</td>
<td>1.427(5)</td>
</tr>
<tr>
<td>CoCP₂⁺[Ir(trop2DAD)] 63b</td>
<td>1.952(5)</td>
<td>1.379(8)</td>
<td>1.343(8)</td>
<td>1.441(7)</td>
</tr>
</tbody>
</table>

The diazadiene complexes 18a,b have an almost pseudo-planar structure with N-C_DAD and C-C_DAD bond distances in the range of C=N double bonds and C-C single bonds. In comparison, the N-C_DAD bond distance of [M(trop2DAD)]CoCP₂⁺ 63a,b is substantially longer and closer to a N-C single bond. At the same time, the C-C_DAD bond length is significantly shortened upon reduction of 18a,b and essentially has C=C double bond character.20 These distances confirm that the diazadiene complexes 18a,b have been reduced to the enediamido complex 63a,b. The nearly identical coordination geometries of 18a,b and 63a,b imply that the oxidation state of the metal centre remained unchanged. Furthermore, the M-N and M-ct bond distances of 63a,b were shortened and the C=C_DAD distances were elongated upon reduction when compared to 18a,b. The elongation of the C=C_DAD bond lengths is a consequence of the amides donating more electron density to the metal centre, which results in stronger back-donation to the coordinated olefins. The calculated bond distances of the paramagnetic complexes 20a,b lie between those of 18a,b and 63a,b as the free electron is delocalized on the diazadiene unit. In conclusion, the diazadiene moiety of 18a,b is a redox-active ligand as the reduction occurs at the ligand and not at the metal centre. As a result, the enediamido complexes 63a,b are both best described as [16+2] complexes.

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20 cht2DAD = 1,4-bis(cycloheptatrienyl)-1,4-diazabutadien
The insolvability of $63a,b$ in commonly used deuterated solvents prohibited the characterization by NMR spectroscopy; only the recording of a $^1$H NMR spectrum was successful.\(^{[89]}\)

### 1.2 Sodium as Reducing Agent

The insolvency of CoC$_2$\textsuperscript{$^1$}M(trop$_2$DAD)] $63a,b$ is largely due to the nature of the counter ion. The use of decamethylocobaltocene was circumvented by using elementary sodium as reducing agent and thus allowing characterization by NMR spectroscopy (Scheme 39).

<table>
<thead>
<tr>
<th>$18a,b$</th>
<th>$\text{OTf}$</th>
<th>$\text{Na}$</th>
<th>THF</th>
<th>$\text{Na}$</th>
<th>THF</th>
<th>$\text{sym-63a,b}$</th>
<th>$\text{asym-64a,b}$</th>
</tr>
</thead>
</table>

Scheme 39: Reduction of [M(trop$_2$DAD)]OTf $18a,b$ with sodium in THF yielding the enediamido complexes Na[M(trop$_2$DAD)] $\text{sym-63a,b}$ and the unidentified complexes $\text{asym-64a,b}$.

Reduction of $18a,b$ was performed in an NMR tube with a small piece of sodium. The reaction mixtures were kept in an ultrasonic bath and were closely monitored by NMR spectroscopy. The colour of the reaction changed from red to bright green for $18a$ and from dark green to bright red for $18b$. The $^1$H NMR data $\text{sym-63a,b}$ confirmed that the obtained spectra were identical with those of $63a,b$. As expected, the sodium ion prohibited the fast crystallization of the complexes $63a,b$ and as a result, characterization by NMR spectroscopy was possible after the sodium had been removed from the reaction mixture. On the basis of the $^1$H NMR spectra, which showed a singlet for the olefinic protons, a symmetric coordination sphere around the metal atom was concluded (\textit{vide infra}). When the reduction was not carefully monitored, longer reaction times in the ultrasonic bath resulted in the formation of a unknown compound, which was denoted as $\text{asym-64a,b}$ based on the NMR data (\textit{vide infra}). During the reduction process the subsequent formation of the different complexes was accompanied by a colour change: starting from the dark green of [Ir(trop$_2$DAD)]OTf $18b$, a light green solution of [Ir(trop$_2$DAD)] $20b$ was observed, which then changed to the red of $\text{sym-63a,b}$ and eventually to a brownish red $\text{asym-64b}$. Due to the measurement of $^1$H NMR spectra during the reduction of $18b$, it was possible to observe the formation of $\text{sym-63a,b}$ and its conversion to $\text{asym-64a,b}$ over time (Figure 33).
Figure 33: 2D-stacked $^1$H NMR spectra, recorded during the reduction of 18b with sodium in [D$_8$]-THF.

At the beginning of the experiment, [Ir(trop$_2$DAD)]OTf 18b is the only observable species. Upon addition of sodium, the NMR tube was kept in an ultrasonic bath and only taken out for NMR measurements. For these measurements, the sodium was removed from the solution to suppress further reduction and to ensure the accuracy of the measurement. The diazadiene complex 18b was readily reduced to the paramagnetic complex 20b within 30 min. After 55 min, the symmetrical complex sym-63a,b was formed, as indicated by the singlet of the olefins at 3.49 ppm. The formation of the asymmetric complex began at this point, as shown by the two distinct singlets of the olefinic protons at 2.56 and 2.69 ppm. The conversion to asym-64a,b could be stopped at this point by removing the sodium from the reaction mixture. When the sodium was re-added and reaction mixture was kept for longer in the ultrasonic bath, the amount of asym-64b formed quickly increased. After two additional hours the conversion from sym-63b to asym-64b was completed. When the experiment was repeated several times, the subsequent complex formation was observed but the reaction times differed. However, the reduction of 18a,b by sodium prohibited the instant crystallisation and allowed characterization by NMR spectroscopy of sym-63a,b and asym-64a,b in [D$_8$]-THF. Selected $^1$H, and $^{13}$C chemical shifts of 18a,b, sym-63a,b and asym-64a,b are listed in Table 24.
Mechanistic Insights – Further Reactivities of Diazadiene Complexes

Table 24: Selected $^1$H and $^{13}$C chemical shifts of $^{18}$a,b, sym-$^{63}$a,b and asym-$^{64}$a,b, measured in [D$_8$]-THF if not otherwise noted. Chemical shifts given on the $\delta$ scale are expressed in ppm.

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ $^1$H$_{HC=N}$</th>
<th>$\delta$ $^{13}$C$_{HC=N}$</th>
<th>$\delta$ $^1$H$_{ol}$</th>
<th>$\delta$ $^{13}$C$_{ol}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{18}$a$^{[a]}$</td>
<td>8.40</td>
<td>165.5</td>
<td>5.47</td>
<td>85.3</td>
</tr>
<tr>
<td>sym-$^{63}$a</td>
<td>5.79</td>
<td>117.6</td>
<td>3.49</td>
<td>67.1</td>
</tr>
<tr>
<td>asym-$^{64}$a</td>
<td>6.85, 7.49</td>
<td>126.7, 143.4</td>
<td>2.61, 2.78</td>
<td>59.7, 62.3</td>
</tr>
<tr>
<td>$^{18}$b</td>
<td>9.47</td>
<td>171.1</td>
<td>5.63</td>
<td>74.5</td>
</tr>
<tr>
<td>sym-$^{63}$b</td>
<td>6.23</td>
<td>120.1</td>
<td>3.07</td>
<td>49.1</td>
</tr>
<tr>
<td>asym-$^{64}$b</td>
<td>6.85, 7.60</td>
<td>129.9, 144.3</td>
<td>2.56, 2.69</td>
<td>44.7, 46.7</td>
</tr>
</tbody>
</table>

$^{[a]}$ Measured in CD$_2$Cl$_2$.

As expected from the crystal structure of CoCp$_2$$^*$[M(tropolDAD)] $^{63}$a,b, the enediamido complexes sym-$^{63}$a,b showed only singlets for the H$_{ol}$, H$_{bz}$ and H$_{HC=N}$ protons, confirming a symmetrical geometry around the metal centre. In the $^{13}$C NMR spectra of sym-$^{63}$a,b, the chemical shifts of the carbon atoms at the backbone were observed between 117 and 121 ppm and are thus in the typical range of a C=C double bond. In contrast, the corresponding resonances of the diazadiene complexes $^{18}$a,b occur at higher frequencies (between 165 and 172 ppm) which is in the typical range for diazadienes binding in a $\sigma$-$N,N$ fashion to a transition metal centre.$^{[204]}$ Furthermore, the formation of a C=C double bond in the backbone of the ligand is also implied by the shift of the imine hydrogen atoms H$_{HC=N}$ (8.0 - 10.0 ppm) to the typical region for non-coordinated olefinic protons (5.5 - 6.5 ppm).

In contrast to sym-$^{63}$a,b, the $^1$H spectrum of asym-$^{64}$a,b showed two distinct singlets for the protons of the backbone and distinct multiplets for each aromatic proton. However, the two singlets of the olefinic protons imply that the complexes have a reduced symmetry in comparison to sym-$^{63}$a,b. It can be assumed that the two distinct singlets of the olefinic protons in the $^1$H NMR spectrum arise from the two olefin centroids and two inequivalent donor atoms lying in the same plane, as discussed in Chapter II.2.2.1 (Figure 7B). Unfortunately, the determination of the structure of asym-$^{64}$a,b based on the NMR data was not possible and all attempts to crystallize asym-$^{64}$a,b were unsuccessful.
2 Pentacoordinated Diazadiene Complexes

The reactivity of the diazadiene complexes [M(trop$_2$DAD)]OTf 18a,b towards a wide range of anionic and neutral nucleophiles has been investigated in previous studies. It has been shown that the reaction of different nucleophiles with 18b leads to the formation of pentacoordinated square pyramidal complexes with the incoming ligand bound to the axial position. In contrast, the corresponding rhodium(I) complex 18a shows no adduct formation (see Introduction).\cite{89} The complex formation constant $K_B$ strongly increases with the polarizability of the ligand; in general, ligands with an anionic charge form more stable complexes than the neutral ligands. We assume that the ability to coordinate a fifth ligand is an important feature of the catalysts and provides a plausible explanation for the lack of catalytic activity of 18a. The reason as to why 18a is incapable of binding a fifth ligand and to what extent the non-innocent diazadiene ligand plays the role of an “electronic buffer” in the pentacoordinated iridium complexes has yet to be determined (see Introduction Scheme 13).

2.1 Pentacoordinated Diazadiene-Olefin Complexes

In order to fill these gaps in understanding, the molecular structures of the pentacoordinated complexes [Ir(trop$_2$DAD)L] (L = Cl, SPh)\cite{89} were compared to [Ir(trop$_2$DAD)]OTf 18b, the reduced complexes [Ir(cht$_2$DAD)] 20b' and the enediamido complex CoCp$_2$’[Ir(trop$_2$DAD)] 63b. Selected bond lengths of 18b, 20b and 63b are compared with those of the pentacoordinated complexes [Ir(trop$_2$DAD)Cl] 65b and [Ir(trop$_2$DAD)SPh] 66b in Table 25.
Table 25: Selected bond length [Å] of [Ir(trop$_2$DAD)]OTf 18b, [Ir(cht$_2$DAD)] 20b, CoCp$_2$-[Ir(trop$_2$DAD)] 63b and the pentacoordinated complexes [Ir(trop$_2$DAD)]Cl 65b and [Ir(trop$_2$DAD)]SPh 66b. The DFT calculated bond length of the pentacoordinated complexes are given in brackets below the experimental values.

<table>
<thead>
<tr>
<th></th>
<th>M-N</th>
<th>N-C$_{DAD}$</th>
<th>C-C$_{DAD}$</th>
<th>M-C$_{Col}$ [a]</th>
<th>C=C$_{Col}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(trop$_2$DAD)]OTf 18b</td>
<td>2.013(1)</td>
<td>1.295(2)</td>
<td>1.457(3)</td>
<td>2.165(2)</td>
<td>1.415(4)</td>
</tr>
<tr>
<td>[Ir(cht$_2$DAD)] 20b</td>
<td>2.004</td>
<td>1.345</td>
<td>1.407</td>
<td>2.155</td>
<td>1.442</td>
</tr>
<tr>
<td>CoCp$_2$-[Ir(trop$_2$DAD)] 63b</td>
<td>1.952(5)</td>
<td>1.379(8)</td>
<td>1.343(8)</td>
<td>2.122(5)</td>
<td>1.441(7)</td>
</tr>
<tr>
<td>[Ir(trop$_2$DAD)]Cl 65b</td>
<td>2.009(3)</td>
<td>1.309(4)</td>
<td>1.429(5)</td>
<td>2.154(3)</td>
<td>1.430(5)</td>
</tr>
<tr>
<td>[Ir(trop$_2$DAD)]SPh 66b</td>
<td>1.987(4)</td>
<td>1.316(6)</td>
<td>1.382(7)</td>
<td>2.173(4)</td>
<td>1.435(7)</td>
</tr>
</tbody>
</table>

[a] Only the average bond length of M-C$_{Col}$ is given.

In the solid state, the N-C$_{DAD}$ and C=C$_{Col}$ bond lengths in the pentacoordinated complexes are about 0.02 Å longer, while the C-C$_{DAD}$ bond distance is shortened by the same extent when compared to the cationic precursor [Ir(trop$_2$DAD)]OTf 18b. The geometric changes in the pentacoordinated complexes imply a discernible electron back-donation into the diazadiene and the olefin units but not to an extent that justifies classification as a full electron transfer. In conclusion, the geometric difference is smaller than expected, implying that the electronic structure of the pentacoordinated complexes is best described as low-spin d$^8$ iridium(I) complexes in a square-pyramidal ligand field (resonance structure I).

Detailed DFT calculations were also performed, in collaboration with Frank Neese and Andreas Hansen$^{21}$, to help determine the reason for the different reactivity of 18a and 18b. These DFT calculations revealed that although the electronic structure of 18a and 18b are quite similar, there is a subtle difference: the metal d-based valence orbitals of the iridium complex are higher in energy than those of 18a. As a result, the metal character of the LUMO is slightly higher for 18b, hence the iridium(I) complex is more electrophilic and forms stronger bonds to the nucleophiles.

$^{21}$ Prof. Frank Neese, University of Bonn, Germany.
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Since $K_B$ is not directly accessible via quantum chemical calculations, the COSMO model (with outlying charge correction) was used, to account for the solvent effects (THF) and calculate the corresponding Gibbs energy $\Delta G_R$ for the reaction of 18a,b with a fifth ligand (Table 26).

Table 26: Calculated Gibbs energy $\Delta G_R$ for the reaction of 18a,b with a fifth ligand in THF (COSMO).

<table>
<thead>
<tr>
<th>Chemical Reaction</th>
<th>$\Delta G_R$ [kcal/mol]</th>
<th>$\Delta G_R$ [kcal/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{M(trop}<em>{2}\text{DAD})]^+ + \text{Cl}^- \rightarrow [\text{M(trop}</em>{2}\text{DAD})\text{Cl}]$</td>
<td>-9.2</td>
<td>-17.7</td>
</tr>
<tr>
<td>$[\text{M(trop}<em>{2}\text{DAD})]^+ + \text{PhTe}^- \rightarrow [\text{M(trop}</em>{2}\text{DAD})\text{TePh}]$</td>
<td>-19.0</td>
<td>-24.2</td>
</tr>
</tbody>
</table>

All the calculated reactions are exothermic and the pentacoordinated iridium(I) complexes are always more than 5 kcal/mol thermodynamically more stable than the corresponding rhodium(I) complexes. This finding is in agreement with the higher electrophilic character of 18b and the consequently stronger bonds to the nucleophiles. Despite the computed exothermicities, the formation of pentacoordinated rhodium complexes was never observed experimentally. This result implies that the calculations overlook some aspects of the reaction, e.g. by neglecting the entropy effects, which are negative for association reactions. Accounting for the entropy effect, would shift the Gibbs energy $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$, towards less negative values.

2.2 Pentacoordinated Diazadiene-Phosphane Complexes

The importance of the olefins in trans position to the diazadiene can be demonstrated by the DFT calculations of a (hypothetical) model diazadiene-phosphane complex $[\text{M([PMe}_{3}\text{]_{2}\text{DAD})}]^+$ 67a,b (Scheme 40).

![Scheme 40](image)

Scheme 40: A) Reaction of the diazadiene complex 67a,b with chloride to the pentacoordinated complex 69a,b. B) Optimized geometric structure of the 69b calculated by DFT (BP86/TZVP, ZORA).

Upon reaction of 67a,b with a chloride, one phosphane is shifted from the equatorial to the axial position of the square pyramidal complex $[\text{M([PMe}_{3}\text{]_{2}\text{DAD})Cl}]$ 69a,b; Scheme 40B displays the
Mechanistic Insights – Further Reactivities of Diazadiene Complexes

optimized structure of 69a,b calculated by DFT. As identical results were obtained for the model complex [M((PH₃)₂DAD)Cl], the structural change was assigned to electronic instead of steric effects. DFT calculations of the pentacoordinated complex 69a,b showed that they have a different electronic structure than the diazadiene-olefin complexes [Ir(trop₂DAD)L] (Table 27).

Table 27: Calculated bond length [Å] of the diazadiene-phosphane complexes [M([PMe₃]₂DAD)]⁺ 67a,b, [M([PMe₃]₂DAD)] 68a,b and their pentacoordinated complexes M([PMe₃]₂DAD)Cl 69a,b.

<table>
<thead>
<tr>
<th></th>
<th>M-P</th>
<th>M-N</th>
<th>N-C_DAD</th>
<th>C-C_DAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh([PMe₃]₂DAD)]⁺ 67a</td>
<td>2.312</td>
<td>2.058</td>
<td>1.310</td>
<td>1.440</td>
</tr>
<tr>
<td>[Rh([PMe₃]₂DAD)] 68a</td>
<td>2.260</td>
<td>2.075</td>
<td>1.345</td>
<td>1.400</td>
</tr>
<tr>
<td></td>
<td>2.253</td>
<td>2.060</td>
<td>1.347</td>
<td></td>
</tr>
<tr>
<td>[Rh([PMe₃]₂DAD)Cl] 69a</td>
<td>2.291</td>
<td>2.015</td>
<td>1.357</td>
<td>1.392</td>
</tr>
<tr>
<td></td>
<td>2.303</td>
<td>2.001</td>
<td>1.351</td>
<td></td>
</tr>
<tr>
<td>[Ir([PMe₃]₂DAD)]⁺ 67b</td>
<td>2.306</td>
<td>2.038</td>
<td>1.317</td>
<td>1.430</td>
</tr>
<tr>
<td>[Ir([PMe₃]₂DAD)] 68a</td>
<td>2.254</td>
<td>2.049</td>
<td>1.349</td>
<td>1.396</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ir([PMe₃]₂DAD)Cl] 69a</td>
<td>2.260</td>
<td>2.006</td>
<td>1.366</td>
<td>1.382</td>
</tr>
<tr>
<td></td>
<td>2.295</td>
<td>1.989</td>
<td>1.363</td>
<td></td>
</tr>
</tbody>
</table>

In agreement with the calculated bond length, the pentacoordinated complexes 69a,b are best described as low-spin M(III) complexes with d⁶ configuration, coordinated to an endiamido ligand. The DFT calculations revealed that the dₓz and dᵧz orbitals are involved in weak back-bonding to the phosphane ligands, while the dₓᵧ is essentially non-bonding. Due to the replacement of the olefin ligand by better σ-donor ligand (PMe₃), the valence d-orbitals are more metal-centred and orbital mixing is less pronounced. Furthermore, different interactions occur as a result of changes to the geometric structure, which modify the symmetry of the corresponding orbitals. The dₓz orbital is energetically lower and can easily donate two electrons to the LUMO of the diazadiene. Similar to 18a,b, the iridium complex 67b is more electrophilic, which results in stronger binding to a fifth ligand.

Inspired by the results obtained using the model complexes [M([PMe₃]₂DAD)]⁺ 67a,b, an attempt was made to synthesize rhodium(I) and iridium(I) complexes with a tetradentate diazadiene-phosphane ligand. The synthesis of the ligand is outlined in Scheme 41 and was based on a literature procedure.[206]
Mechanistic Insights – Further Reactivities of Diazadiene Complexes

\[
\begin{align*}
\text{NH}_2\text{HCl} & \quad \text{i} \quad 87\% \quad \text{Ph}_2\text{P} & \quad \text{NH}_2 \quad \text{ii} \quad 45\% \quad \text{Ph}_2\text{P} & \quad \text{N} & \quad \text{N} \quad \text{P} & \quad \text{P} & \quad \text{P} & \quad \text{P} \\
\text{Cl} & \quad \text{70} & \quad \text{71}
\end{align*}
\]

Scheme 41: Synthesis of the diazadiene-phosphane ligand 71. Reaction conditions: i) HPPh₂, KO²Bu, THF, reflux, 24 h; ii) 2,3-butanedione, EtOH, 39 h.

Reaction of 2-chloroethaneamine hydrochloride with diphenylphosphane under basic conditions gave 2-(diphenylphosphino)ethanamine 70 in 87% yield. The desired diazadiene-phosphane ligand 71 was obtained by condensation of 70 with 2,3-butanedione. In the next step, 71 was coordinated to rhodium(I) by reacting it with the metal precursor [Rh₂(µ-Cl)₂(C₅H₄)₄] in the presence of thallium(I) hexafluorophosphate (Scheme 42). Unfortunately, the synthesis of the corresponding iridium(I) complex was unsuccessful.

\[
\begin{align*}
\text{Ph}_2\text{P} & \quad \text{i} \quad \text{PF}_6 \quad \text{72} & \quad \text{73} \\
\text{N} & \quad \text{N} & \quad \text{P} & \quad \text{P} & \quad \text{P} & \quad \text{P} \\
\text{rt} & \quad 82:18 \ (72 : 73) & \quad \text{reflux} & \quad 38.62 \ (72 : 73)
\end{align*}
\]

Scheme 42: Synthesis of the rhodium(I) diazadiene-phosphane complex 72 and its isomer 73. Reaction condition: i) [Rh₂(µ-Cl)₂(C₅H₄)₄], TiPF₆, THF, rt, 1 h.

In addition to the rhodium diazadiene complex 72, which gave a doublet at 51.3 ppm in the ³¹P NMR spectrum, a second complex was formed at room temperature, visible as two doublet of doublets at 54.8 and 54.9 ppm (Figure 34).
Mechanistic Insights – Further Reactivities of Diazadiene Complexes

Figure 34: Section of the $^{31}$P spectrum of a mixture of 72 and 73.

The $^{31}$P signal at 51.3 ppm is a doublet with a coupling constant $^{1}J_{Rh,P} = 166$ Hz, implying a symmetric geometry around the metal centre, as expected for 72. In contrast, the $^{31}$P signals at 54.9 and 54.8 ppm are a doublet of doublets, implying that the complex has no C$_2$-symmetry.

Reaction at room temperature gave a product distribution of 82 : 18 (72 : 73). Although refluxing changed the ratio to 38 : 62 (72 : 73), even longer reaction times did not lead to full conversion to 73. Detailed 1D and 2D NMR spectroscopic studies of 73 in the mixture revealed that one of the C=N double bonds has been rearranged so that the two C=N double bonds are no longer conjugated. This result is likely to be due to steric strain imposed on the ligand. Selected $^1$H, and $^{13}$C chemical shifts 72 and 73 are listed in Table 28.

Table 28: Selected $^1$H, and $^{13}$C chemical shifts of 72 and asym-73, measured in [D$_8$]-THF. The chemical shifts given on the δ scale are expressed in ppm.

<table>
<thead>
<tr>
<th></th>
<th>$\delta^{1}H_{CH_3}$</th>
<th>$\delta^{13}C_{CH_3}$</th>
<th>$\delta^{13}C_{CH_2P}$</th>
<th>$\delta^{13}C_{CH}$</th>
<th>$\delta^{1}H_{HC=N}$</th>
<th>$\delta^{13}C_{HC=N}$</th>
<th>$\delta^{13}C_{MeC=N}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>2.12</td>
<td>17.0</td>
<td>34.8</td>
<td></td>
<td>172.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>1.67</td>
<td>15.6</td>
<td>36.3</td>
<td>76.5</td>
<td>8.41</td>
<td>170.7</td>
<td>183.2</td>
</tr>
</tbody>
</table>

As the geometry around the rhodium(I) atom of complex 72 is symmetrical, the phosphorus atoms are equivalent, resulting in a doublet as they couple with the $^{103}$Rh atom ($^{1}J_{RhP} = 166$ Hz). Due to the rearrangement of the C=N double bond, a signal of an imine proton $H_{HC=N}$ at 8.41 ppm was observed in
the $^1$H NMR spectrum of complex 73. Furthermore, the signal for the methyl group at 1.67 ppm splits up into a doublet in the $^1$H NMR spectrum: it couples to the CH group at the backbone of the ligand, which was formed during the rearrangement. In the $^{13}$C NMR spectrum, two distinct signals for the imino groups, the CH$_2$P groups and the methyl groups are visible and one signal of the CH group at 76.5 ppm. Due to the rearrangement, the two phosphorus atoms are inequivalent and as a result, two doublets of doublets are present in the $^1$H NMR spectrum: they couple with the rhodium atom ($^1$$J_{HbP} = 166$ Hz) and with each other ($^2$$J_{PP} = 33$ Hz).

When the reaction of the ligand with the rhodium(I) precursor was performed in the absence of thallium(I) hexafluorophosphate, identical NMR spectra were obtained when compared to complexes 72 and 73 with hexafluorophosphate as counter ion. This finding implies that the chloride is the counter ion and not coordinated to the metal centre. As a result, the formation of a pentacoordinated complex could be excluded. Despite the prediction for the model complex 67a,b, the diazadiene-phosphane complex 72 did not form stable pentacoordinated complexes with chloride. This could be due to the tetradentate ligand circumventing the geometric rearrangement, with one phosphane in the axial position and the chloride in the equatorial position. Unfortunately, attempts to synthesize a diazadiene complexes with bidentate phosphane ligands were unsuccessful.

In conclusion, these results support the assumption that the ability of the pseudo-planar [Ir(trop$_2$DAD)OTf 18b to coordinate a fifth ligand in the axial position is the key to its catalytic activity. Furthermore, these results show that both the diazadiene and the olefins of 18b are equally important for stabilizing the extra electron density from the fifth ligand. The calculated structure of [M((PMe$_3$)$_2$DAD)Cl] 69a,b showed that in the absence of olefins, the chloride occupies an equatorial position. Due to this geometry, a substantial back-donation from the metal to the diazadiene results so that 69a,b are best described as enediamido M(III) complexes with d$^6$ configuration. In particular, in catalysis it is crucial that the incoming substrate binds weakly to the metal centre and that the resulting product is easily replaced again after the transformation by a substrate molecule. On the basis of these results, it is assumed that the tetradentate ligand of 18b favours the weak coordination of the substrate in the axial position of the square pyramid. In this context, it is interesting that [Ir(c-hex)$_2$DAD]CODPF$_6$ 58, which is a poor catalyst for the alcohol oxidation, forms stable trigonal bipyramidal pentacoordinated complexes with triphenylphosphine in which the diazadiene is occupying the axial positions.$^{[127]}$ Undeniably, the iridium(I) atom and the tetradentate diazadiene-olefin ligand are well matched; changing the metal centre or modifying the ligand results in reduced catalytic activity or complete deactivation. In the following section, the reaction of 18b with alcohols and alcoholates will be investigated.
3 Reaction of Diazadiene Complexes with Alcohols and Alcoholates

As studies into the ability of [Ir(trop₂DAD)]OTf 18b to form pentacoordinated complexes were performed before its catalytic activity in alcohol oxidation had been discovered, the reaction with alcohols and alcoholates has not yet been investigated.

3.1 Reaction of Diazadiene Complexes with Alcohols

In order to gain an insight into the catalytic cycle of the oxidation of alcohols, the reaction of [Ir(trop₂DAD)]OTf 18b with different alcohols, such as ethanol, iso-propanol, benzylic alcohol and cyclo-hexanol was investigated. The reaction of 18b in THF with these alcohols gave [Ir(trop₂MIMA)]OTf 53b (Scheme 43) in all cases. This complex was discovered as the intermediate in the oxidative dehydrogenation of the amino-olefin complexes [M(trop₂DAE)]PF₆ 40a,b (see Chapter IV).

Based on previous discoveries for different nucleophiles, it was assumed that the alcohol coordinates to the iridium atom, forming the pentacoordinated species TS in a transition state. In the next step, a hydride transfer from the alcohol to the electrophilic C=N double bond, along with the protonation of the formed amide, produces 53b and the corresponding aldehyde. DFT calculations for iridium(I) transfer hydrogenation catalysts have shown that the methoxide coordinated iridium(I) complexes formed are highly unlikely to undergo β-elimination to formaldehyde and the iridium-hydride complex: the energy barrier was calculated to be in the order of 26-30 kcal/mol. A mechanism via an
iridium-hydride intermediate could therefore be excluded for the dehydrogenation of alcohols with [Ir(trop₂DAD)]OTf 18b. Unlike in catalysis, the reaction of 18b to 53b requires long reaction times at elevated temperatures and an excess of alcohol (100 equivalents). Furthermore, the reaction of 18b with secondary alcohols, such as cyclo-hexanol and iso-propanol, also gave 53b at a comparable reaction rate. However, under catalytic conditions the transformation of a primary alcohol to the corresponding aldehyde is much faster and the conversion of a secondary alcohol to the ketone was never completed (see Table 19).

Interestingly, the reaction of [Ir(trop₂DAD)]OTf 18b with the alcohol stopped at the partially hydrogenated complex [Ir(trop₂MIMA)]OTf 53b and did not proceed further to the amino-olefin complex [Ir(trop₂DAE)]OTf 40b. Furthermore, the corresponding rhodium(I) complex 18a is unreactive, which supports the assumption that the formation of pentacoordinated alcohol-complex is a crucial intermediate in the catalytic cycle. Reaction of isolated 53b with p-benzoquinone instantaneously regenerated 18b again.

### 3.1.1 Reaction of Diazadiene Complexes with Deuterated Alcohol

Further insight into the mechanism of the catalytic cycle can be obtained from deuteration studies, i.e. determining the position(s) at which the deuterium is incorporated in the resulting [Ir(trop₂MIMA)]OTf 53b by means of ¹H, ²H and ¹³C NMR spectroscopy. To perform this study, the reaction of 18b was repeated using deuterated ethanol. The reaction of 18b with an excess [D₆]-ethanol (20 equivalents) led to the formation of more than one product after 7 d of refluxing. The prolonged reaction time for deuterated compared to non-deuterated ethanol implies an isotope effect. The resulting deuterated complexes are displayed in Figure 35; enantiomers and diastereomers are not mentioned separately.

![Figure 35: Complexes D1-D4 that have been obtained as products of the reaction of 18b with [D₆]-ethanol.](image-url)
Overall, the complexes formed incorporated between one (D1) and four deuterium atoms (D4). In the case of irreversibility and the absence of proton-deuterium exchange, two deuterium atoms should theoretically be integrated into the backbone of the ligand: one at the nitrogen atom and the other at the α-carbon next to the nitrogen atom. In the $^1$H NMR spectrum, the absence of the NH peak at 7.16 ppm, implies an incorporation of deuterium. The integrals of $H_{NC,N}$ and CH$_2$ are much lower in intensity than the olefinic or benzylic protons. In the $^{13}$C NMR spectrum, carbon atoms with no bonded deuterium appear as singlets, as the carbon nucleus is decoupled from the hydrogen nucleus. In contrast, multiplicity arises as a result of the carbon nucleus coupling with a deuterium atom. The $^{13}$C NMR spectrum clearly shows that no deuterium is incorporated at the olefinic, benzylic and aromatic carbon atoms. As a result, it can be concluded that the deuterium only took place on the backbone of the ligand. Besides the CH$_2$-type carbon atoms, CHD- and CD$_2$-type carbon atoms were also identified in the $^{13}$C NMR spectrum in addition to the $C_{NC,N}$ and $C_{BC,N}$ carbon atoms. The incorporation of multiple deuterium atoms implies that the reductive hydrogenation is reversible or that 53b undergoes proton-deuterium exchange (Scheme 44).

This assumption was confirmed by reacting 53b with an excess of acetone, which produced merely 30% of the iridium(I) diazadiene complex 18b after 3 d at room temperature.

The reaction with [D$_6$]-ethanol was repeated for the corresponding rhodium(I) diazadiene complex 18a to eliminate the possibility that the equilibrium of the reaction lies almost entirely on the side of the diazadiene complex. However, the incorporation of deuterium into the diazadiene complex 18a will be detectable by $^2$H NMR spectroscopy. The reaction conditions were identical to those used for 18b, but the reaction time was prolonged to eliminate the possibility that the reaction is much slower. After 3 weeks, the sample was examined by $^1$H and $^2$H NMR spectroscopy. In the $^1$H NMR spectrum, neither the formation of a (mono)imine(mono)amine complex nor an intensity loss of the imine protons compared to the olefinic, benzylic and aromatic protons was observed. To be absolutely sure, a $^2$H NMR spectrum was measured, which did not show any resonances. It can therefore be concluded with certainty that 18a does not react with alcohols.
3.2 Reaction of Diazadiene Complexes with Alcoholates

To complement this work, the reaction of \([\text{Ir(trop}_2\text{DAD})\text{OTf}] 18b\) with alcoholates was investigated. Instead of producing a pentacoordinated complex, the enediamido complex \(\text{Na}[\text{Ir(trop}_2\text{DAD})] \text{ sym-63b}\) was formed (Scheme 45).

![Scheme 45: Proposed mechanism of the reaction of 18b with alkoxides in THF.](image)

The iridium(I) diazadiene complex 18b reacts with an excess of cyclo-hexanolate or benzyl alcoholate (4 equivalents) to sym-63b in less than 15 min in THF. Upon addition of only one equivalent of benzylalcoholate to 18b, the formation of small amounts of benzaldehyde was observed, which decreased with the addition of larger amounts of benzyl alcoholate, as the equilibrium shifted towards the side of the hemiacetal. Similar to the reaction of 18b with different alcohols, the corresponding rhodium(I) complex 18a did not react with any alcoholate. The formation of sym-63b under non-protic conditions can be attributed to a hydride transfer from the alcohol to the C=N double bond over a pentacoordinated complex (Scheme 43 TS) in the first step, giving I-1. The subsequent 1,2-H shift results in the formation of I-2, which is deprotonated by the excess of alcoholate.

In order to prove that the formation of sym-63b results from the rearrangement of the proposed intermediate I-1 and subsequent deprotonation of I-2, the deprotonation of \([\text{Ir(trop}_2\text{MIMA})\text{OTf}] 53b\) was studied (Scheme 46).
Mechanistic Insights – Further Reactivities of Diazadiene Complexes

Scheme 46: Deprotonation of [Ir(trop₂MIMA)]OTf 53b with two equivalents of sodium alkoxide.

The double deprotonation of 53b with two equivalents of NaO’Bu gave the expected product sym-63b within a few minutes.

3.3 DFT-Calculations

The reaction of the alcohol with [Ir(trop₂DAD)]OTf 18b to [Ir(trop₂MIMA)]OTf 53b requires an excess of alcohol (100 equivalents) and lengthy reaction times (24 h) at elevated temperatures. This result is not in agreement with the reaction rates of the catalysis, which takes only between 90 s to 20 min, depending on the substrate (Table 19). In comparison, the reoxidation of 53b with p-benzoquinone to 18b takes less than a minute. When the two separate steps were scrutinized by NMR spectroscopy, it was observed that once 53b was formed quantitatively, the second step was very fast: reoxidation to 18b and the oxidation of the excess of alcohol occurred within seconds to full conversion. This mismatch between the reaction time for the formation of [Ir(trop₂MIMA)]OTf 53b and the oxidation of alcohols under catalytic conditions prompted an investigation into the formation of 53b using DFT calculations, conducted by Jean-Valère Naubron²² (B3PW91/6-311G(d): Lanl2dz). Preliminary DFT calculations have shown that the nitrogen atoms of the diazadiene complex are not basic and therefore the O-H bond of the alcohol must be cleaved prior to the catalysis. This result might explain the necessity of 0.01 mol% NaO’Bu for full conversion of the alcohol with low catalysts loadings (see Chapter V). Figure 36 displays the reaction of the model complex [Ir(cht₂DAD)]OTf 18b²³ with ethanolate.

²² Dr. Jean-Valère Naubron, University of Marseille, FR.
²³ For the DFT calculation, the trop ligand was simplified: cht = cycloheptatrienyl. These complex complexes are denoted by an apostrophe ‘: [Ir(trop₂DAD)]OTf 18b and [Ir(cht₂DAD)]OTf 18b’.
The reaction of [Ir(cht₂DAD)]OTf 18b′ with ethanolate leads to the formation of the ethoxide complex [Ir(cht₂DAD)OEt] 74b′ in which the ethanolate binds to the iridium via the oxygen atom. This adduct 74b′ was assigned a zero energy level. Subsequently, the α-C-H bond is broken via TS and hydride transfer to the C=N double bond occurs. This reaction step is endothermic and the activation barrier is 13.1 kcal mol⁻¹. The dissociation of the acetaldehyde leads to the formation of 53b′, a step which is very exothermic.

Given that the diazadiene-olefin complex [Ir(trop₂DAD)]OTf 18b is reduced by NaO'Bu to the radical complex [Ir(trop₂DAD)] 20b (which shows the same catalytic activity in the dehydrogenation of alcohols), its involvement in the catalytic cycle cannot be excluded. Consequently, DFT calculations were used to analyse the reaction of ethanolate with the model radical complex [Ir(cht₂DAD)] 20b′. In this scenario, the activation barrier was found to be significantly lower than for [Ir(cht₂DAD)]OTf 18b′ (E_a = 9.0 kcal mol⁻¹).

The mismatch between the slow formation of [Ir(trop₂MIMA)]OTf 53b from the reaction of 18b with alcohol and the subsequent faster reoxidation and dehydrogenation of the excessive alcohol can be attributed to the dual function of the p-benzoquinone added as co-oxidant and base. Note: an important feature of this catalytic system might be the re-aromatization energy and the re-conjugation
energy that results from the oxidation of \( p \)-benzquinone to \( p \)-hydroquinone and \( 53b \) to diazadiene \( 18b \). During the course of the catalysis, the reaction vessel heated up to 90 °C; given the extremely exothermic nature of the dehydrogenation of alcohols, it is conceivable that the elevated temperatures needed to initiate the first step are produced during later stages of the reaction.

Two conclusions can be drawn from the DFT calculations. Firstly, the long reaction times and the elevated temperature required for the reaction of the cationic complex \( 18b \) with alcohols can be attributed to the absence of base. Secondly, the lower activation energy for the reaction of the radical complex \( 20b \) with ethanolate strongly implies an involvement of \([\text{Ir(trop}_2\text{DAD})]\) \( 20b \) in the catalytic cycle. The implication of this section’s findings for the mechanism will be discussed in detail in Section VI.6.

4 Reaction of Diazadiene Complexes with Molecular Hydrogen

During the reductive hydrogenation of \([\text{Ir(trop}_2\text{DAD})]\)OTf \( 18b \) to \([\text{Ir(trop}_2\text{MIMA})]\)OTf \( 53b \) by alcohols, a hydride and a proton is transferred from the alcohol to the diazadiene complex. This process can in principle be regarded as the transfer of dihydrogen (\textit{vide supra}). The hydrogenation of small molecules containing C-N multiple bonds is, in general, not a facile process and normally requires elevated temperature and high pressures.\(^{125, 209}\) To date, only a few examples have been reported of the hydrogenation of binuclear diazadiene complexes (see Introduction).\(^{123-126, 210}\) As a result, the question arose whether the mononuclear complex \( 18b \) reacts with molecular hydrogen (Scheme 47).

![Scheme 47: Reaction of \([\text{Ir(trop}_2\text{DAD})]\)OTf \( 18b \) with 1 bar molecular hydrogen in THF.](image)

Preliminary experiments were made using 40 bar hydrogen pressure. These experiments showed that \( 18b \) was instantaneously hydrogenated to \( 53b \). Further experimentation showed that high pressures were not necessary: the hydrogenation of \( 18b \) also proceeds with 1 bar hydrogen pressure at room temperature. Within one hour, this reaction was completed, yielding exclusively \( 53b \). It is remarkable that the hydrogenation does not produce the fully hydrogenated complex \([\text{Ir(trop}_2\text{DAE})]\)OTf \( 40b \). In agreement with the previous studies of the reactivity of \( 18a, b \) towards a wide range of nucleophiles, the rhodium(I) diazadiene complex \( 18a \) is not hydrogenated to the corresponding (mono)imino(mono)amine \( 53a \) or amino-olefin complex \( 40a \). In conclusion, it is assumed that the key
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step is the coordination of dihydrogen to the iridium diazadiene complex, as 18a is not able to coordinate a fifth ligand. The proposed mechanism for the hydrogenation is displayed in Scheme 48.

Scheme 48: Proposed mechanism for the hydrogenation of [Ir(trop₂DAD)]OTf 18b with molecular dihydrogen.

In the proposed mechanism, molecular hydrogen coordinates to the iridium complex in the first step; it is thought to form a non-classical dihydrogen complex I-3. The heterolytic splitting of dihydrogen across the iridium and the carbon at the backbone of the ligand occurs via the transition state TS resulting in the iridium hydride complex I-4 which rearranges to form [Ir(trop₂MIMA)]OTf 53b. Further investigation will be necessary to confirm this proposed mechanism.

5 Reaction of [Ir(trop₂MIMA)]OTf with Oxygen

Due to environmental considerations (see Chapter V), the substitution of p-benzoquinone for a less hazardous oxidizing reagent is desirable. In order to do so, two conditions must be fulfilled: firstly, it must have a suitable redox potential and secondly, it has to be basic. With the isolated intermediate of the catalytic cycle, the reaction [Ir(trop₂MIMA)]OTf 53b with oxygen was investigated by ¹H NMR spectroscopy (Scheme 49).

Scheme 49: Reoxidation of [Ir(trop₂MIMA)]OTf 53b to [Ir(trop₂DAD)]OTf 18b with air.
Complete conversion to 18b was observed after 7 d at room temperature. No decomposition of the complex was observed after this time. It is assumed that the transfer of the hydride and proton to the oxygen is the reaction-determining step. To facilitate this step, pyridine was added as an external base, resulting in a significant increase of the reaction rate: instead of 7 d it now took only 3 d.

In conclusion, it has been shown that the aerobic oxidation of 53b to 18b is possible even though it proceeds slowly. However, the reaction rate was still too slow for using oxygen as co-oxidant; experiments conducted accordingly for the oxidation of 1-octanol with 1 mol% 18b gave merely 1% conversion after 48 h.

6 Catalytic Cycle of Alcohol Dehydrogenation

In this chapter, the reactivity of the diazadiene complexes [M(trop2DAD)]OTf 18a,b towards different reagents was investigated, in an attempt to determine the key difference between the rhodium(I) and iridium(I) complexes. The only difference found was in their ability to coordinate a fifth ligand. This ability is pivotal for the catalytic activity, as it is assumed that the alcohol has to bind weakly to the iridium atom prior to the catalysis.

The amount of substrate required is many times that of the catalyst, hindering observation of the catalytic intermediates. To overcome this problem, the interaction of [Ir(trop2DAD)]OTf 18b with alcohol was investigated under slightly different reaction conditions. In this process, instead of the metal centre, the diazadiene ligand was reduced, producing the hydrogenated complex [Ir(trop2MIMA)]OTf 53b (see Section VI.3.1). Reacting isolated 53b with p-benzoquinone regenerated 18b again. While attempting to prove the correctness of a proposed mechanism, it must taken into consideration that even small changes in the reaction conditions may alter some delicate balance and thereby change the mechanism and the selectivity of the reaction. This might explain why the reaction of secondary alcohols with 18b also led to the formation of 53b with similar reaction rates. This is not in agreement with the observed reactivity of 18b towards secondary alcohols under catalytic conditions (see Chapter V). As a result, it is assumed that the use of additional base and p-benzoquinone under catalytic conditions might have a stronger influence on the mechanism than expected. Based on these findings, a mechanism for the catalytic oxidation of alcohols is proposed, in which the diazadiene ligand behaves as a cooperating ligand.

The DFT calculations and the fact that [Ir(trop2DAD)] 20b can be used as catalyst in the dehydrogenation of alcohols imply that, in all likelihood, the diazadiene radical complex 20b is the catalytically active species (see Section VI.3). Moreover, it has been shown that the addition of NaO'Bu
to [Ir(trop₂DAD)]OTf 18b gives a strong EPR signal for the diazadiene radical complex [Ir(trop₂DAD)] 20b in the EPR spectrum. This observation implies that the diazadiene radical complex is the catalytically active species, which is formed by reaction with the base under catalytic conditions (see Section V.1.2). In general, the dehydrogenation of a primary alcohol to the corresponding aldehyde can be regarded as an elimination of a proton and a hydride from the substrate (formally dihydrogen), whilst forming the corresponding aldehyde. The removal of the hydride (a poor leaving group) is aided by the catalyst, which captures the pair of electrons and converts the hydride into a proton. The proposed catalytic cycle for the dehydrogenation of alcohols is displayed in Scheme 50.

Scheme 50: Proposed catalytic cycle for the dehydrogenation of alcohols with [Ir(trop₂DAD)]OTf 18b.

On the basis of the results presented so far, the diazadiene radical complex [Ir(trop₂DAD)] 20b is the catalytically active species and therefore has to be formed in situ when using [Ir(trop₂DAD)]OTf 18b as precursor. In the next step, an alcololate coordinates to 20b resulting in the formation of the
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pentacoordinated intermediate 1-5, which has a square pyramidal structure. In this geometrical arrangement, the α hydrogen of the substrate is in close proximity to the radical delocalized in the backbone of the diazadiene ligand. The intramolecular hydrogen atom transfer leads to the ketyl radical complex 1-6. Rapid intramolecular redox processes form the intermediate 1-7 and the aldehyde. Oxidation with ρ-benzoquinone (BQ) and subsequent deprotonation by the ρ-semiquinone radical formed (SQ⁻) give the enediamido complex 63b, which is the deprotonated form of [Ir(trop)MIMA]OTf 53b (see Section VI.3.3). In the final stage of the catalytic cycle, the enediamido complex 63b is reoxidized to [Ir(trop,DAD)] 20b. In this case, the diazadiene ligand is best described as a *cooperating ligand* which participates directly in the C-H bond activation and undergoes a reversible chemical transformation in the catalysis.\[^{64}\]

In the proposed catalytic cycle, the catalyst [Ir(trop,DAD)] 20b is reductively hydrogenated by the primary alcohol and then undergoes oxidative dehydrogenation upon reaction with ρ-benzoquinone, in accordance with the mechanism presented in Chapter IV.

The presence of 0.01 mol% NaO'Bu in the reaction mixture is needed to initiate the catalysis by reducing the catalyst precursor [Ir(trop,DAD)]OTf 18b to [Ir(trop,DAD)] 20b. In addition, small amounts of NaO'Bu are needed to deprotonate the alcohol and so enabling the formation of 1-5 until enough deprotonated hydroquinone has been formed to fulfil this role. The function of ρ-benzoquinone is to regenerate the catalyst 20b by formally abstracting a hydride and a proton. Furthermore, the deprotonated hydroquinones (HQ \(^1\)H and HQ \(^2\)H) and SQ⁻ play an important role in the deprotonation of the intermediate complex 1-7 and the hydroxyl groups of the substrate. In principle, the following equilibrium between [Ir(trop,DAD)] 20b and [Ir(trop,DAD)]OTf 18b can be assumed in the presence of ρ-benzoquinone (Scheme 51).

\[
\text{[Ir(trop,DAD)]}^{+} + \text{HQ} \rightarrow \text{[Ir(trop,DAD)]}^{2+} + \text{HQ}^{+}
\]

Scheme 51: Proposed equilibrium between [Ir(trop,DAD)] 20b and [Ir(trop,DAD)]OTf 18b in the presence of ρ-benzoquinone.

In this context, the unsuitability of DDQ as co-oxidant (see Section V.1.3.1) can be readily explained by the equilibrium shown in Scheme 51: if the co-oxidant is too strongly oxidizing, the equilibrium lies on the side of the catalyst precursor [Ir(trop,DAD)]OTf 18b, which results in the deactivation of the catalyst. However, if the co-oxidant is not strong enough, then the rapid regeneration of [Ir(trop,DAD)] 20b at the end of the catalytic cycle is hindered. This conjecture is supported by the redox potentials of 18b and ρ-benzoquinone (Table 12 and Table 20). Furthermore, if the
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$p$-hydroquinone is too acidic, then the formation of alcoholates will be strongly suppressed and as a result, the catalysis will become significantly slower or not proceed at all, as only the alcoholate is able to coordinate to 20b. In this context, another important feature may be the solubility of hydroquinone. Since concentrations of these build up during the catalytic reaction, the complex’s proton transfer and redox equilibria will be shifted towards the side of the less active forms of the catalyst. However, if the HQ and SQ precipitate during the course of the reaction, then a concentration of catalytically active diazadiene radical anion complex sufficiently high to achieve high reaction rates will result.

The presented mechanism explains the role of the metal, the ligand, the co-oxidant and the dual function of the added base. Irrefutably, the iridium(I) atom, the diazadiene-olefin ligand trop₂DAD, sodium tert-butoxide and $p$-benzoquinone form a perfectly balanced, winning combination: even slight modifications to the catalytic system can significantly reduce the reaction rate or even deactivate it completely.

7    Outlook

In conclusion, the chemoselective oxidation method for the catalytic oxidation of alcohols with the established amino-olefin catalyst [Ir(trop₂DACH)]OTf 6b [2] was advanced and a 2nd generation catalyst which reduces the limitations of the former catalytic system was developed. The detailed mechanistic investigation showed that [M(trop₂DACH)]OTf 6a,b and the newly prepared amino-olefin complexes [M(trop₂DAE)]PF₆ 40a,b undergo oxidative dehydrogenation to the corresponding diazadiene complexes [M(trop₂DICH)]OTf 52a,b and [M(trop₂DAD)]OTf 18a,b prior to catalysis. As a result, by employing the diazadiene complex 18b in catalysis, the scope could be expanded considerably to more complex primary alcohols with sensitive functional groups. However, the dehydrogenation of highly polar alcohols with more than two unprotected hydroxyl groups, such as unprotected carbohydrates, was unsuccessful. To overcome this disadvantage and to broaden the scope, the synthesis of a water-soluble catalyst is desirable. For this purpose, modifying the ligand framework by introducing sulfonate groups in the meta position of the benzo groups seems promising, resulting in the diazadiene-olefin ligand 75 (Figure 37).
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![Figure 37: Proposed ligand framework of a water-soluble diazadiene-olefin ligand 75 for the dehydrogenation of highly polar alcohols.]

Further challenges lie in the field of asymmetric alcohol oxidation, as the demand for enantiomerically pure compounds in the pharmaceutical industry has increased significantly. To date, only a few effective oxidation catalysts are able to discriminate between two alcohols on the basis of their chiral environment (see Introduction). To broaden the application of the presented chemoselective [Ir(trop₂DAD)]OTf 18b catalytic system to the desymmetrization of meso-diols and the kinetic resolution (KR) of primary alcohols with a chiral centre at the β-carbon atom, a chiral version of the diazadiene ligand trop₂DAD 28 is desirable. Figure 38 displays a selection of possible tri- and tetradentate chiral diazadiene ligands.

![Figure 38: Possible chiral diazadiene-olefin ligand frameworks for application in asymmetric oxidation chemistry.]

One possible ligand framework is represented by the tridentate ligand 76 where the chiral information is embedded in the oxazoline ring. The catalytic activity of 76, however, might be affected by the sterically demanding substituent at the diazadiene moiety (see Chapter V). As a result, the synthesis of ligand 77 and 78 might be more promising, as chirality arises from the coordination of the olefins to the metal centre. Furthermore, the C₂ symmetry of these ligands might be advantageous, as the substrate experiences the same chirality regardless of how it binds.

The main drawback of the kinetic resolution is that as the maximum theoretical yield is limited to 50%, half the material is wasted. This limitation has recently been overcome by combining an enzyme with a
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racemisation catalyst, which enhances the theoretical yield of an enantiomerically pure alcohol to 100%.\textsuperscript{[211]} This method, known as dynamic kinetic resolution (DRK), was recently extended by Bäckvall et al. to primary alcohols with a chiral centre in the β-position. (Scheme 52).\textsuperscript{[212]}

\begin{center}
\textbf{Scheme 52: Proposed mechanism for the dynamic kinetic resolution of primary β-aryl substituted alcohols by Bäckvall et al.}\textsuperscript{[212]}
\end{center}

A similar reaction could potentially be developed for [Ir(trop\textsubscript{2}DAD)]OTf 18b, providing 18b is a sufficiently good racemisation catalyst and compatible with a suitable enzyme.

Besides its reactivity in the catalytic dehydrogenation of alcohols, [Ir(trop\textsubscript{2}DAD)]OTf 18b reacts smoothly with molecular hydrogen to form the partially hydrogenated (mono)imino(mono)amino complex [Ir(trop\textsubscript{2}MIMA)]OTf 53b (see Chapter VI). Based on this result, the catalytic application of [Ir(trop\textsubscript{2}DAD)]OTf 18b in the catalytic hydrogenation of aldehydes, ketones and imines with molecular hydrogen might be possible, proceeding via the catalytic cycle displayed in Scheme 53.
The successful realization of the catalytic hydrogenation of aldehydes, ketones and imines with the established alcohol dehydrogenation catalyst [Ir(trop₂DAD)]OTf 18b would render 18b a multifunctional catalyst. Depending on the chosen reaction conditions, it would then be possible to control whether the oxidation of alcohols or reduction of carbonyl compounds occurs. Furthermore, good results for the hydrogenation of ketones and secondary imines with 18b would emphasise the necessity of a chiral diazadiene-olefin iridium(I) catalyst for the enrichment of enantiomerically pure secondary alcohols and amines.
VII. Experimental Section
**General Comments**

**General Techniques**

All syntheses and catalyses were performed under an argon atmosphere using standard Schlenk techniques. Glassware was flame dried under high vacuum or dried at 120 °C overnight prior to use. Air sensitive compounds were stored and handled in a glove box (Braun MB 150 B-G system). Small-scale reactions were performed in 15 mL glass vials directly in the glove box. Solvents were freshly distilled under argon from sodium/benzophenone (THF, diethylether, DME), sodium/benzophenone/tetraglyme (hexane, toluene) or calcium hydride (DCM) prior to use and stored over 3 Å molecular sieves.

**Chemicals**

Basic chemicals were ordered from ABCR, Acros, Aldrich, Fluker, Lancaster or STREM. Solid alcohols were used as received without further purification, whereas the liquid alcohols were dried over a small amount of sodium and additionally distilled under argon. Sodium tert-butoxide and benzoquinone were purified by sublimation and stored under argon. The following organic compounds and metal precursors were prepared by literature methods: tropNH$_2$ (N-(5H-dibenzo[a,d]cyclohepten-5-yl)-amine),$^{[89, 213]}$ tropCl,$^{[169]}$ tropOH,$^{[169]}$ trop$_2$DAD,$^{[132]}$ trop$_2$MeDAD,$^{[214]}$ N,N'-bis(trimethylsilyl)-ethylendiamin,$^{[215]}$ [Rh$_2$(μ-Cl)$_2$(C$_2$H$_4$)$_4$],$^{[216, 217]}$ [Ir$_3$(μ-Cl)$_2$(COD)$_3$],$^{[218]}$ and [Ir$_3$(μ-Cl)$_2$(COE)$_4$]$^{[218]}$.

**NMR Spectroscopy**

NMR spectra were recorded using Bruker Avance 700, 500, 400, 300 and 250 spectrometers at room temperature if not otherwise noted. Chemical shifts (δ) are given as dimensionless values in ppm relative to TMS, CD$_3$NO$_2$, H$_3$PO$_4$, CFCl$_3$ and [Rh(ACAC)$_3$] for $^1$H, $^2$H, $^{13}$C, $^{19}$F, $^{31}$P and $^{103}$Rh respectively. Coupling constants $J$ are given in Hertz [Hz] as absolute values unless specifically stated. The multiplicity of the signals is indicated as s, d, t, q and m for singlets, doublets, triplets, quartets and multiplets, respectively. The abbreviation br is given for broadened signals. Quaternary carbons are indicated as C$_{quat}$, aromatic units as C$_{ar}$ and H$_{ar}$; olefinic carbons of the trop unit are indicated as C$_{ol}$ and the corresponding protons as H$_{ol}$. The benzylic protons and carbons in the seven-membered ring are denoted as H$_{bz}$ and C$_{bz}$. When all NMR signals of two or more isomers were assignable, the characterization is separated; otherwise the assignable peaks are marked with A, B, C etc.
IR Spectroscopy

IR spectra were recorded using a Perkin-Elmer-Spectrum 2000 FT-IR-Raman spectrometer with KBr beam splitter (range 500-4000 cm\(^{-1}\)). The ATR technique was applied to solid compounds. The absorption bands are described as follows: strong \(s\), middle \(m\) or weak \(w\). When possible, assignments are given in brackets.

UV/Vis Spectroscopy

UV/Vis spectra were measured with a Perkin-Elmer Lambda 19 spectrometer in 2 mm quartz cuvettes (200-1000 nm) if not otherwise noted.

Gas Chromatography

Gas chromatography was performed on a Hewlett Packard HP 6890 Series GC system equipped with an EPC split injector. Most measurements were carried out with an inlet pressure of 4.88 psi; a 50:1 split resulted in a split flow of 108 mL/min and a HP-5 cross-linked 5% phenyl methyl siloxane column (30 m × 0.32 mm, film thickness 0.25 μm), flow rate 27.2 mL/min with hydrogen as the carrier gas. The temperature program: initial temperature 80 °C (hold 1 min), increase to 180 °C at a rate of 4 °C/min and hold for a further 40 min.

Cyclic Voltammetry

Cyclic voltammograms were measured with a Princeton Applied Research potentiostat/galvanostat, model 263 A or 283. The device was designed by Heinze et al.[219] A platinum electrode (approximate surface area of the working electrode is 0.785 mm\(^2\)), a silver reference electrode and a platinum wire as the counter electrode were applied. At the end of each measurement, ferrocene was added as an internal standard for calibration (+ 0.352 V versus Ag/AgCl).

X-Ray

X-ray diffraction was measured using an Oxford XCalibur or Bruker Smart Apex diffractometer with a CCD area detector; Mo\(_{K\alpha}\) radiation (0.71073 Å) at \(T = 293\) K, if not otherwise noted. The refinement against the full matrix (versus \(F^2\)) was performed using SHELXL (version 6.12) and SHELXTL-97. Empirical absorption corrections were done using SADABS (version 2.03). All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model.
Melting Points
Melting points $M_p$ were determined with Büchi melting point apparatus and were not corrected. Samples were prepared in sealed glass capillaries.

Mass Spectrometry (MS) and (GC-MS)
Mass spectra were recorded using a Finnigan MAT SSQ 7000 mass spectrometer in El mode (70 eV) equipped with a solid probe inlet. Alternatively, the attached GCQ gas chromatograph with a Macherey Nagel Optima 5 Accent column (30 m × 0.32 mm × 0.25 μm) and helium as carrier gas was used as the inlet for the MS device. High resolution ESI MS (HiRes MS) was measured by the mass spectroscopy service of ETH Zürich.

EPR Spectroscopy
The S-band spectra were measured at room temperature on a bespoke instrument with a split ring resonator (mw frequency 2.64 GHz), using a microwave power of 11 mW, a modulation amplitude of 0.2 mT and a modulation frequency of 200 kHz. The X-band spectra were measured on a Bruker Elex500 using SHQ cavity with a microwave power of 5 mW, modulation amplitude of 0.1 mT and a modulation frequency of 100 kHz. The Q-band (~ 35.3 GHz) experiments were carried out on a custom instrument [220] equipped with a helium gas flow cryostat from Oxford Inc. At Q-band, measurements were performed using a Bruker Elex600 with the following parameters: mw pulses of length of $t_{\pi/2} = t_{\pi} = 16$ ns, starting times of 96 ns for $t_1$ and $t_2$, and time increments $\Delta t = 12$ ns (data matrix $300 \times 300$). Spectra with $\tau$ values of 124 ns were recorded. Measurements performed on a X- and Q-band used an eight-step cycle to eliminate unwanted echoes. The HYSCORE data were processed using MATLAB 7.0. The time traces were baseline corrected with an exponential, apodized with a Gaussian window and zero filled. After the two-dimensional Fourier transform, absolute-value spectra were calculated. EPR spectra were simulated using the EasySpin software [221] and HYSCORE spectra using a program developed in-house [222].
Experimental Section

Preparation and Characterization

1 Compounds of Section II

1.1 Syntheses of Oxygen-Donor Olefin Ligands

(5-H-dibenzo[a,d]cyclohepten-5-yl)ethylether (tropOEt) (32)

\[ \text{C}_{17} \text{H}_{16} \text{O} \]

\( M_w: 236.12 \text{ g/mol} \)

Colourless solid

\( R_f: 0.78 \) (Hex/EtOAc 9 : 1)

\( M_p: 93 \degree \text{C} \)

Potassium carbonate (91 mg, 6.58 mmol) was added to a solution of (5-H-dibenzo-[a, d]cyclohepten-5-yl)chloride \(^{[223]}\) (500 mg, 2.20 mmol) in 5 mL ethanol. The reaction mixture was refluxed for 6 h. All insoluble compounds were filtered out over Celite. The solvent was evaporated under reduced pressure to give a colourless solid (0.42 g, 1.78 mmol, 81%). Two conformers were formed in a 1 : 4 ratio, which were inseparable.

**Endo-Conformer**

\(^1\text{H} \) NMR (500 MHz, CD\(_2\)Cl\(_2\), -80 °C): \( \delta = 1.06 \) (t, \( ^3J_{HH} = 7.0 \text{ Hz}, 3\text{H}, \text{CH}_3 \)), 3.14 (q, \( ^3J_{HH} = 7.0 \text{ Hz}, 2\text{H}, \text{CH}_2 \)), 5.51 (s, 1H, Hbz), 7.12 (s, 2H, Hol), 7.28-7.55 (m, 8H, Har);

\(^{13}\text{C} \) NMR (126 MHz, CD\(_2\)Cl\(_2\), -80 °C): \( \delta = 15.7 \) (s, 1C, CH\(_3\)), 64.0 (s, 1C, CH\(_2\)), 86.6 (s, 1C, Cbz), 128.5 (s, 2C, C\(_{ar}\)), 128.9 (s, 2C, C\(_{ar}\)), 130.4 (s, 2C, C\(_{ar}\)), 130.5 (s, 2C, C\(_{ar}\)), 130.7 (s, 2C, C\(_{ar}\)), 134.4 (s, 2C, C\(_{quart}\)), 137.3 (s, 2C, C\(_{quart}\)).

**Exo-Conformer**

\(^1\text{H} \) NMR (500 MHz, CD\(_2\)Cl\(_2\), -80 °C): \( \delta = 1.45 \) (t, \( ^3J_{HH} = 7.0 \text{ Hz}, 3\text{H}, \text{CH}_3 \)), 3.70 (q, \( ^3J_{HH} = 7.0 \text{ Hz}, 2\text{H}, \text{CH}_2 \)), 4.77 (s, 1H, Hbz), 7.18 (s, 2H, Hol), 7.30 (t, \( ^3J_{HH} = 7.5 \text{ Hz}, 2\text{H}, \text{H}_{ar} \)), 7.38 (d, \( ^3J_{HH} = 7.5 \text{ Hz}, 2\text{H}, \text{H}_{ar} \)), 7.48 (t, \( ^3J_{HH} = 7.5 \text{ Hz}, 2\text{H}, \text{H}_{ar} \)), 7.73 (d, \( ^3J_{HH} = 7.5 \text{ Hz}, 2\text{H}, \text{H}_{ar} \));
13C NMR (126 MHz, CD₂Cl₂, -80 °C): δ = 16.1 (s, 1C, CH₃), 65.8 (s, 1C, CH₂), 78.1 (s, 1C, Cbz), 122.5 (s, 2C, Caryl), 126.7 (s, 2C, Caryl), 128.2 (s, 2C, Caryl), 129.2 (s, 2C, Caryl), 131.5 (s, 2C, Cquat), 132.7 (s, 2C, Cquat), 139.7 (s, 2C, Cquat);

ATR IR (ν in cm⁻¹): 2970 w (C-H st), 2887 w (C-H st), 2160 w, 1482 m, 1440 m, 1332 m, 1200 m, 1115 s (C-O-C st as), 1081 s, 795 s (C-O-C st sy), 774 s, 741 s;

HRMS (EI+) m/z: 236.1196 (calculated: 236.1196).

1.2 Syntheses of Alcohol- and Ether-Olefin Complexes

[Rh(tropOH)₂OTf (33)]

C₃₁H₂₄F₇O₅RhS

Mₙ: 688.04 g/mol

Yellow solid

M_p: 205-210 °C dec.

(5-H-dibenzo[a,d]cyclohepten-5-yl)alcohol (107 mg, 0.52 mmol) and thallium(I) triflate (91 mg, 0.26 mmol) were added to a solution of [Rh₂(μ-Cl)₂(C₂H₄)₄] (50 mg, 0.13 mmol) in 3 mL THF. The reaction mixture was stirred at room temperature for 1 h. The solvent was evaporated and the crude product was dissolved in 2 mL DCM. Afterwards, the solution was filtered over Celite and covered with a layer of hexane to yield yellow crystals (155 mg, 0.23 mmol, 90%).

¹H NMR (300 MHz, CD₂Cl₂, rt): δ = 4.30 (s, 4H, Hol), 5.87 (s, 2H, Hbz), 7.43 (m, 12H, Haryl), 7.83 (m, 4H, Haryl), 8.64 (d, ³J_HH = 3.5 Hz, 2H, OH);

¹³C NMR (75 MHz, CD₂Cl₂, rt): δ = 72.3 (d, ¹J_RHC = 14.0 Hz, 4C, Caryl), 78.1 (s, 2C, Cbz), 128.3 (s, 4C, Caryl), 129.5 (s, 4C, Caryl), 130.1 (s, 4C, Caryl), 134.5 (s, 4C, Cquat), 138.0 (s, 4C, Cquat);

¹⁰³Rh NMR (16 MHz, CD₂Cl₂, rt): δ = 1315;

¹H NMR (400 MHz, [D₈]-THF, rt): δ = 4.64 (s, 4H, Hol), 6.08 (s, 2H, Hbz), 7.18-7.57 (m, 12H, Haryl), 7.90 (m, ³J_HH = 7.5 Hz, 4H, Haryl), 8.64 (d, ³J_HH = 2.0 Hz, 2H, OH);
Thallium(I) hexafluorophosphate (47 mg, 0.14 mmol) was added to a solution of (5-H-dibenzo[a,d]cyclohepten-5-y)ethylether 32 (67 mg, 0.28 mmol) and [Rh2(µ-Cl)2(C2H4)4] (26 mg, 0.07 mmol) in 3 mL dichloromethane. The reaction mixture was refluxed over night. All insoluble compounds were filtered out using Celite and the solvent was evaporated under reduced pressure. The obtained product was recrystallized from dichloromethane/hexane yielding red crystals (91 mg, 0.13 mmol, 94%), which were suitable for X-ray diffraction analysis.

$^{1}$H NMR (500 MHz, CD$_2$Cl$_2$, -80 °C): $\delta = 1.02$ (t, $^{3}J_{HH} = 7.0$ Hz, 6H, CH$_3$), 3.32 (m, 2H, CH$_2$), 3.48 (m, 2H, CH$_3$), 3.84 (d, $^{3}J_{HH} = 9.0$ Hz, 2H, CH$_3$), 4.83 (d, $^{3}J_{HH} = 9.0$ Hz, 2H, CH$_3$), 5.61 (s, 2H, H$_{ar}$), 7.48 (m, 12H, H$_{ar}$), 7.86 (m, 4H, H$_{ar}$);

$^{13}$C NMR (126 MHz, CD$_2$Cl$_2$, -80 °C): $\delta = 14.4$ (s, 2C, CH$_3$), 67.0 (d, $^{3}J_{CH} = 10.0$ Hz, 2C, CH$_3$), 71.9 (s, 2C, CH$_3$), 75.8 (d, $^{3}J_{CH} = 10.0$ Hz, 2C, CH$_3$), 84.0 (s, 2C, C$_{ar}$), 128.6 (s, 2C, C$_{ar}$), 130.0 (s, 2C, C$_{ar}$), 130.4 (s, 2C, C$_{ar}$), 130.4 (s, 2C, C$_{ar}$), 130.9 (s, 2C, C$_{ar}$), 131.1 (s, 2C, C$_{ar}$), 131.2 (s, 2C, C$_{ar}$), 131.7 (s, 2C, C$_{ar}$), 134.3 (s, 2C, C$_{ar}$), 134.5 (s, 2C, C$_{ar}$), 135.4 (s, 2C, C$_{ar}$), 136.2 (s, 2C, C$_{ar}$);

$^{103}$Rh NMR (16 MHz, CD$_2$Cl$_2$, -80 °C): $\delta = 1411$;
Experimental Section

ATR IR (ν in cm\(^{-1}\)): 2942\(w\) (C-H st), 1983\(w\), 1494\(w\), 1464\(w\), 1386\(w\), 1249\(w\), 1164\(m\), 1010\(m\) (C-O-C st as), 934\(m\), 881\(m\), 831\(s\) (PF\(_6\)), 762\(s\) (C-O-C st sy);

UV/Vis (λ\(_{\text{max}}\) in nm): 327, 281;

HRMS (ESI+) \(m/z\): 575.1451 (calculated: 575.1452) \([\text{C}_{34}\text{H}_{32}\text{O}_2\text{Rh}]^+\).

\(\text{Na[Rh(tropO)}_2]\) \(\text{(36)}\)

Sodium \textit{tert}-butoxide (5.6 mg, 58 \(\mu\)mol) was added to a solution of \([\text{Rh(tropOH)}_2]\)OTf 33 (20 mg, 29 \(\mu\)mol) in 0.4 mL \([\text{D}_8]-\text{THF}\). The deprotonation reaction was completed within minutes. The product was not isolated and characterized \textit{in situ} by NMR spectroscopy.

\(^1\text{H}\) NMR (400 MHz, \([\text{D}_8]-\text{THF},\ \text{rt})\): \(\delta = 3.79\ (s, 4\text{H, }\text{H}_{\text{ol}}), 5.64\ (s, 2\text{H, }\text{H}_{\text{bz}}), 7.08\ (m, 8\text{H, }\text{H}_{\text{ar}}), 7.23\ (m, 4\text{H, }\text{H}_{\text{ar}}), 7.50\ (m, 4\text{H, }\text{H}_{\text{ol}});

\(^{13}\text{C}\) NMR (75 MHz, \([\text{D}_8]-\text{THF},\ \text{rt})\): \(\delta = 71.2\ (d, \quad^{1}J_{\text{RhC}} = 13.0 \text{ Hz, } 4\text{C, }\text{C}_{\text{ol}}), 81.5\ (s, 2\text{C, }\text{C}_{\text{bz}}), 124.6\ (s, 4\text{C, }\text{C}_{\text{ar}}), 125.8\ (s, 4\text{C, }\text{C}_{\text{ar}}), 125.9\ (s, 4\text{C, }\text{C}_{\text{ar}}), 127.5\ (s, 4\text{C, }\text{C}_{\text{ar}}), 138.6\ (s, 4\text{C, }\text{C}_{\text{quat}}), 147.1\ (s, 4\text{C, }\text{C}_{\text{quat}});

\(^{103}\text{Rh-NMR}\) (16 MHz, \([\text{D}_8]-\text{THF},\ \text{rt})\): \(\delta = 1065\).
2 Compounds of Section III

2.1 Synthesis of an Ethylenediamin Based Ligand and its Complexes

\(N,N’\)-bis(5\(H\)-dibenzo[\(a,d\]cyclohepten-5-yl]-1,2-diaminoethane (trop\(2\)DAE) (39)

\[
\text{C}_{32}\text{H}_{28}\text{N}_2
\]

\(M_w: 440.23 \text{ g/mol}\)

Colourless solid

\(R_f: 0.56 \text{ (DCM/MeOH 9 : 1)}\)

\(M_p: 134 \, ^\circ\text{C}\)

\(N,N’\)-Bis(trimethylsilyl)ethylenediamine\(^{[215]}\) (5.1 g, 25.0 mmol) in 100 mL toluene was added to a solution of (5\(H\)-dibenzo[\(a,d\]cyclohepten-5-yl])chloride\(^{[223]}\) (11.4 g, 50.3 mmol) in 200 mL toluene. The reaction mixture was refluxed for 2 h. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (DCM/MeOH = 19 : 1) to give a colourless solid (8.25 g, 18.7 mmol, 75%). Three different conformers were formed in a 1 : 1 : 2 ratio.

\(^1\text{H} \text{NMR (700 MHz, [D}_2\)]-THF, -40 \, ^\circ\text{C}}\): \(\delta = 2.48 \, (\text{br s, 6H, CH}_2), 2.92 \, (\text{br s, 6H, CH}_2), 3.77 \, (s, 2H, H_{boz}), 4.14 \, (s, 2H, H_{boz}), 4.98 \, (s, 2H, H_{boz}), 6.92 \, (s, 4H, H_{ol}), 7.16 \, (s, 4H, H_{ol}), 7.23 \, (s, 4H, H_{ol}), 7.18-7.78 \, (m, 48H, H_{ar});\)

\(^{13}\text{C} \text{NMR (178 MHz, [D}_2\)]-THF, -40 \, ^\circ\text{C}}\): \(\delta = 46.3 \, (s, 2C, CH_2), 47.7 \, (s, 2C, CH_2), 48.7 \, (s, 2C, CH_2), 60.6 \, (s, 2C, C_{boz}), 61.0 \, (s, 2C, C_{boz}), 69.3 \, (s, 2C, C_{boz}), 122.6 \, (s, 4C, C_{ar}), 122.7 \, (s, 4C, C_{ar}), 125.1 \, (s, 4C, C_{ar}), 122.3 \, (s, 4C, C_{ar}), 126.6 \, (s, 4C, C_{ar}), 127.3 \, (s, 4C, C_{ar}), 127.4 \, (s, 4C, C_{ar}), 128.0 \, (s, 4C, C_{ar}), 128.1 \, (s, 4C, C_{ar}), 128.3 \, (s, 4C, C_{ar}), 129.5 \, (s, 4C, C_{ar}), 129.7 \, (s, 4C, C_{ar}), 130.3 \, (s, 4C, C_{ar}), 130.9 \, (s, 4C, C_{ar}), 131.6 \, (s, 4C, C_{ar}), 133.7 \, (s, 4C, C_{quar}), 133.8 \, (s, 4C, C_{quar}), 133.9 \, (s, 4C, C_{quar}), 140.3 \, (s, 4C, C_{quar}), 140.5 \, (s, 4C, C_{quar}), 140.6 \, (s, 4C, C_{quar});\)

ATR IR (\(v \text{ in cm}^{-1}\)): 3302\(w\) (NH st), 3022\(w\), 2962\(w\), 2836\(w\), 2360.6\(w\), 1598\(w\), 1484\(m\), 1438\(m\), 1261\(m\), 1192\(m\), 1087\(m\), 1032\(m\), 885\(m\), 793\(s\), 778\(s\), 760\(s\), 734\(s\), 637\(m\), 615\(m\);

HRMS (EI+) \(m/z: 440.2246 \text{ (calculated: 440.2247) [C}_{32}\text{H}_{28}\text{N}_2]^+}\).
[Rh(trop₂DAE)]PF₆ (40a)

\[
\text{C}_{32} \text{H}_{28} \text{F}_{6} \text{N}_3 \text{PRh}
\]

\[
\text{M}_w: 688.09 \text{ g/mol}
\]

Orange solid

\[
\text{M}_p: 186-191 \degree \text{C}
\]

[Rh₂(μ-Cl₂)(C₅H₄)₄] (66 mg, 0.17 mmol) and thallium(I) hexafluorophosphate (125 mg, 0.36 mmol) were added to a solution of trop₂DAE 39 (150 mg, 0.34 mmol) in 5 mL THF. The reaction mixture was stirred at room temperature for 1 h. Afterwards the solution was filtered over Celite. The solvent was removed under reduced pressure to obtain a powder, which was recrystallized from dichloromethane/hexane yielding orange crystals (220 mg, 0.32 mmol, 94%). Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of n-hexane into a solution of dichloromethane. Two different inseparable diastereomers were formed; \( \text{dr} = 62 : 38 \) (\( \text{rac} : \text{meso} \)). Mass spectrometric, IR- and UV/Vis-spectroscopic measurements were taken of the mixture of diastereomers.

meso-[Rh(trop₂DAE)]PF₆ (meso-40a)

\(^1\text{H} \text{NMR (500 MHz, [D₆]-THF, -5 °C):} \delta = 2.31 \text{ (m, 2H, CH}_2\text{), 3.08 \text{ (m, 2H, CH}_2\text{), 4.85 \text{ (br s, 2H, NH), 4.91 \text{ (m, 4H, H}_ω\text{), 5.19 \text{ (s, 2H, H}_β\text{), 7.22-7.82 \text{ (m, 16H, H}_α\text{);}}\n\]

\(^{13}\text{C} \text{NMR (126 MHz, [D₆]-THF, -5 °C):} \delta = 45.7 \text{ (s, 2C, CH}_2\text{), 65.5 \text{ (s, 2C, C}_β\text{), 77.1 \text{ (d, } J_{\text{HH}} = 12.0 \text{ Hz, 2C, C}_α\text{), 81.7 \text{ (d, } J_{\text{HH}} = 12.0 \text{ Hz, 2C, C}_β\text{), 128.1 \text{ (s, 2C, C}_α\text{), 128.3 \text{ (s, 2C, C}_α\text{), 128.4 \text{ (s, 2C, C}_ω\text{), 128.5 \text{ (s, 2C, C}_α\text{), 129.2 \text{ (s, 2C, C}_α\text{), 129.4 \text{ (s, 2C, C}_ω\text{), 129.5 \text{ (s, 2C, C}_ω\text{), 130.8 \text{ (s, 2C, C}_ω\text{), 135.8 \text{ (s, 2C, C}_ω\text{), 137.3 \text{ (s, 2C, C}_ω\text{), 137.4 \text{ (s, 2C, C}_ω\text{), 139.1 \text{ (s, 2C, C}_ω\text{);}}\n\]

\(^{103}\text{Rh NMR (15.8 MHz, [D₆]-THF, -5 °C):} \delta = 773.\n\]

rac-[Rh(trop₂DAE)]PF₆ (rac-40a)

\(^1\text{H} \text{NMR (500 MHz, [D₆]-THF, -5 °C):} \delta = 2.24-2.47 \text{ (m, 2H, CH}_2\text{), 3.01-3.16 \text{ (m, 4H, CH}_2\text{), 4.30 \text{ (d, } J_{\text{HH}} = 8.8 \text{ Hz, 2H, H}_ω\text{), 5.05 \text{ (s, 2H, H}_β\text{), 5.40 \text{ (d, } J_{\text{HH}} = 8.8 \text{ Hz, 2H, H}_ω\text{), 6.01 \text{ (d, } J_{\text{HH}} = 7.2 \text{ Hz, 2H, NH), 7.22-7.82 \text{ (m, 16H, H}_α\text{);}}\n\]

\(^{13}\text{C} \text{NMR (126 MHz, [D₆]-THF, -5 °C):} \delta = 50.6 \text{ (s, 2C, CH}_2\text{), 67.7 \text{ (s, 2C, C}_β\text{), 71.4 \text{ (d, } J_{\text{HH}} = 11.5 \text{ Hz, 2C, C}_α\text{), 84.0 \text{ (d, } J_{\text{HH}} = 11.5 \text{ Hz, 2C, C}_ω\text{), 127.3 \text{ (s, 2C, C}_α\text{), 128.5 \text{ (s, 2C, C}_ω\text{), 128.7 \text{ (s, 2C, C}_ω\text{), 128.8 \text{ (s, 2C,}}\n
135
Experimental Section

$^{13}C_{\text{ar}}$, 129.3 (s, 2C, $C_{\text{ar}}$), 129.4 (s, 2C, $C_{\text{ar}}$), 130.1 (s, 2C, $C_{\text{ar}}$), 130.6 (s, 2C, $C_{\text{ar}}$), 136.7 (s, 2C, $C_{\text{quart}}$), 137.0 (s, 2C, $C_{\text{quart}}$), 137.9 (s, 2C, $C_{\text{quart}}$), 139.3 (s, 2C, $C_{\text{quart}}$); $^{103}$Rh NMR (15.8 MHz, [D$_8$]-THF, -5 °C): δ = 862;

ATR IR (ν in cm$^{-1}$): 3192 w (NH st), 2159 w, 1620 w 1491 w, 1281 w, 1135 m, 833 s, 775 s, 755 s, 742 s, 633 m, 615 m;

UV/Vis (λ$_{\text{max}}$ in nm): 449, 326, 279 (THF);

HRMS (ESI+) m/z: 543.1298 (calculated: 543.1302) [C$_{32}$H$_{28}$N$_2$Rh]$^+$. 

[Ir(trop$_2$DAE)]PF$_6$ (40b)

\[
\begin{align*}
C_{32}H_{28}F_6\text{IrN}_2P \\
M_w: 778.15 \text{ g/mol} \\
\text{Red solid} \\
M_p: 220 \degree \text{C dec.}
\end{align*}
\]

[Ir$_3$(µ-Cl)$_3$(COE)$_4$] (153 mg, 0.17 mmol) and thallium(I) hexafluorophosphate (125 mg, 0.36 mmol) were added to a solution of trop$_2$DAE 39 (150 mg, 0.34 mmol) in 5 mL THF. The reaction mixture was stirred at room temperature for 1 h. Afterwards, the solution was filtered over Celite to remove the formed thallium(I) chloride. All solvents were removed under reduced pressure to obtain a powder, which was recrystallized from dichloromethane/hexane yielding red crystals (220 mg, 0.32 mmol, 94%). Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of $n$-hexane into a solution of 40b in dichloromethane. Two inseparable diastereomers (rac : meso) were formed in a 9 : 1 ratio. Mass spectrometric, IR- and UV/Vis-spectroscopic measurements were taken of the mixture of diastereomers.

meso-[Ir(trop$_2$DAE)]PF$_6$ (meso-40b)

$^1$H NMR (500 MHz, [D$_8$]-THF, rt): δ = 2.33 (m, 2H, CH$_2$), 3.24 (m, 2H, CH$_2$), 4.29 (d, $^3J_{HH} = 8.5$ Hz, 2H, H$_{aa}$), 4.43 (d, $^3J_{HH} = 8.5$ Hz, 2H, H$_{ab}$), 5.71 (s, 2H, H$_{bb}$), 6.08 (br s, 1H, NH), 7.20-7.69 (m, 16H, H$_{ar}$);

$^{13}$C NMR (126 MHz, [D$_8$]-THF, rt): δ = 46.7 (s, 2C, CH$_2$), 61.3 (s, 2C, C$_{ao}$), 65.2 (s, 2C, C$_{bo}$), 66.9 (s, 2C, C$_{bo}$), 125.6 (s, 2C, C$_{ao}$), 126.9 (s, 2C, C$_{ao}$), 127.0 (s, 2C, C$_{ao}$), 127.5 (s, 2C, C$_{ao}$), 128.7 (s, 2C, C$_{ao}$), 128.9 (s, 2C,
C\textsubscript{ar}, 129.2 (s, 2C, C\textsubscript{ar}), 130.9 (s, 2C, C\textsubscript{ar}), 134.9 (s, 2C, C\textsubscript{quart}), 136.5 (s, 2C, C\textsubscript{quart}), 138.3 (s, 2C, C\textsubscript{quart}), 138.4 (s, 2C, C\textsubscript{quart}).

\textit{rac-[Irtrop\textsubscript{2}DAE]PF\textsubscript{6} (rac-40b)}

\textsuperscript{1}H NMR (500 MHz, [D\textsubscript{6}]-THF, rt): \(\delta = 2.50\) (m, 2H, CH\textsubscript{2}), 3.52 (dd, \(\mathbf{\textit{J}_{HH}} = 7.5\) Hz, \(\mathbf{\textit{J}_{HH}} = 5.0\) Hz, 2H, CH\textsubscript{2}), 3.95 (d, \(\mathbf{\textit{J}_{HH}} = 8.5\) Hz, 2H, H\textsubscript{ol}), 4.72 (d, \(\mathbf{\textit{J}_{HH}} = 8.5\) Hz, 2H, H\textsubscript{el}), 5.54 (s, 2H, H\textsubscript{b2}), 6.66 (d, \(\mathbf{\textit{J}_{HH}} = 7.5\) Hz, 1H, NH), 7.20-7.69 (m, 16H, H\textsubscript{ar});

\textsuperscript{13}C NMR (126 MHz, [D\textsubscript{6}]-THF, rt): \(\delta = 52.2\) (s, 2C, CH\textsubscript{2}), 54.5 (s, 2C, C\textsubscript{ar}), 66.7 (s, 2C, C\textsubscript{el}), 69.2 (s, 2C, C\textsubscript{ol}), 126.1 (s, 2C, C\textsubscript{ar}), 127.6 (s, 2C, C\textsubscript{ol}), 128.1 (s, 2C, C\textsubscript{el}), 128.5 (s, 2C, C\textsubscript{ol}), 128.6 (s, 2C, C\textsubscript{ar}), 129.0 (s, 2C, C\textsubscript{ar}), 129.1 (s, 2C, C\textsubscript{ar}), 130.6 (s, 2C, C\textsubscript{ar}), 136.3 (s, 2C, C\textsubscript{quart}), 137.7 (s, 2C, C\textsubscript{quart}), 138.2 (s, 2C, C\textsubscript{quart}), 138.3 (s, 2C, C\textsubscript{quart});

ATR IR (\(\nu\) in cm\(^{-1}\)): 3178 w (NH st), 2962 w, 2361 m, 2342 m, 2159 w, 219 w, 1602 w, 1490 m, 1469 m, 1350 w, 1260 m, 1190 m, 1131 m, 1019 m, 957 w, 824 s (PF\textsubscript{6}), 755 s, 742 s, 711 m;

HRMS (ESI+) m/z: 633.1877 (calculated: 633.1876) \([\text{C}_{32}\text{H}_{28}\text{N}_{2}\text{Ir}]^{+}\);

UV/Vis (\(\lambda_{\text{max}}\) in nm): 477, 389, 299, 216 (THF).

\textbf{[Rh(trop\textsubscript{2}DAE-1H)] (41a)}

\begin{center}
\includegraphics[width=0.5\textwidth]{C32H28N2Rh.png}
\end{center}

\(M_w: 542.12\) g/mol

Sodium tert-butoxide (1.4 mg, 0.015 mmol) was added to a solution of [Rh(trop\textsubscript{2}DAE)]PF\textsubscript{6} \textbf{40a} (10 mg, 0.015 mmol) in 0.4 mL [D\textsubscript{6}]-THF. The deprotonation reaction was completed within minutes. The product was not isolated and characterized \textit{in situ} by NMR and UV/Vis spectroscopy.

\textsuperscript{1}H NMR (500 MHz, [D\textsubscript{6}]-THF, -80 °C): \(\delta = 2.12\) (m, 1H, CH\textsubscript{2}), 2.76 (m, 1H, CH\textsubscript{2}), 2.97 (m, 1H, CH\textsubscript{2}), 3.14 (d, \(\mathbf{\textit{J}_{HH}} = 9\) Hz, 1H, H\textsubscript{b2}), 3.37 (m, 1H, CH\textsubscript{2}), 3.70 (d, 1H, H\textsubscript{b2} under THF), 4.35 (d, \(\mathbf{\textit{J}_{HH}} = 9\) Hz, 1H, H\textsubscript{b2}), 4.54 (s, 1H, H\textsubscript{b2}), 4.83 (s, 1H, H\textsubscript{b2}), 4.92 (d, \(\mathbf{\textit{J}_{HH}} = 9\) Hz, 1H, H\textsubscript{b2}), 5.70 (d, \(\mathbf{\textit{J}_{HH}} = 12\) Hz, 1H, NH), 6.87-7.61 (m, 16H, H\textsubscript{ar});

\textsuperscript{13}C NMR (126 MHz, [D\textsubscript{6}]-THF, -80 °C): \(\delta = 51.9\) (s, 1C, CH\textsubscript{2}), 59.2 (s, 1C, CH\textsubscript{2}), 66.2 (s, 1C, C\textsubscript{b2} under THF), 68.1 (s, 1C, C\textsubscript{b2}), 71.1 (br s, 2C, C\textsubscript{el}), 75.2 (s, 1C, C\textsubscript{el}), 81.1 (d, \(\mathbf{\textit{J}_{HH}} = 13.0\) Hz, 1C, C\textsubscript{el}), 123.6 (s, 1C, C\textsubscript{ar}), 137.
UV/Vis (λ in nm): 469, 387, 312 (THF).

[S]Rh NMR (15.8 MHz, [D₈]-THF, -80 °C): δ = 656;

UV/Vis (λₑₓ in nm): 485, 408, 337, 261 (THF).

[S]Ir(trop₂DAE-1H)] (42b)

Sodium tert-butoxide (1.2 mg, 12.8 μmol) was added to a solution of [Ir(trop₂DAE)]PF₆ 40b (10 mg, 12.8 μmol) in 0.4 mL [D₈]-THF. The deprotonation reaction was completed within minutes. The product was characterized in situ by NMR spectroscopy.

¹H NMR (500 MHz, [D₈]-THF, -40 °C): δ = 2.17 (m, 1H, CH₃), 2.78 (d, 3Jₙₙ = 8.5 Hz, 1H, Hₐ), 2.86 (m, 1H, CH₂), 3.24 (m, 1H, CH₂), 3.28 (d, 3Jₙₙ = 8.5 Hz, 1H, Hₐ), 3.61 (1H, Hₐ under THF), 3.91 (m, 1H, CH₂), 4.16 (d, 3Jₙₙ = 8.5 Hz, 1H, Hₐ), 5.11 (s, 1H, Hₐ), 5.29 (s, 1H, Hₐ), 6.28 (d, 3Jₙₙ = 12 Hz, 1H, NH), 6.90-7.54 (m, 16H, Hₐ);

¹³C NMR (126 MHz, [D₈]-THF, -40 °C): δ = 46.5 (s, 1C, Cₐ), 51.1 (s, 1C, Cₐ), 54.2 (s, 1C, CH₂), 57.0 (s, 1C, Cₐ), 59.4 (s, 1C, CH₂), 63.4 (s, 1C, Cₐ), 67.8 (s, 1C, Cₐ), 72.7 (s, 1C, Cₐ), 123.6 (s, 1C, Cₐ), 123.9 (s, 1C, Cₐ), 124.2 (s, 1C, Cₐ), 124.7 (s, 1C, Cₐ), 125.9 (s, 1C, Cₐ), 126.0 (s, 1C, Cₐ), 126.2 (s, 1C, Cₐ), 126.3 (s, 1C, Cₐ), 127.6 (s, 1C, Cₐ), 127.8 (s, 1C, Cₐ), 128.0 (s, 1C, Cₐ), 128.1 (s, 1C, Cₐ), 128.3 (s, 1C, Cₐ), 128.7 (s, 1C, Cₐ), 129.7 (s, 1C, Cₐ), 135.7 (s, 1C, Cₐ), 136.7 (s, 1C, Cₐ), 139.8 (s, 1C, Cₐ), 140.1 (s, 1C, Cₐ), 143.9 (s, 1C, Cₐ), 144.1 (s, 1C, Cₐ), 146.6 (s, 1C, Cₐ), 149.8 (s, 1C, Cₐ);

UV/Vis (λₑₓ in nm): 469, 387, 312 (THF).
Na[Rh(trop₂DAE-2H)] (42a)

C₃₂H₂₆N₃NaRh

Mᵣ: 564.10 g/mol

Sodium tert-butoxide (2.9 mg, 0.03 mmol) was added to a solution of [Rh(trop₂DAE)]PF₆ 40a (10 mg, 0.015 mmol) in 0.4 mL [D₈]-THF in a NMR-tube. The deprotonation reaction was completed within minutes. The product was not isolated and characterized in situ by NMR and UV/Vis spectroscopy.

¹H NMR (500 MHz, [D₈]-THF, -80 °C): δ = 2.91 (m, 4H, CH₂), 3.66 (br, 4H, Hₐ), 4.46 (s, 2H, H₈), 6.88-7.07 (m, 10H, H₉), 7.31-7.41 (m, 6H, H₁₀);

¹³C NMR (126 MHz, [D₈]-THF, -80 °C): δ = 58.2 (s, 2C, CH₂), 71.2 (br s, 4C, C₉), 75.5 (s, 2C, C₈), 123.6 (s, 2C, C₇), 125.8 (s, 2C, C₇), 126.6 (s, 4C, C₆), 127.3 (s, 4C, C₆), 128.6 (s, 2C, C₆), 128.7 (s, 2C, C₆), 141.5 (s, 4C, C₅), 146.2 (s, 4C, C₅);

¹⁰³Rh NMR (15.8 MHz, [D₈]-THF, -80 °C): δ = 523;

Na[Ir(trop₂DAE-2H)] (42b)

C₃₂H₂₆IrN₃Na

Mᵣ: 654.16 g/mol

Sodium tert-butoxide (2.4 mg, 25.6 μmol) was added to a solution of [Ir(trop₂DAE)]PF₆ 40b (10 mg, 12.8 μmol) in 0.4 mL [D₈]-THF in a NMR-tube. The deprotonation reaction was completed within minutes. The product was not isolated and characterized in situ by NMR- and UV/Vis spectroscopy.

¹H NMR (500 MHz, [D₈]-THF, -50 °C): δ = 3.09 (br s, 4H, CH₂), 3.25 (s, 4H, Hₗ), 4.92 (s, 2H, H₈), 6.85 (t, 3Jₗₗ = 7.0 Hz, 4H, H₉), 6.93 (t, 3Jₗₗ = 7.0 Hz, 4H, H₉), 7.02 (d, 3Jₗₗ = 7.0 Hz, 4H, H₉), 7.33 (d, 3Jₗₗ = 7.0 Hz, 4H, H₉);
2.2 Synthesis of an Aminoethanol Based Ligand and its Complexes

2-Ethyl-((5H-dibenzo[a, d]cyclohepten-5-yl)amino)ethanoate (44)

\[ \text{C}_{19} \text{H}_{19} \text{NO}_2 \]

\[ M_w: 293.14 \text{ g/mol} \]

Colourless oil

\[ R_f: 0.36 \text{ (Hex/EtOAc 8 : 2)} \]

Triethylamine (3.0 g, 29.4 mmol, 4.1 mL) and ethylchloroacetate (2.0 g, 15.9 mmol, 1.7 mL) were added to a solution of (5H-dibenzo[a, d]cyclohepten-5-yl)amine (3.0 g, 14.5 mmol) in 30 mL THF. The reaction mixture was refluxed for 45 h, then diluted with 120 mL water and subsequently extracted twice with 150 mL diethylether. The combined organic phases were dried over MgSO₄ and concentrated to dryness in vacuum. Purification by flash chromatography (Hex/EtOAc 8 : 2) gave a colourless oil (3.46 g, 11.8 mmol, 81%), which consisted of two dynamic conformers (exo : endo) in a 2.6 : 1 ratio.

**Endo-Conformer**

\[ ^1\text{H} \text{ NMR (500 MHz, [D₆]-THF, -40 °C):} \delta = 1.18 \text{ (t, } ^3J_{HH} = 7.0 \text{ Hz, } \text{CH}_3), \] 3.11 (s, 1H, NH), 2.98 (s, 2H, CH₂N), 4.03 (q, \(^3J_{HH} = 7.0 \text{ Hz, } 2\text{H, CH}_2\text{O}), 5.00 (s, 1H, \text{H}_\alpha), 7.06 (s, 2H, \text{H}_\beta), 7.33-7.48 (m, 8H, \text{H}_\omega); \]

\[ ^13\text{C} \text{ NMR (126 MHz, [D₆]-THF, -40 °C):} \delta = 14.0 \text{ (s, } 1\text{C, CH}_3), 48.1 \text{ (s, } 1\text{C, CH}_2\text{O), 60.3 \text{ (s, } 1\text{C, CH}_2\text{O), 68.7 \text{ (s, 1C, C}_\omega), 127.3 \text{ (s, } 2\text{C, C}_\omega), 128.5 \text{ (s, } 2\text{C, C}_\omega), 130.1 \text{ (s, } 2\text{C, C}_\omega), 130.2 \text{ (s, } 2\text{C, C}_\omega), 130.7 \text{ (s, } 2\text{C, C}_\omega), 134.5\text{(s, 2C, C}_\omega), 139.9 \text{ (s, } 2\text{C, C}_\omega), 171.8 \text{ (s, } 1\text{C, C}_\omega). \]

**Exo-Conformer**

\[ ^1\text{H} \text{ NMR (500 MHz, [D₆]-THF, -40 °C):} \delta = 1.22 \text{ (t, } ^3J_{HH} = 7.0 \text{ Hz, } \text{CH}_3), \] 3.11 (s, 1H, NH), 3.52 (s, 2H, CH₂N), 4.12 (q, \(^3J_{HH} = 7.0 \text{ Hz, } 2\text{H, CH}_2\text{O), 4.16 (s, 1H, } \text{H}_\alpha), 7.21 (s, 2H, \text{H}_\beta), 7.23 (m, 2H, \text{H}_\omega), 7.33-7.48 \text{ (m, 4H, } \text{H}_\omega), 7.71 (d, \(^3J_{HH} = 7.5 \text{ Hz, } 2\text{H, } \text{H}_\omega); \]
Experimental Section

\[^{13}\text{C} \text{NMR} (126 \text{ MHz}, [D_8]-\text{THF}, -40 \text{ °C}): \delta = 14.0 \,(s, 1\text{C}, \text{CH}_3),\, 48.8 \,(s, 1\text{C}, \text{CH}_2\text{N}),\, 60.3 \,(s, 1\text{C}, \text{C}_\text{ar}),\, 60.6 \,(s, 1\text{C}, \text{CH}_2\text{O}),\, 122.7 \,(s, 2\text{C}, \text{C}_\text{ar}),\, 125.8 \,(s, 2\text{C}, \text{C}_\text{ar}),\, 127.9 \,(s, 2\text{C}, \text{C}_\text{ar}),\, 128.7 \,(s, 2\text{C}, \text{C}_\text{ar}),\, 131.3 \,(s, 2\text{C}, \text{C}_\text{ar}),\, 134.3 \,(s, 2\text{C}, \text{C}_\text{quat}),\, 140.2 \,(s, 2\text{C}, \text{C}_\text{quat}),\, 172.3 \,(s, 1\text{C}, \text{C}=\text{O});\]

ATR IR (\nu in \text{cm}^{-1}): 2980w, 1723s (C=O st), 13439, 1237s, 1141m, 1024m, 1087m, 987w, 876m, 833m, 798s, 762s, 740s, 641w, 606w;

El-MS (70 eV, \text{m/z}): 293 (15, [M^+]), 206 (47, [M^+-\text{C}_2\text{H}_2\text{O}_2]), 191 (100), 144 (11), 99 (88), 56 (55).

2-((5H-Dibenzo[a, d]cyclohepten-5-yl)amino)ethanol (45)

\[
\text{C}_{17}\text{H}_{17}\text{NO} \\
M_w: 251.13 \text{ g/mol} \\
\text{Colourless solid} \\
R_f: 0.19 (\text{Hex/EtOAc 3 : 7}) \\
M_p: 108 \text{ °C}
\]

Lithium aluminium hydride (1.1 g, 27.8 mmol) was added in small portions over a period of 5 min to a solution of 2-Ethyl-((5H-dibenzo[a, d]cyclohepten-5-yl)amino)ethanoate 44 (3.4 g, 11.6 mmol) in 80 mL THF at -10 \text{ °C}. The reaction mixture was allowed to warm to room temperature and was then stirred for 3 h. The mixture was cooled to 0 \text{ °C}, carefully quenched with 5 mL sat. NaHCO\text{3} and diluted with 100 mL ethylacetate. Subsequently, the solution was washed with 50 mL sat. NaHCO\text{3}, 50 mL water and 50 mL brine. The organic phase was then dried over MgSO\text{4} and the solvent was removed under reduced pressure. Purification by flash chromatography (DCM/EtOH 97 : 3 to 95 : 5) gave a colourless solid (1.92 g, 7.75 mmol, 66%), consisting of two dynamic conformers (exo : endo) in a 3.3 : 1 ratio.

**Endo-Conformer**

\[^{1}\text{H} \text{NMR} (500 \text{ MHz}, [D_8]-\text{THF}, -70 \text{ °C}): \delta = 2.23 \,(t, J_{HH} = 5.0 \text{ Hz}, 2\text{H}, \text{CH}_2\text{N}),\, 2.85 \,(s, 1\text{H}, \text{NH}),\, 3.38 \,(t, J_{HH} = 5.0 \text{ Hz}, 2\text{H}, \text{CH}_2\text{O}),\, 4.52 \,(s, 1\text{H}, \text{OH}),\, 4.93 \,(s, 1\text{H}, \text{H}_\text{ar}),\, 7.07 \,(s, 2\text{H}, \text{H}_\text{ar}),\, 7.33 \,(m, 2\text{H}, \text{H}_\text{ar}),\, 7.36-7.53 \,(m, 6\text{H}, \text{H}_\text{ar});\]

\[^{13}\text{C} \text{NMR} (126 \text{ MHz}, [D_8]-\text{THF}, -70 \text{ °C}): \delta = 49.9 \,(s, 1\text{C}, \text{CH}_3\text{N}),\, 61.4 \,(s, 1\text{C}, \text{CH}_2\text{O}),\, 69.4 \,(s, 1\text{C}, \text{C}_\text{ar}),\, 125.8 \,(s, 2\text{C}, \text{C}_\text{ar}),\, 127.2 \,(s, 2\text{C}, \text{C}_\text{ar}),\, 130.0 \,(s, 2\text{C}, \text{C}_\text{ar}),\, 130.1 \,(s, 2\text{C}, \text{C}_\text{ar}),\, 130.8 \,(s, 2\text{C}, \text{C}_\text{ar}),\, 134.0 \,(s, 2\text{C}, \text{C}_\text{quat}),\, 140.7 \,(s, 2\text{C}, \text{C}_\text{quat}).\]

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**Exo-Conformer**

$^1$H NMR (500 MHz, [D$_8$]-THF, -70 °C): $\delta = 2.71$ (t, $^3$J$_{H'H} = 5.0$ Hz, 2H, CH$_2$N), 2.85 (s, 1H, NH), 3.75 (t, $^3$J$_{H'H} = 5.0$ Hz, 2H, CH$_2$O), 4.04 (s, 1H, H$_{5b}$), 4.52 (s, 1H, OH), 7.23 (m, 2H, H$_{ar}$), 7.24 (s, 2H, H$_{ar}$), 7.36-7.53 (m, 4H, H$_{ar}$), 7.71 (d, $^3$J$_{H'H} = 7.5$ Hz, 2H, H$_{ar}$);  

$^{13}$C NMR (126 MHz, [D$_8$]-THF, -70 °C): $\delta =$ 51.1 (s, 1C, CH$_2$N), 61.4 (s, 2C, CH$_2$O/C$_{5b}$), 123.0 (s, 2C, C$_{ar}$), 125.8 (s, 2C, C$_{ar}$), 127.9 (s, 2C, C$_{ar}$), 128.7 (s, 2C, C$_{ar}$), 131.4 (s, 2C, C$_{ar}$), 134.3 (s, 2C, C$_{ar}$), 140.7 (s, 2C, C$_{ar}$);  

ATR IR (v in cm$^{-1}$): 3100w (NH st, OH st), 2953w, 2360m, 1492m, 1435m, 1352w, 1185w, 1079m, 1021m, 973w, 932w, 890w, 860w, 831w, 803s, 763s, 739s, 694w, 626w;  

EI-MS (70 eV, m/z %): 251 (59, [M$^+$]), 220 (20, [M$^+$-CH$_3$O]), 192 (100, [M$^+$-C$_2$H$_5$NO]), 165 (45), 115 (5), 94 (5), 49 (6).  

**N-(2-(5H-Dibenzo[a, d]cyclohepten-5-yl)oxy)ethyl-(5H-dibenzo[a, d]cyclohepten-5-yl)amine (trop$_2$EEA) (46)**

![Structure of trop$_2$EEA](image)

C$_{12}$H$_{22}$NO  

$\text{M}_w$: 441.21 g/mol  

Colourless solid  

$R_f$: 0.40 (Hex/EtOAc 8 : 2)  

$\text{M}_p$: 61 °C  

Triethylamine (2.3 g, 22.8 mmol, 3.2 mL) and (5H-dibenzo[a,d]cyclohepten-5-yl)chloride (1.8 g, 7.9 mmol) were added to a solution of 44 (1.9 g, 7.6 mmol) in 30 mL THF. The reaction mixture was refluxed for 16 h. The solution was diluted with 80 mL water and subsequently extracted three times with 100 mL diethylether. The combined organic phases were dried over MgSO$_4$ and the solvent was removed under reduced pressure. Purification by flash chromatography (Hex/EtOAc 8 : 2) gave a colourless solid (2.83 g, 6.4 mmol, 84%). Three different conformers (A : B : C) were formed in a 1.8 : 4.5 : 1 ratio.  

$^1$H NMR (400 MHz, [D$_8$]-THF, -50 °C): $\delta =$ 2.41 (br s, 1H, NH$^\delta$), 2.53 (t, $^3$J$_{H'H} = 4.6$ Hz, 2H, CH$_2$N$^\delta$), 2.58 (br s, 2H, CH$_2$N$^\delta$), 2.92 (br s, 1H, NH$^\delta$), 3.05 (s, 2H, CH$_2$N$^\delta$), 3.14 (br s, 1H, NH$^\delta$), 3.28 (t, $^3$J$_{H'H} = 4.6$ Hz, 2H,
Experimental Section

CH$_3$O$^+$: 3.57 (t, $^3$J$_{HH}$ = 4.6 Hz, 2H, CH$_2$O$^+$), 3.76 (s, 1H, H$_{arb}$), 3.91 (t, $^3$J$_{HH}$ = 4.6 Hz, 2H, CH$_2$O$^+$), 4.21 (s, 1H, H$_{arb}$), 4.55 (s, 1H, H$_{arb}$), 4.85 (s, 1H, H$_{arb}$), 4.99 (s, 1H, H$_{arb}$), 5.59 (s, 1H, H$_{arb}$), 6.95 (s, 2H, H$_{arb}$), 7.08 (s, 2H, H$_{arb}$), 7.14 (s, 2H, H$_{arb}$), 7.15 (s, 2H, H$_{arb}$), 7.22 (s, 2H, H$_{arb}$), 7.25 (s, 2H, H$_{arb}$), 7.19-7.84 (m, 48H, H$_{arb}$);

$^{13}$C NMR (100 MHz, [D$_6$]-THF, -50 °C): δ = 46.7 (s, 1C, CH$_2$N$^+$), 48.0 (s, 1C, CH$_2$N$^+$), 48.2 (s, 1C, CH$_2$N$^+$), 60.5 (s, 1C, C$_{arb}$), 61.2 (s, 1C, C$_{arb}$), 65.8 (s, 1C, CH$_2$O$^+$), 69.4 (s, 1C, C$_{arb}$), 69.8 (s, 1C, CH$_2$O$^+$), 70.0 (s, 1C, CH$_2$O$^+$), 78.3 (s, 1C, C$_{arb}$), 78.8 (s, 1C, C$_{arb}$), 86.0 (s, 1C, C$_{arb}$), 122.6 (s, 2C, C$_{arb}$), 122.7 (s, 2C, C$_{arb}$), 123.0 (s, 2C, C$_{arb}$), 125.7 (s, 2C, C$_{arb}$), 125.8 (s, 2C, C$_{arb}$), 126.3 (s, 4C, C$_{arb}$), 127.0 (s, 2C, C$_{arb}$), 127.8 (s, 2C, C$_{arb}$), 127.9 (s, 4C, C$_{arb}$), 128.0 (s, 4C, C$_{arb}$), 128.3 (s, 2C, C$_{arb}$), 128.6 (s, 4C, C$_{arb}$), 128.7 (s, 4C, C$_{arb}$), 128.8 (s, 4C, C$_{arb}$), 129.8 (s, 2C, C$_{arb}$), 129.9 (s, 2C, C$_{arb}$), 130.1 (s, 2C, C$_{arb}$), 130.2 (s, 2C, C$_{arb}$), 130.7 (s, 2C, C$_{arb}$), 130.8 (s, 2C, C$_{arb}$), 131.2 (s, 2C, C$_{arb}$), 131.4 (s, 2C, C$_{arb}$), 132.9 (s, 2C, C$_{quad}$), 133.0 (s, 2C, C$_{quad}$), 133.9 (s, 2C, C$_{quad}$), 134.3 (s, 2C, C$_{quad}$), 134.4 (s, 2C, C$_{quad}$), 134.8 (s, 2C, C$_{quad}$), 138.1 (s, 2C, C$_{quad}$), 139.6 (s, 2C, C$_{quad}$), 139.8 (s, 2C, C$_{quad}$), 140.6 (s, 2C, C$_{quad}$), 140.7 (s, 2C, C$_{quad}$), 141.0 (s, 2C, C$_{quad}$), 141.5 (s, 2C, C$_{quad}$), 141.0 (s, 2C, C$_{quad}$);

ATR IR (v in cm$^{-1}$): 3016w, 2360w, 1484m, 1438m, 1267w, 1198w, 1083m, 946w, 891w, 830w, 796s, 766s, 735s, 644m;

EI-MS (70 eV, m/z, %): 441 (7, [M$^+$]), 250 (51, [M$^+$-C$_{16}$H$_{14}$]), 191 (100), 129 (4), 74 (11).

[Rh(trop$_2$EEA)]PF$_6$ (47b)

C$_{32}$H$_{37}$F$_6$NOPRh

M$_w$: 689.08 g/mol

Orange solid

M$_p$: 205-210 °C

$N$-(2-[(5H-dibenzo[a, d]cyclohepten-5-yl)oxy]ethyl)-(5H-dibenzo[a, d]cyclohepten-5-yl)amine 46 (75 mg, 170 µmol) and thallium(I) hexafluorophosphate (69 mg, 178 µmol) were added to a solution of [Rh$_2$(μ-Cl)$_2$(C$_7$H$_7$)$_4$] (33 mg, 85 µmol) in 2 mL THF. The reaction mixture was stirred at room temperature for 1 h. The precipitate was filtered over Celite and the solvent removed under reduced pressure. The crude product was washed with 1 mL diethylether and twice with 1 mL n-hexane to give an orange solid (113 mg, 164 µmol, 97%).
Experimental Section

$^1$H NMR (300 MHz, [D$_8$]-THF, rt): $\delta = 2.44$ (qd, $^2J_{HH} = 12.0$ Hz, $^3J_{HH} = 5.5$ Hz 1H, CH$_2$N), 2.94 (dt, $^3J_{HH} = 12.0$ Hz, $^4J_{HH} = 3.0$ Hz, 1H, CH$_2$N), 3.88 (ddd, $^4J_{HH} = 12.0$ Hz, $^5J_{HH} = 9.0$ Hz, $^6J_{HH} = 3.0$ Hz, 1H, CH$_2$O), 4.01 (dd, $^7J_{HH} = 9.0$ Hz, $^8J_{HH} = 5.5$ Hz, 1H, CH$_2$O), 4.31 (dd, $^9J_{HH} = 9.0$ Hz, $^{10}J_{HH} = 1.0$ Hz, 1H, H$_{\text{ar-N}}$), 4.58 (d, $^{11}J_{HH} = 9.0$ Hz, 1H, H$_{\text{ar-O}}$), 4.96 (m, 1H, H$_{\text{ar-N}}$/1H, H$_{\text{ar-O}}$), 5.29 (d, $^{12}J_{HH} = 9.0$ Hz, 1H, H$_{\text{ar-O}}$), 5.89 (d, $^{13}J_{HH} = 12.0$ Hz, 1H, NH), 5.99 (s, 1H, H$_{\text{ar-O}}$), 7.24-7.50 (m, 10H, H$_{\text{ar}}$), 7.57 (dd, $^{14}J_{HH} = 7.0$ Hz, $^{15}J_{HH} = 1.0$ Hz, 1H, H$_{\text{ar}}$), 7.65 (m, 1H, H$_{\text{ar}}$), 7.70-7.83 (m, 3H, H$_{\text{ar}}$), 7.87 (m, 1H, H$_{\text{ar}}$);

$^{13}$C NMR (75 MHz, [D$_8$]-THF, rt): $\delta = 49.3$ (s, 1C, CH$_2$N), 65.0 (d, $^{1}J_{C-H} = 15.0$ Hz, 1C, C$_{\text{ar-N}}$), 65.5 (s, 1C, C$_{\text{ar-N}}$ under THF), 73.3 (s, 1C, CH$_2$O), 75.2 (d, $^{1}J_{C-H} = 15.0$ Hz, 1C, C$_{\text{ar-N}}$), 77.9 (d, $^{1}J_{C-H} = 11.5$ Hz, 1C, C$_{\text{ar-O}}$), 83.1 (d, $^{1}J_{C-H} = 11.5$ Hz, 1C, C$_{\text{ar-O}}$), 86.9 (s, 1C, C$_{\text{ar-O}}$), 127.2 (s, 1C, C$_{\text{ar}}$), 127.5 (s, 1C, C$_{\text{ar}}$), 128.3 (s, 1C, C$_{\text{ar}}$), 128.4 (s, 1C, C$_{\text{ar}}$), 128.5 (s, 1C, C$_{\text{ar}}$), 128.6 (s, 1C, C$_{\text{ar}}$), 128.7 (s, 1C, C$_{\text{ar}}$), 129.1 (s, 1C, C$_{\text{ar}}$), 129.2 (s, 1C, C$_{\text{ar}}$), 129.3 (s, 1C, C$_{\text{ar}}$), 129.5 (s, 1C, C$_{\text{ar}}$), 129.7 (s, 1C, C$_{\text{ar}}$), 129.9 (s, 2C, C$_{\text{ar}}$), 130.0 (s, 1C, C$_{\text{ar}}$), 130.3 (s, 1C, C$_{\text{ar}}$), 134.9 (s, 1C, C$_{\text{quart}}$), 135.7 (s, 1C, C$_{\text{quart}}$), 135.8 (s, 1C, C$_{\text{quart}}$), 136.5 (s, 1C, C$_{\text{quart}}$), 137.1 (s, 1C, C$_{\text{quart}}$), 137.4 (s, 1C, C$_{\text{quart}}$), 137.5 (s, 1C, C$_{\text{quart}}$), 137.6 (s, 1C, C$_{\text{quart}}$);

$^{103}$Rh NMR (15.8 MHz, [D$_8$]-THF, rt): $\delta = 1001$;

ATR IR (v in cm$^{-1}$): 3648w (NH st), 2877w, 1601w, 1492w, 1281w, 1049w, 1008w, 827s (PF$_6$), 756m, 741m, 616w;

UV/Vis ($\lambda_{\text{max}}$ in nm): 429, 277, 233 (THF);

HRMS (ESI+) m/z: 544.1142 (calculated: 544.1134) [C$_{32}$H$_{27}$NORh]$^+$. 
Experimental Section

[\text{Ir(tropol}_2\text{EEA)}]\text{PF}_6 (47b)

\[
\text{C}_{32}\text{H}_{27}\text{IrNOP}
\]

\[
M_w: 779.14 \text{ g/mol}
\]

Red solid

\[
M_p: 201-206 ^\circ\text{C}
\]

\(N\)-(2-(5H-dibenz[a , d]cyclohepten-5-yl)oxy)ethyl-(5H-dibenz[a, d]cyclohepten-5-yl)amine 46

(50.0 mg, 113.3 \text{ \mu mol}) and thallium hexafluorophosphate (41.6 mg, 119 \text{ \mu mol}) were added to a solution of \([\text{Ir}_2(\mu-\text{Cl})_2(\text{COE})_2]\) (50.7 mg, 56.6 \text{ \mu mol}) in 2 mL THF. The reaction mixture was stirred at room temperature for 1 h. The precipitate was filtered over Celite and the solution concentrated to dryness. The crude product was washed with 1 mL diethylether and twice with 1 mL n-hexane to give a red solid (84 mg, 107.8 \text{ \mu mol}, 96 %).

\(^1\text{H} \text{ NMR (300 MHz, [D}_8\text{-THF, rt})}: \delta = 2.59 (m, 1H, CH_2N), 3.17 (d, \text{ }^3J_{HH} = 12.0 \text{ Hz}, 1H, CH_2N), 4.07 (d, \text{ }^3J_{HH} = 8.5 \text{ Hz}, 1H, H_{b1-N}), 4.23-4.32 (m, 2H, CH_2O / 1H, H_{a1-C}), 4.34 (d, \text{ }^3J_{HH} = 8.5 \text{ Hz}, 1H, H_{a1-N}), 4.68 (d, \text{ }^3J_{HH} = 8.5 \text{ Hz}, 1H, H_{a2-C}), 5.49 (s, 1H, H_{b2-N}), 6.53 (s, 1H, H_{b2-C}), 6.64 (d, \text{ }^3J_{HH} = 12.0 \text{ Hz}, 1H, NH), 7.20-7.51 (m, 10H, H_{ar}), 7.59 (d, \text{ }^3J_{HH} = 7.0 \text{ Hz}, 1H, H_{wa}), 7.67 (m, 3H, H_{ar}), 7.75 (dd, \text{ }^3J_{HH} = 10.5 \text{ Hz}, \text{ }^3J_{HH} = 7.0 \text{ Hz}, 2H, H_{wa});

\(^{13}\text{C} \text{ NMR (75 MHz, [D}_8\text{-THF, rt})}: \delta = 49.1 (s, 1C, C_{a1-N}), 50.6 (s, 1C, CH_2N), 59.4 (s, 1C, C_{a1-N}), 62.7 (s, 1C, C_{a1-C}), 65.5 (s, 1C, C_{b2-N} \text{ under THF}), 67.4 (s, 1C, C_{a1-C}), 76.7 (s, 1C, CH_2O), 89.1 (s, 1C, C_{b1-C}), 126.5 (s, 2C, C_{ar}), 127.5 (s, 2C, C_{ar}), 128.6 (s, 1C, C_{ar}), 128.8 (s, 2C, C_{ar}), 128.9 (s, 1C, C_{ar}), 129.0 (s, 1C, C_{ar}), 129.1 (s, 1C, C_{ar}), 129.2 (s, 1C, C_{ar}), 129.3 (s, 1C, C_{ar}), 129.6 (s, 1C, C_{ar}), 129.7 (s, 1C, C_{ar}), 130.1 (s, 1C, C_{ar}), 130.2 (s, 1C, C_{ar}), 135.2 (s, 1C, C_{quart}), 136.5 (s, 1C, C_{quart}), 136.7 (s, 2C, C_{quart}), 136.9 (s, 2C, C_{quart}), 138.0 (s, 1C, C_{quart}), 138.3 (s, 1C, C_{quart});

\text{ATR IR (\nu in cm}^{-1}): 3652w, 2921w, 2360w, 1601w, 1490w, 1467w, 1280w, 1047w, 996w, 830s, 756m, 741m, 620w;

\text{UV/Vis (\lambda_{max} in nm)}: 486, 444, 356, 298, 274 (THF);

\text{HRMS (ESI+) m/z: 634.1710 (calculated: 634.1710) [C}_{32}\text{H}_{27}\text{IrNOP}^+}.
Sodium tert-butoxide (2 mg, 22 μmol) was added to a solution of [Rh(trop₂EEA)]PF₆ 47a (15 mg, 22 μmol) in 0.4 mL [D₈]-THF. The deprotonation reaction was completed within minutes. The product was characterized in situ by NMR- and UV/Vis-spectroscopy.

$^1$H NMR (300 MHz, [D₈]-THF, rt): $\delta = 2.99$ (t, $^3$Jₕₚₚ = 5.0 Hz, 2H, CH₂N), 3.60 (t, $^3$Jₕₚₚ = 5.0 Hz, 2H, CH₂O), 3.85 (s, 2H, Hₜₜₜ-O), 4.11 (d, $^3$Jₕₚₚ = 2.4 Hz, 2H, Hₜₜₜ-N), 4.35 (s, 1H, Hₜₜₜ-N), 5.49 (s, 1H, Hₜₜₜ-O), 6.93-7.11 (m, 6H, Hₜₜₜ), 7.16 (td, $^3$Jₕₚₚ = 7.5 Hz, $^3$Jₕₚₚ = 1.0 Hz, 2H, Hₜₜₜ), 7.21-7.32 (m, 4H, Hₜₜₜ), 7.48 (dd, $^3$Jₕₚₚ = 7.0 Hz, $^4$Jₕₚₚ = 1.0 Hz, 2H, Hₜₜₜ), 7.56 (d, $^3$Jₕₚₚ = 7.5 Hz, 2H, Hₜₜₜ);

$^{13}$C NMR (75 MHz, [D₈]-THF, rt): $\delta = 57.2$ (s, 1C, CH₂N), 68.1 (d, $^1$J₁₉ = 18.0 Hz, 2C, Cₚₚₚ-N), 71.6 (d, $^1$J₁₉ = 10.0 Hz, 2C, Cₚₚₚ-O), 74.8 (s, 1C, CH₂O), 74.9 (s, 1C, Cₜₜₜ-N), 88.5 (s, 1C, Cₜₜₜ-O), 124.6 (s, 2C, Cₜₜₜ), 124.8 (s, 2C, Cₜₜₜ), 125.9 (s, 2C, Cₜₜₜ), 126.1 (s, 2C, Cₜₜₜ), 127.6 (s, 2C, Cₜₜₜ), 128.5 (s, 4C, Cₜₜₜ), 128.9 (s, 2C, Cₜₜₜ), 135.0 (s, 2C, Cₜₜₜ), 138.4 (s, 2C, Cₜₜₜ), 139.6 (s, 2C, Cₜₜₜ), 147.5 (s, 2C, Cₜₜₜ);

$^{103}$Rh NMR (15.8 MHz, [D₈]-THF, rt): $\delta = 839$;

UV/Vis ($\lambda_{max}$ in nm): 471, 405, 272, 236 (THF).
Sodium tert-butoxide (1.2 mg, 12.8 μmol) was added to a solution of [Ir(trop₂EEA)]PF₆ 47b (10 mg, 12.8 μmol) in 0.4 mL [D₈]-THF. The deprotonation reaction was completed within minutes. The product was characterized in situ by NMR- and UV/Vis spectroscopy.

$^1$H NMR (300 MHz, [D₈]-THF, rt): $\delta = 3.18$ (s, 2H, Hₘₒₜₔ), 3.54 (t, $^3$Jₜₜ = 5.5 Hz, 2H, CH₂N), 3.78 (s, 2H, Hₘₒₜₔ-N), 3.83 (t, $^3$Jₜₜ = 5.5 Hz, 2H, CH₂O), 5.07 (s, 1H, Hₘₑ₋ₑₙ), 5.81 (s, 1H, Hₘₑ₋ₑₙ), 6.96 (m, 4H, Hₘₑ), 7.07 (t, $^3$Jₜₜ = 7.5 Hz, 4H, Hₘₑ);

$^{13}$C NMR (75 MHz, [D₈]-THF, rt): $\delta = 51.2$ (s, 2C, Cₘₒₜₔ), 52.3 (s, 2C, Cₘₒₜₔ-N), 57.6 (s, 1C, CH₂N), 72.7 (s, 1C, Cₘₑ₋ₑₙ), 79.5 (s, 1C, CH₂O), 91.0 (s, 1C, Cₘₑ₋ₑₙ), 123.4 (s, 2C, Cₘₑ), 124.2 (s, 2C, Cₘₑ), 125.6 (s, 2C, Cₘₑ), 126.0 (s, 2C, Cₘₑ), 127.7 (s, 2C, Cₘₑ), 127.8 (s, 2C, Cₘₑ), 128.2 (s, 2C, Cₘₑ), 129.3 (s, 2C, Cₘₑ), 133.9 (s, 2C, Cₘₑ), 139.1 (s, 2C, Cₘₑ), 142.3 (s, 2C, Cₘₑ), 148.1 (s, 2C, Cₘₑ);

UV/Vis (λₑₜₙ in nm): 456, 383, 307, 248 (THF).
3 Compounds of Section IV

3.1 General Procedures for the Oxidative Dehydrogenation of Amino-Olefin Complexes

Procedure A1

Four equivalents of sodium tert-butoxide were added to a solution of \([M(trop_2DAE)]PF_6\) \textit{40a,b} in 2 mL THF. The reaction mixture was stirred for 5 min, then four equivalents of silver(I) triflate were added and the reaction mixture was stirred for 15 min at room temperature. The solution was then filtered over Celite and the solvent was removed under reduced pressure, quantitatively yielding the corresponding diazadiene complex \textit{18a,b}.

Procedure A2

Two equivalents of \(p\)-benzoquinone were added to a solution of \([M(trop_2DAE)]PF_6\) \textit{40a,b} in 1 mL THF. The reaction mixture was stirred at room temperature for 15 minutes. Afterwards the solvent was evaporated, quantitatively yielding the corresponding diazadiene complex \textit{18a,b}.

Procedure A3

\(p\)-Benzoquinone (0.7 mg, 6.4 μmol) was added to \([Ir(trop_2MIMA)]OTf\) \textit{53b} (5.0 mg, 6.4 μmol) in 0.4 mL \([D_8]\)-THF. The oxidation was completed within minutes, quantitatively yielding \([Ir(trop_2DAD)]OTf\textit{18b}].
3.2 Characterization of the Oxidative Dehydrogenation Products

\([\text{Ir(trop}_2\text{MIMA})\text{OTf (53b)}]\)

\[
\begin{align*}
\text{C}_{33}\text{H}_{26}\text{F}_3\text{IrN}_2\text{O}_5\text{S} \\
M_\omega: 780.12 \text{ g/mol}
\end{align*}
\]

Red solid

\(M_p: 170 ^\circ \text{C}\)

Sodium tert-butoxide (1.2 mg, 12.8 μmol) and silver(I) triflate (3.3 mg, 12.8 μmol) were added to a solution of [Ir(trop$_2$DAD)OTf (5.0 mg, 6.4 μmol) in 2 mL THF. The reaction mixture was stirred in the dark for 1 h and then filtered over Celite, yielding a red solid in quantitative yield.

\(^1\text{H} \text{ NMR (500 MHz, [D$_8$]-THF, rt):} \delta = 3.33 \ (dd, \ J_{\text{HH}} = 18.0 \text{ Hz}, \ J_{\text{HH}} = 9.0 \text{ Hz, 1H, CH$_2$}), 4.16 \ (d, \ J_{\text{HH}} = 8.5 \text{ Hz, 1H, H$_{ol}$}), 4.43 \ (d, \ J_{\text{HH}} = 8.5 \text{ Hz, 1H, H$_{ar}$}), 4.72 \ (ddd, \ J_{\text{HH}} = 18.0 \text{ Hz, J$_{\text{HH}}$ = 4.5 Hz, J$_{\text{HH}}$ = 1.5 Hz, 1H, CH$_2$}), 4.77 \ (d, \ J_{\text{HH}} = 8.5 \text{ Hz, 1H, H$_{ol}$}), 4.92 \ (d, \ J_{\text{HH}} = 8.5 \text{ Hz, 1H, H$_{ar}$}), 5.71 \ (s, 1H, H$_{bs}$), 6.72 \ (s, 1H, H$_{bs}$), 7.16 \ (dd, \ J_{\text{HH}} = 9.0 \text{ Hz, J$_{\text{HH}}$ = 4.5 Hz, 1H, NH}), 7.19-7.40 \ (m, 8H, H$_{ar}$), 7.50 \ (d, \ J_{\text{HH}} = 7.5 \text{ Hz, 1H, H$_{ar}$}), 7.53-7.70 \ (m, 7H, H$_{ar}$), 9.10 \ (br s, 1H, H$_{N=CN}$);

\(^{13}\text{C} \text{ NMR (126 MHz, [D$_8$]-THF, rt):} \delta = 58.4 \ (s, 1C, CH$_3$), 60.9 \ (s, 1C, C$_{ol}$), 62.8 \ (s, 1C, C$_{ol}$), 65.5 \ (s, 1C, C$_{bs}$), 66.7 \ (s, 1C, C$_{ol}$, under THF), 73.8 \ (s, 1C, C$_{ol}$), 73.9 \ (s, 1C, C$_{bs}$), 126.9 \ (s, 1C, C$_{ol}$), 127.2 \ (s, 1C, C$_{ar}$), 127.8 \ (s, 1C, C$_{ar}$), 128.0 \ (s, 1C, C$_{ar}$), 128.2 \ (s, 1C, C$_{ar}$), 128.6 \ (s, 1C, C$_{ar}$), 128.7 \ (s, 1C, C$_{ar}$), 128.9 \ (s, 2C, C$_{ar}$), 129.0 \ (s, 3C, C$_{ar}$), 129.1 \ (s, 1C, C$_{ar}$), 129.2 \ (s, 1C, C$_{ar}$), 130.0 \ (s, 1C, C$_{ar}$), 130.8 \ (s, 1C, C$_{ar}$), 130.8 \ (s, 1C, C$_{ar}$), 136.4 \ (s, 1C, C$_{quat}$), 137.4 \ (s, 1C, C$_{quat}$), 137.7 \ (s, 1C, C$_{quat}$), 138.1 \ (s, 1C, C$_{quat}$), 138.6 \ (s, 1C, C$_{quat}$), 138.7 \ (s, 1C, C$_{quat}$), 138.8 \ (s, 1C, C$_{quat}$), 139.3 \ (s, 1C, C$_{quat}$), 182.0 \ (s, 1C, C$_{CN}$);

ATR IR (ν in cm$^{-1}$): 2871w, 1621w, 1489m, 1471m, 1254s (SO$_3$), 1223s, 1154s, 1028s, 900m, 811w, 787m, 756s, 714m, 636s;

UV/Vis (λ$_{max}$ in nm): 537, 484, 391, 304 (THF);

HRMS (ESI+) m/z: 631.1706 (calculated: 631.1721) [C$_{33}$H$_{26}$IrN$_2$]$.^+$.
Experimental Section

[Rh(trop$_2$DAD)]OTf (18a)

\[
\text{C}_{33}\text{H}_{24}\text{F}_3\text{IrN}_2\text{O}_3\text{S}
\]

\[M_w: 688.05 \text{ g/mol}\]

Red solid

[Rh(trop$_2$DAD)]OTf (18a) was oxidized with silver(I) triflate (15.0 mg, 58.0 μmol) in the presence of potassium tert-butoxide (6.5 mg, 58.0 μmol) according to procedure A1.

\(^1\)H NMR (250 MHz, CD$_2$Cl$_2$, rt): \(\delta = 5.59 (s, 4H, H_{ol}), 6.02 (s, 2H, H_{bc}), 7.36-7.81 (m, 16H, H_{ar}), 8.50 (d, J_{Rh,H} = 2.8 \text{ Hz}, 2H, H_{CH=N})\).

The \(^1\)H-NMR data is in perfect agreement with previously published data for [Rh(trop$_2$DAD)]OTf.\[132\]

[Ir(trop$_2$DAD)]OTf (18b)

\[
\text{C}_{33}\text{H}_{24}\text{F}_3\text{IrN}_2\text{O}_3\text{S}
\]

\[M_w: 778.11 \text{ g/mol}\]

Green solid

[Ir(trop$_2$DAE)]PF$_6$ (10.0 mg, 12.8 μmol) was oxidized with silver(I) triflate (13.2 mg, 51.2 μmol) in the presence of potassium tert-butoxide (5.3 mg, 51.2 μmol) according to procedure A1.

\(^1\)H NMR (250 MHz, CD$_2$Cl$_2$, rt): \(\delta = 5.77 (s, 4H, H_{ol}), 6.41 (s, 2H, H_{bc}), 7.36-7.75 (m, 16H, H_{ar}), 9.36 (s, 2H, H_{CH=N})\).

The \(^1\)H-NMR data is in perfect agreement with previously published data for [Ir(trop$_2$DAD)]OTf.\[132\]
4 Compounds of Section V

4.1 General Procedures for the Oxidation of Alcohols

Procedure A1
Sodium tert-butoxide (2.5 μmol, 0.1 mL of a 25 mM stock solution in THF), alcohol (25 mmol) and p-benzoquinone (3.0 g, 27.5 mmol) were added in this order to a solution of [Ir(tropDAD)OTf] (2.0 mg, 2.5 μmol, 1.0 mL of a 2.5 mM stock solution in THF) in 1.9 mL THF. The reaction mixture was stirred at room temperature unless otherwise noted and monitored by gas chromatography and/or NMR spectroscopy.

Procedure A2
Sodium tert-butoxide (1.25 μmol, 0.1 mL of a 12.5 mM stock solution in THF), alcohol (12.5 mmol) and p-benzoquinone (1.5 g, 13.75 mmol) were added in this order to a solution of [Ir(tropDAD)OTf] (1.0 mg, 1.25 μmol, 0.5 mL of a 2.5 mM stock solution in THF) in 2.4 mL THF. The reaction mixture was stirred at room temperature unless otherwise noted and monitored by gas chromatography and/or NMR spectroscopy.

4.2 General Procedure for the Identification of Catalysis Products

Chromatographic Conditions: Separation of alcohols, aldehydes, p-benzoquinone and p-hydroquinone; Column: Hewlett-Packard HP-5 phenylmethylsiloxane (30 m × 0.32 mm × 0.25 μm).

Method 1
Temperature: 5 min at 35 °C, then 10 °C/min to 180 °C, 20 min at 180 °C; hydrogen pressure 0.5 bar; retention times [min]: glycidol 3.22; glycinal 2.22.

Method 2
Temperature: 1 min at 80 °C then 4 °C/min to 180 °C; hydrogen pressure 0.5 bar; retention times [min]: 1,3-butanediol 2.68; 3-hydroxy-1-butanal 1.95; 3-methylthio-1-propanol 3.85; 3-methylthio-1-propanal 2.93; 1,4-benzoquinone 3.10; 1,4-hydroquinone 10.66; 4-hydroxybenzylic alcohol 13.00; 4-hydroxybenzaldehyde 13.59; 4-(methylthio)-benzylic alcohol 16.70; 4-(methylthio)benzaldehyde 15.37; n-octanol 5.43; n-octanal 4.20; 2 phenyl-1-propanol 7.81; 2-phenyl-1-propanal 6.15; geraniol 10.33; geranial 10.50; lavandulol 7.65; lavandulal 5.95; (2,2,7,7-tetramethyltetrahydro-3aH-bis[1,3]-
dioxolo[4,5-b:4',5'-d]pyran-5-yl)methanol 20.68; 2,2,7,7-tetramethyltetrahydro-3aH-bis[1,3]dioxolo-[4,5-b:4',5'-d]pyran-5-carbaldehyde 18.77.

4.3 General Procedure for the Isolation of the Catalysis Products

Isolation Procedure B1 (Isolation as Aldehyde)

After the reaction was completed, the reaction mixture was poured into 25 mL n-pentane. The precipitate was filtered over Celite and washed thoroughly with 40 mL dichloromethane. Afterwards, the solvent was removed under reduced pressure and the residue was resolved in 30 mL dichloromethane. Subsequently, the organic phase was washed twice with 15 mL water and then the aqueous phase was extracted once with 10 mL dichloromethane. The combined organic phases were dried over MgSO₄ and the solvent was removed under reduced pressure to give the pure aldehyde.

Isolation Procedure B2 (Isolation as 2,4-Dinitro-phenylhydrazones)

For isolation a hydrazine solution was prepared by carefully adding 18 mL water and 60 mL ethanol to a solution of 2,4-dinitro-phenylhydrazine (2.5 g, 12.5 mmol) in 12 mL concentrated sulphuric acid. The solution was stirred for 10 min at room temperature and filtered. The reaction mixture was then added slowly to the clear orange hydrazine solution. The formed hydrazone was filtered off, washed with water and dried under reduced pressure. Variations of this procedure are noted in the characterization of the aldehydes.

4.4 Preparation of the Catalyst

[Ir(trop₂DAD)]OTf (18b)

\[
\text{C}_{33}\text{H}_{24}\text{F}_{3}\text{IrN}_{2}\text{O}_{4}\text{S} \\
M_w: 778.11 \text{ g/mol} \\
\text{Green solid}
\]

A solution of [Ir₂(μ-Cl)₂(COE)₄] (0.25 g, 0.29 mmol) in 40 mL THF was added to a solution of trop₂DAD (0.26 g, 0.60 mmol) in 40 mL THF. The reaction mixture was stirred at room temperature for 1h, then silver(I) triflate (0.16 g, 0.62 mmol) was added and stirred for another hour in the dark. The solvent was removed under reduced pressure and the crude product was resolved in 20 mL DCM. The solution
was filtered through Celite and the residue was washed with 100 mL DCM. The solvent was concentrated to 20 mL and overlaid with 50 mL hexane. A precipitate formed over night; the solution on top was decanted and the product was dried under reduced pressure, yielding a dark green solid (0.42 g, 0.54 mmol, 93%).

\(^1\)H NMR (250 MHz, CDCl\(_2\), rt): \(\delta = 5.77 \) (s, 4H, H\(_{\text{ol}}\)), 6.41 (s, 2H, H\(_{\text{bz}}\)), 7.36-7.75 (m, 16H, H\(_{\text{ar}}\)), 9.36 (s, 2H, H\(_{\text{HC=N}}\)).

### 4.5 Characterization of the Catalysis Products

#### Octanal

\[ \text{C}_8\text{H}_{16}\text{O} \]

\[ M_w: 128.12 \text{ g/mol} \]

Yellowish oil

1-Octanol (3.25 g, 25 mmol, 3.9 mL) was oxidized according to procedure A1. The reaction was finished after 2.5 min at room temperature. Isolation according to procedure B1 yielded 1-octanal (3.02 g, 23.5 mmol, 94%) as a yellowish oil.

\(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 0.9 \) (t, \( ^3J_{\text{HH}} = 6.5 \) Hz, 3H, CH\(_3\)), 1.23-1.39 (m, 8H, CH\(_2\)), 1.64 (quint, \( ^3J_{\text{HH}} = 7.5 \) Hz, 2H, CH\(_2\)), 2.43 (dt, \( ^3J_{\text{HH}} = 7.5 \) Hz, \( ^3J_{\text{HH}} = 2.0 \) Hz, 2H, CH\(_2\)), 9.78 (t, \( ^3J_{\text{HH}} = 2.0 \) Hz, 1H, H\(_{\text{CHO}}\));

\(^13\)C NMR (63 MHz, CDCl\(_3\)): \(\delta = 14.0 \) (s, 1C, CH\(_3\)), 22.1 (s, 1C, CH\(_2\)), 22.6 (s, 1C, CH\(_2\)), 29.1 (s, 2C, CH\(_2\)), 31.6 (s, 1C, CH\(_2\)), 43.9 (s, 1C, CH\(_2\)), 203.0 (s, 1C, C\(_{\text{CHO}}\));

ATR IR (\(\nu \) in cm\(^{-1}\)): 2926s (C-H st), 2857m (C-H st), 1726s (C=O st), 1466m (CH\(_3\) \(\delta\) as, CH\(_2\) \(\delta\)), 1114w, 915w, 734s;

GC-MS (70 eV, \(m/z\), %): 130 (1, [M\(^+\)]), 110 (16, [M\(^+\)-CHO]), 100 (22), 84 (90, [M\(^+\)-C\(_3\)H\(_5\)O]), 56 (100, [M\(^+\)-C\(_3\)H\(_2\)O]).
2-Phenyl-1-propanal

![Structural formula of 2-Phenyl-1-propanal]

\[ C_9H_{10}O \]

\[ M_w: 134.07 \text{ g/mol} \]

Yellowish oil

2-Phenyl-1-propanol (3.4 g, 25 mmol, 3.5 mL) was oxidized according to procedure A1. The catalytic reaction was completed after 2.5 min at room temperature. 2-Phenyl-1-propanal was isolated, as stated in procedure B1, as a yellowish oil (3.22 g, 24.0 mmol, 96%).

\[^1\text{H} \text{NMR} \text{ (250 MHz, CDCl}_3\text{): } \delta = 1.49 \text{ (d, } ^3\text{J}_{HH} = 7.0 \text{ Hz, } 3\text{H, CH}_3\text{)}, 3.67 \text{ (dq, } ^3\text{J}_{HH} = 7.0 \text{ Hz, } ^4\text{J}_{HH} = 1.0 \text{ Hz, } 1\text{H, CH})\text{, } 7.25 \text{ (dd, } ^3\text{J}_{HH} = 8.0 \text{ Hz, } ^4\text{J}_{HH} = 1.0 \text{ Hz, } 2\text{H, } H_{ar}\text{), 7.28-7.48 \text{ (m, } 3\text{H, } H_{ar}\text{), } 9.72 \text{ (d, } ^3\text{J}_{HH} = 1.0 \text{ Hz, } 1\text{H, } H_{CHO}\text{);}}\]

\[^{13}\text{C} \text{NMR} \text{ (63 MHz, CDCl}_3\text{): } \delta = 14.6 \text{ (s, } 1\text{C, CH}_3\text{)}, 53.0 \text{ (s, } 1\text{C, CH})\text{, } 127.6 \text{ (s, } 2\text{C, } C_{ar}\text{), } 128.4 \text{ (s, } 2\text{C, } C_{ar}\text{), } 129.1 \text{ (s, } 2\text{C, } C_{ar}\text{), } 137.7 \text{ (s, } 1\text{C, } C_{ quart}\text{), } 201.2 \text{ (s, } 1\text{C, } C_{CHO}\text{);}}\]

ATR IR \((\nu \text{ in cm}^{-1})\): 2977w \((\text{C-H st})\), 1720s \((\text{C=O st})\), 1602w, 1493m, 1452s, 1391w, 1066m, 1021m, 865w, 758m, 698s;

GC-MS (70 eV, \(m/z\), %): 134 (45, [M\(^+\)]), 105 (100, [M\(^+\)-CHO]), 91 (20, [M\(^+\)-C\(_2\)H\(_4\)O]), 77 (38), 51 (18).

Lavandulol

![Structural formula of Lavandulol]

\[ C_{10}H_{16}O \]

\[ M_w: 152.12 \text{ g/mol} \]

Yellowish oil

Lavandulol (3.85 g, 25 mmol, 4.4 mL) was oxidized as detailed in procedure A1. The reaction was finished after 5.0 min at room temperature. Isolation performed according to procedure B1 gave lavandulol (3.64 g, 24.0 mmol, 96%) as a yellowish oil.
Geraniol (3.85 g, 25 mmol, 4.4 mL) was oxidized according to procedure A1. The catalytic reaction was completed after 2.5 min at room temperature. Isolation as detailed in procedure B1 yielded geranial (3.70 g, 24.0 mmol, 97%) as a yellowish oil.

\(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 1.62 \) (s, 3H, CH\(_3\)), 1.70 (s, 3H, CH\(_3\)), 2.18 (s, 3H, CH\(_3\)), 2.24 (m, 4H, CH\(_2\)), 5.08 (m, 1H, H\(_{al}\)), 5.90 (d, \(^3\)J\(_{HH}\) = 8.0 Hz, 1H, H\(_{al}\)), 10.01 (d, \(^3\)J\(_{HH}\) = 8.0 Hz, 1H, H\(_{CHO}\));

\(^13\)C NMR (63 MHz, CDCl\(_3\)): \(\delta = 17.6 \) (s, 1C, CH\(_3\)), 25.7 (s, 2C, CH\(_3\)), 40.6 (s, 2C, CH\(_3\)), 122.6 (s, 1C, C\(_o\)), 127.4 (s, 1C, C\(_o\)), 132.9 (s, 1C, C\(_{quad}\)), 163.9 (s, 1C, C\(_{quad}\)), 191.3 (s, 1C, C\(_{CHO}\));

ATR IR (\(\nu\) in cm\(^{-1}\)): 2917w (C-H st), 1671s (C=O st), 1633w (C=C st), 1442w (C=O), 1379w, 1194w, 1121m, 820w;

GC-MS (70 eV, \(m/z\), %): 152 (9, [M\(^+\)]), 137 (14, [M\(^+\)-CH\(_3\)]), 123 (22, [M\(^+\)-CHO]), 109 (33, [M\(^+\)-C\(_2\)H\(_4\)O]), 84 (44), 69 (100).

Geranial

\[\text{C}_{10}\text{H}_{16}\text{O}\]

\(M_w: 152.12 \text{ g/mol}\)

Yellowish oil
Experimental Section

4-Hydroxybenzaldehyde

\[ \text{C}_6\text{H}_7\text{O}_2 \]

\[ M_w: 122.04 \text{ g/mol} \]

Colourless solid

\[ M_p: 115 ^\circ \text{C} \]

\[ R_f: 0.53 \text{ (Hex/EtOAc 7 : 3)} \]

4-Hydroxybenzyl alcohol (1.55 g, 12.5 mmol) was oxidized according to procedure A2. The reaction was finished after 2.5 minutes at room temperature. The solvent of the reaction mixture was removed under reduced pressure. Purification by flash chromatography (Hex/EtOAc 9 : 1) gave 4-hydroxybenzylaldehyde (1.38 g, 11.37 mmol, 91%) as a colourless solid.

\(^1\text{H NMR} \text{ (250 MHz, [D}_6\text{-DMSO)}: \delta = 6.94 (d, \ ^3J_{HH} = 8.5 \text{ Hz, 2H, H}_{\text{ar}}),\ 7.77 (d, \ ^3J_{HH} = 8.5 \text{ Hz, 2H, H}_{\text{ar}}),\ 9.80 \text{ (s, 1H, H}_{\text{CHO}}),\ 10.61 \text{ (br s, 1H, OH);} \]

\(^{13}\text{C NMR} \text{ (63 MHz, [D}_6\text{-DMSO)}: \delta =116.3 \text{ (s, 2C, C}_{\text{ar}}),\ 128.9 \text{ (s, 1C, C}_{\text{quart}}),\ 132.6 \text{ (s, 2C, C}_{\text{ar}}),\ 163.8 \text{ (s, 1C, C}_{\text{quart}}),\ 191.4 \text{ (s, 1C, C}_{\text{CHO}});} \]

ATR IR (v in cm\(^{-1}\)): 3157m (OH st), 1663s (C=O st), 1589s, 1450s, 1385m, 1282s, 1216s, 1157s, 1114m, 832s, 788m, 699s;

EI-MS (70 eV, m/z, %): 122 (81, [M\(^+\)]), 121 (100, [M\(^+\)-H]), 105 (1, [M\(^+\)-OH]), 93 (34, [M\(^+\)-CHO]), 74 (5, [M\(^+\)-CH\(_2\)O\(_2\)])}, 65 (55).
4-(Methylthio)benzaldehyde

\[
\text{C}_8\text{H}_8\text{OS} \\
M_w: 152.03 \text{ g/mol} \\
\text{Yellowish oil}
\]

4-(Methylthio)benzylic alcohol (3.85 g, 25 mmol) was oxidized according to procedure A1. The catalytic reaction completed after 2.5 min at room temperature; the resulting oxidation product, 4-Methylthiobenzaldehyde, was isolated, as described in procedure B1, as a yellowish oil (3.38 g, 22.2 mmol, 89%).

\[\begin{align*}
\text{H NMR} & : \delta = 2.55 (s, 3H, \text{CH}_3), 7.34 (d, J_{HH} = 8.3 \text{ Hz}, 2H, \text{H}_ar), 7.78 (d, J_{HH} = 8.3 \text{ Hz}, 2H, \text{H}_ar), 9.94 (s, 1H, \text{H}_CHO) \\
\text{C NMR} & : \delta = 14.7 (s, 1C, \text{CH}_3), 125.2 (s, 2C, \text{C}_ar), 130.0 (s, 2C, \text{C}_ar), 133.0 (s, 1C, \text{Cquart}), 147.9 (s, 1C, \text{Cquart}), 191.3 (s, 1C, \text{CCHO})
\end{align*}\]

ATR IR (v in cm\(^{-1}\)): 2829w (C-H st), 1691s (C=O st), 1589s, 1560s, 1389w, 1214m, 1169m, 1091s, 836s, 809s, 691w (C-S st);

GC-MS (70 eV, m/z, %): 152 (100, [M\(^+\)]), 123 (30, [M\(^+\)-CHO]), 79 (21), 45 (26).

3-(Methylthio)propanal(2,4-dinitrophenyl)hydrazone

\[
\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_4\text{S} \\
M_w: 284.06 \text{ g/mol} \\
\text{Orange solid} \\
\text{M}_p: 110 ^\circ\text{C}
\]

3-Methylthio-1-propanol (1.33 g, 12.5 mmol, 1.2 mL) was oxidized as stated in procedure A2. The reaction mixture was stirred at 50 °C for 20 min. Isolation according to procedure B2 gave 3-(Methylthio)propanal(2,4-dinitrophenyl)hydrazone (2.57 g, 9.0 mmol, 72%) as an orange solid.
Experimental Section

\(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 2.20 (s, 3H, CH_3), 2.81 (m, 4H, CH_2), 7.61 (t, \(^3J_{HH} = 5.0\) Hz, 1H, H\(_{HC=HN}\)), 7.96 (d, \(^3J_{HH} = 10.0\) Hz, 1H, H\(_{ar}\)), 8.34 (dd, \(^3J_{HH} = 10.0\) Hz, \(^3J_{HH} = 2.5\) Hz, 1H, H\(_{ar}\)), 9.14 (d, \(^3J_{HH} = 2.5\) Hz, 1H, H\(_{ar}\)); 11.10 (br s, 1H, NH);

\(^{13}\)C NMR (63 MHz, CDCl\(_3\)): \(\delta = 15.6 (s, 1C, CH_3), 30.8 (s, 1C, CH_2), 31.9 (s, 1C, CH_2), 116.5 (s, 1C, C\(_{ar}\)), 123.5 (s, 1C, C\(_{ar}\)), 129.0 (s, 1C, C\(_{quart}\)), 130.0 (s, 1C, C\(_{ar}\)), 138.0 (s, 1C, C\(_{quart}\)), 145.1 (s, 1C, C\(_{quart}\)), 150.1 (s, 1C, C\(_{HC=HN}\));

ATR IR (v in cm\(^{-1}\)): 3295\(m\) (NH st), 3091\(w\) (C-H st), 2916\(w\) (C-H st), 2360\(w\), 1615\(s\) (C=N st), 1591\(s\) (NO\(_2\) st as), 1516\(s\) (NO\(_2\) st as), 1421\(s\), 1310\(s\) (NO\(_2\) st sy), 1269\(s\) (NO\(_2\) st sy), 1221\(s\), 1133\(s\), 1075\(s\), 1054\(m\) (N-N st), 924\(m\), 830\(m\), 742\(m\), 723\(m\), 687\(w\) (C-S st);

El-MS (70 eV, m/z, %): 284 (26, [M\(^+\)]), 237 (12, [M\(^+\)-CH\(_3\)])], 159 (7), 102 (7, [M\(^+\)-C\(_6\)H\(_4\)N\(_2\)O\(_4\)])], 61 (100).

**Oxirane-2-carbaldehyde (2,4-dinitrophenyl)hydrazone**

\[\text{C}_9\text{H}_8\text{N}_4\text{O}_5\]

M\(_w\): 252.05 g/mol

Orange solid

M\(_p\): 105 °C

Glycidol (0.92 g, 12.5 mmol, 0.83 mL) was oxidized according to procedure A2. The reaction was completed after 5 min at room temperature. For the isolation of the aldehyde, 2,4-dinitrophenylhydrazone (2.5 g, 12.5 mmol) was dissolved in acetic acid (12 mL) and ethanol (180 mL). The mixture was refluxed for 5 min and then filtered warm. Afterwards, the filtrate was allowed to cool to room temperature and the reaction mixture was then slowly added to this clear orange solution while stirring. A yellow solid was formed when left overnight at 0 °C, which was filtered off and washed with cooled ethanol to yield oxirane-2-carbaldehyde-(2,4-dinitrophenyl)hydrazone (2.3 g, 9.16 mmol, 73%) as a yellow solid.

\(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 2.99 (dd, ^3J_{HH} = 5.0\) Hz, \(^3J_{HH} = 2.5\) Hz, 1H, CH\(_2\)), 3.22 (dd, \(^3J_{HH} = 5.0\) Hz, \(^3J_{HH} = 2.5\) Hz, 1H, CH\(_2\)), 3.76 (ddd, \(^3J_{HH} = 7.5\) Hz, \(^3J_{HH} = 5.0\) Hz, \(^3J_{HH} = 2.5\) Hz, 1H, CH), 7.05 (d, \(^3J_{HH} = 7.5\) Hz, 1H, H\(_{HC=HN}\)), 8.04 (d, \(^3J_{HH} = 9.5\) Hz, 1H, H\(_{ar}\)), 8.39 (dd, \(^3J_{HH} = 9.5\) Hz, \(^3J_{HH} = 2.5\) Hz, 1H, H\(_{ar}\)), 9.16 (d, \(^3J_{HH} = 2.5\) Hz, 1H, H\(_{ar}\)), 11.23 (br s, 1H, NH);
Experimental Section

$^{13}$C NMR (63 MHz, CDCl$_3$): $\delta = 47.1$ (s, 1C, CH$_2$), 50.5 (s, 1C, CH), 116.7 (s, 1C, C$_{ar}$), 123.3 (s, 1C, C$_{ar}$), 129.6 (s, 1C, C$_{quart}$), 130.2 (s, 1C, C$_{ar}$), 138.8 (s, 1C, C$_{quart}$), 144.6 (s, 1C, C$_{quart}$), 147.6 (s, 1C, C$_{HC=N}$);

ATR IR (v in cm$^{-1}$): 3296 w (N-H st), 3108 w (C-H st), 2360 w, 1614 s (C=N st), 1584 s (NO$_2$ st as), 1498 s (NO$_2$ st as), 1419 s, 1331 s (NO$_2$ st sy), 1315 s (NO$_2$ st sy), 1268 s, 1223 s (epoxide st as), 1142 m, 1078 m (N-N st), 946 m, 922 m (epoxide st sy), 859 m, 833 m, 742 m (epoxide $\delta$);

EI-MS (70 eV, m/z, %): 252 (32, [M$^+$]), 235 (18, [M$^+$-O]), 193 (10, [M$^+$-C$_3$H$_4$O]), 158 (20, [M$^+$-N$_2$O$_4$]), 131 (10), 122 (20, [M$^+$-C$_3$H$_5$N$_2$O]), 75 (100).

3-Hydroxybutanal(2,4-dinitrophenyl)hydrazone

$\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_5$

$M_w$: 268.08 g/mol

Orange solid

$M_p$: 95 °C

1,3-Butanediol (1.13 g, 12.5 mmol, 1.1 mL) was oxidized according to procedure A2. The reaction mixture was stirred at 50 °C for 10 min. For isolation of the aldehyde, 2,4-dinitrophenylhydrazone (2.5 g, 12.5 mmol) was dissolved in 12 mL concentrated sulphuric acid and 64 mL water. The resulting orange solution was then stirred for 10 min and filtered. The ice cooled reaction mixture was then slowly added to the hydrazone solution at 0 °C. The orange solid obtained was filtered off and washed with water. The precipitation was resolved in 100 mL dichloromethane and washed three times with 70 mL water. The organic phase was dried over MgSO$_4$ and the solvent removed under reduced pressure to give 3-hydroxybutanal(2,4-dinitrophenyl)hydrazone (2.62 g, 9.75 mmol, 78%). ($E$)- and ($Z$)-3-Hydroxybutanal(2,4-dinitrophenyl)hydrazone were formed in a 7.3 : 1 ratio and were not separated, and as a result, the characterization by mass spectrometry, infrared spectroscopy and the melting point refer to the mixture of isomers.
**Experimental Section**

(Z)-3-Hydroxybutanal (2,4-dinitrophenyl)hydrazone

\(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 1.43\) (\(d, J_{HH} = 6.0\) Hz, 3H, CH\(_3\)), 1.91 (br s, 1H, OH), 2.61 (m, 2H, CH\(_2\)), 4.28 (m, 1H, CH), 7.19 (t, \(^3\)J\(_{HH}\) = 6.0 Hz, 1H, H\(_{HC\text{-N}}\)), 7.95 (d, \(^3\)J\(_{HH}\) = 9.5 Hz, 1H, H\(_{ar}\)), 8.34 (dd, \(^3\)J\(_{HH}\) = 9.5 Hz, \(^3\)J\(_{HH}\) = 2.5 Hz, 1H, H\(_{ar}\)), 9.14 (d, \(^3\)J\(_{HH}\) = 2.5 Hz, 1H, H\(_{ar}\)), 11.52 (br s, 1H, NH);

\(^13\)C NMR (63 MHz, CDCl\(_3\)): \(\delta = 24.0\) (s, 1C, CH\(_3\)), 36.9 (s, 1C, CH\(_3\)), 66.2 (s, 1C, CH), 116.2 (s, 1C, C\(_{ar}\)), 116.6 (s, 1C, C\(_{ar}\)), 123.4 (s, 1C, C\(_{ar}\)), 126.9 (s, 1C, C\(_{ar}\)), 138.2 (s, 1C, C\(_{ar}\)), 145.5 (s, 1C, C\(_{ar}\)), 148.3 (s, 1C, C\(_{HC\text{-N}}\)).

(E)-3-Hydroxybutanal (2,4-dinitrophenyl)hydrazone

\(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 1.37\) (\(d, J_{HH} = 6.0\) Hz, 3H, CH\(_3\)), 2.00 (br s, 1H, OH), 2.61 (m, 2H, CH\(_2\)), 4.28 (m, 1H, CH), 7.67 (t, \(^3\)J\(_{HH}\) = 6.0 Hz, 1H, H\(_{HC\text{-N}}\)), 7.93 (d, \(^3\)J\(_{HH}\) = 9.5 Hz, 1H, H\(_{ar}\)), 8.34 (dd, \(^3\)J\(_{HH}\) = 9.5 Hz, \(^3\)J\(_{HH}\) = 2.5 Hz, 1H, H\(_{ar}\)), 9.14 (d, \(^3\)J\(_{HH}\) = 2.5 Hz, 1H, H\(_{ar}\)), 11.11 (br s, 1H, NH);

\(^13\)C NMR (63 MHz, CDCl\(_3\)): \(\delta = 23.5\) (s, 1C, CH\(_3\)), 41.5 (s, 1C, CH\(_3\)), 65.8 (s, 1C, CH), 116.4 (s, 1C, C\(_{ar}\)), 123.5 (s, 1C, C\(_{ar}\)), 129.0 (s, 1C, C\(_{ar}\)), 130.1 (s, 1C, C\(_{ar}\)), 138.0 (s, 1C, C\(_{ar}\)), 145.0 (s, 1C, C\(_{ar}\)), 150.0 (s, 1C, C\(_{HC\text{-N}}\)).

ATR IR (v in cm\(^{-1}\)): 3296m (N-H st, O-H st), 3092w (C-H st), 2968w (C-H st), 2360w, 1614s (C=N st), 1585s, 1517s (NO\(_2\) st as), 1499s (NO\(_2\) st as), 1421m, 1325s (NO\(_2\) st sy), 1310s (NO\(_2\) st sy), 1269s, 1220m, 1132s, 1074s (N-N st), 951m, 924m, 830m, 742m, 725m;

EI-MS (70 eV, m/z, %): 268 (100, [M\(^+\)]), 252 (10, [M\(^+\)-OH]), 235 (10, [M\(^+\)-CH\(_4\)O]), 224 (38, [M\(^+\)C\(_2\)H\(_5\)O]), 206 (92, [M\(^+\)-C\(_3\)H\(_7\)O]), 177 (22, [M\(^+\)-N\(_2\)O\(_3\)]), 149 (56), 122 (35), 103 (61, [M\(^+\)-C\(_6\)H\(_4\)N\(_2\)O\(_3\)]), 77 (84), 55 (41).
Experimental Section

1-(2,4-Dinitrophenyl)-2-(((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetra-hydro-3aH-bis[1,3]dioxolo[4,5-b:4',5'-d]pyran-5-yl)methylene)hydrazine (62)

\[ C_{18}H_{23}N_4O_9 \]

\[ M_w: 438.14 \text{ g/mol} \]

Orange solid

\[ R_f (Z): 0.50 \text{ (Hex/EtOAc 7:3)} \]

\[ R_f (E): 0.64 \text{ (Hex/EtOAc 7:3)} \]

\[ M_p (Z): 151-160 ^\circ \text{C} \]

\[ M_p (E): 72-80 ^\circ \text{C} \]

[Ir(trop2DAD)]OTf (2.0 mg, 2.5 μmol) and NaO'Bu (0.2 mL of a 26 mM stock solution, 5 μmol) were added to a solution of 1,2:3,4-di-O-isopropylidene-D-galactopyranose (650 mg, 2.5 mmol) in 1.3 mL THF. The reaction mixture was stirred until the sugar was completely dissolved, then \( \rho \)-benzoquinone (300 mg, 2.75 mmol) was added. The reaction mixture was refluxed for 2 h. After the addition of 2,4-dinitrophenylhydrazin (500 mg, 2.5 mmol), the reaction mixture was refluxed for another 15 min. The solvent was evaporated and the crude product purified by flash chromatography (Hex/EtOAc 95:5 to 9:1). The desired product was obtained as a yellow solid (0.92 g, 2.1 mmol, 84%); the (E)- and (Z)-isomers were formed in a 3.7 : 1 ratio and were separated by flash chromatography.

(Z)-Isomer

\(^1\text{H} \text{NMR (300 MHz, CDCl}_3\):} \delta = 1.36 (s, 3H, CH\textsubscript{3}), 1.40 (s, 6H, CH\textsubscript{3}), 1.58 (s, 3H, CH\textsubscript{3}), 4.46 (m, 2H, CH\textsubscript{2}O/D), 4.72 (dd, \( ^3\text{J}_{\text{HH}} = 7.8 \text{ Hz}, ^3\text{J}_{\text{HH}} = 2.5 \text{ Hz}, 1H, CH\textsubscript{3})), 4.82 (t, \( ^3\text{J}_{\text{HH}} = 2.5 \text{ Hz}, 1H, CH\textsubscript{3})), 5.85 (d, \( ^3\text{J}_{\text{HH}} = 5.0 \text{ Hz}, 1H, CH\textsubscript{3})), 6.81 (d, \( ^3\text{J}_{\text{HH}} = 2.5 \text{ Hz}, 1H, H\text sub G)), 7.93 (d, \( ^3\text{J}_{\text{HH}} = 9.5 \text{ Hz}, 1H, H\text sub G)), 8.29 (dd, \( ^3\text{J}_{\text{HH}} = 9.5 \text{ Hz}, ^3\text{J}_{\text{HH}} = 2.5 \text{ Hz}, 1H, H\text sub G)), 9.11 (d, \( ^3\text{J}_{\text{HH}} = 2.5 \text{ Hz}, 1H, H\text sub G)), 12.93 (br s, 1H, NH);\n
\(^{13}\text{C} \text{NMR (75 MHz, CDCl}_3\):} \delta = 24.1 (s, 1C, CH\textsubscript{3}), 24.7 (s, 1C, CH\textsubscript{3}), 25.8 (s, 1C, CH\textsubscript{3}), 26.1 (s, 1C, CH\textsubscript{3}), 69.8 (s, 1C, CH\textsubscript{3}), 70.2 (s, 1C, CH\textsubscript{3}), 70.3 (s, 1C, CH\textsubscript{3}), 71.2 (s, 1C, CH\textsubscript{3}), 96.0 (s, 1C, CH\textsubscript{3}), 109.5 (s, 1C, CH\textsubscript{3}), 110.0 (s, 1C, CH\textsubscript{3}), 116.0 (s, 1C, CH\textsubscript{3}), 123.4 (s, 1C, CH\textsubscript{3}), 129.6 (s, 1C, CH\textsubscript{3}), 129.9 (s, 1C, CH\textsubscript{3}), 138.0 (s, 1C, CH\textsubscript{3}), 140.5 (s, 1C, CH\textsubscript{3}), 145.2 (s, 1C, CH\textsubscript{3});
Experimental Section

ATR IR (v in cm⁻¹): 3232m (N-H st), 3076w, 2982w, 2937w, 2448w, 2161m, 2029m, 1620s (C=N st), 1579s, 1519s (NO₂ st as), 1501s (NO₂ st as), 1459m, 1426s, 1388m, 1377m, 1328s (NO₂ st sy), 1310s (NO₂ st sy), 1262s, 1212s, 1165s, 1138s, 1193s, 1052s (N-N st), 1037s, 1014s, 946s, 921m, 901s, 856s, 837s, 794s, 785s, 764m, 747s, 704s, 692s, 655m, 639m, 628m;

EI-MS (70 eV, m/z, %): 438 (11, [M⁺]), 423 (12, [M⁺-CH₃]), 305 (3), 277 (5), 251 (6), 222 (3, [M⁺-C₁₀H₁₆O₃⁺]), 193 (7), 159 (4), 141 (21), 113 (54), 71 (24), 59 (100).

(Φ)-Isomer

¹H NMR (300 MHz, CDCl₃): δ = 1.37 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.52 (s, 3H, CH₃), 1.62 (s, 3H, CH₃), 4.41 (m, 2H, CH₂), 5.38 (dd, 3JHxH₂ = 6.0 Hz, 3JHxH₂ = 1.5 Hz, 1H, CH₂), 4.71 (dd, 3JHxH₂ = 7.5 Hz, 3JHxH₂ = 2.5 Hz, 1H, CH₂), 5.61 (d, 3JHxH₂ = 5.0 Hz, 1H, CH₃), 7.51 (d, 3JHxH₂ = 6.0 Hz, 1H, H₁), 7.93 (d, 3JHxH₂ = 9.5 Hz, 1H, H₂), 8.31 (dd, 3JHxH₂ = 9.5 Hz, 3JHxH₂ = 2.5 Hz, 1H, H₃), 9.11 (d, 3JHxH₂ = 2.5 Hz, 1H, H₄), 11.10 (br s, 1H, NH);

¹³C NMR (75 MHz, CDCl₃): δ = 24.3 (s, 1C, CH₃), 24.9 (s, 1C, CH₃), 25.9 (s, 1C, CH₃), 26.2 (s, 1C, CH₃), 68.4 (s, 1C, C₆), 70.2 (s, 1C, C₆), 70.6 (s, 1C, C₆), 73.1 (s, 1C, C₆), 96.2 (s, 1C, C₆), 109.1 (s, 1C, C₆), 109.9 (s, 1C, C₆), 116.6 (s, 1C, C₆), 123.3 (s, 1C, C₆), 129.5 (s, 1C, C₆), 129.9 (s, 1C, C₆), 134.4 (s, 1C, C₆), 144.9 (s, 1C, C₆);

ATR IR (v in cm⁻¹): 3298w (N-H st), 3110w, 2988w, 2936w, 2447w, 2160m, 2029m 1615s (C=N st), 1590s, 1505s, 1425m, 1383m, 1333s (NO₂ st sy), 1313s (NO₂ st sy), 1283s, 1255s, 1210s, 1165s, 1136s, 1065s, 998s, 944m, 920m, 890m, 833m, 743m, 686w, 634w;

EI-MS (70 eV, m/z, %): 438 (5, [M⁺]), 423 (4, [M⁺-CH₃]), 305 (1), 277 (1), 251 (5), 222 (3, [M⁺-C₁₀H₁₆O₃⁺]), 193 (4), 141 (27), 113 (87), 71 (15), 59 (100).
5 Compounds of Section VI

5.1 Reduction of the Diazadiene-Olef in Complexes

Na[Rh(trop₂DAD)] (63a)

A small piece of sodium was added to a solution of [Rh(trop₂DAD)]OTf (10 mg, 14.5 μmol) in 0.4 mL [D₈]-THF in a NMR tube. The reaction mixture was kept in an ultrasonic bath for approximately 23 min. This procedure yielded the symmetric complex sym-63a. Longer reaction times in the ultrasonic bath led to the formation of the asymmetric compound asym-64a. Reaction monitoring is important as the reaction times differ.

**Symmetric complex (sym-63a)**

$^1$H NMR (500 MHz, [D₈]-THF, rt): δ = 3.49 (s, 4H, H₉), 4.92 (d, $^3$J₉H = 2.0 Hz, 2H, H₈b), 5.79 (d, $^3$J₉H = 2.0 Hz, 2H, H₈a), 6.72 (dt, $^3$J₉H = 7.5 Hz, $^3$J₉H = 1.0 Hz, 4H, H₉), 6.88 (dt, $^3$J₉H = 7.5 Hz, $^3$J₉H = 1.0 Hz, 4H, H₉), 6.98 (d, $^3$J₉H = 7.5 Hz, 4H, H₉), 7.32 (d, $^3$J₉H = 7.5 Hz, 4H, H₉);

$^{13}$C NMR (126 MHz, [D₈]-THF, rt): δ = 67.1 (d, $^2$J₉C = 11.5 Hz, 4C, C₉), 75.5 (s, 2C, C₈), 117.6 (d, $^2$J₉C = 2.5 Hz, 2C, C₉C=N), 122.2 (s, 4C, C₉), 125.6 (s, 4C, C₉), 127.1 (s, 4C, C₉), 144.2 (s, 4C, C₉), 148.2 (s, 4C, C₉);

$^{103}$Rh NMR (15.8 MHz, [D₈]-THF, rt): δ = 374.

**Asymmetric complex (asym-64a)**

$^1$H NMR (500 MHz, [D₈]-THF, rt): δ = 2.61 (s, 2H, H₉), 2.78 (s, 2H, H₈), 3.80 (s, 1H, H₈), 4.82 (s, 1H, H₉), 5.31 (t, $^3$J₉H = 7.0 Hz, 2H, H₈), 5.77 (d, $^3$J₉H = 7.5 Hz, 2H, H₈b), 5.98 (t, $^3$J₉H = 7.0 Hz, 2H, H₈b), 6.55 (m, 4H, H₀), 6.77 (dt, $^3$J₉H = 7.5 Hz, $^3$J₉H = 1.0 Hz, 2H, H₀), 6.85 (d, $^3$J₉H = 2.0 Hz, 1H, H₉C=N), 6.90 (d, $^3$J₉H = 7.5 Hz, 2H, H₀), 7.11 (d, $^3$J₉H = 7.5 Hz, 2H, H₀), 7.49 (d, $^3$J₉H = 4.0 Hz, 1H, H₉C=N);

$^{13}$C NMR (126 MHz, [D₈]-THF, rt): δ = 59.7 (d, $^2$J₉C = 11.0 Hz, 2C, C₉), 62.3 (d, $^2$J₉C = 11.0 Hz, 2C, C₉), 77.2 (s, 1C, C₈), 77.6 (br s, 1C, C₈), 108.6 (s, 2C, C₉), 119.7 (s, 2C, C₉), 121.0 (br s, 2C, C₉), 122.9 (br s,
Experimental Section

2C, C$_{ar}$, 125.1 (s, 2C, C$_{ar}$), 125.5 (s, 2C, C$_{ar}$), 125.6 (s, 2C, C$_{ar}$), 126.7 (br s, 1C, C$_{HC=N}$), 127.9 (s, 2C, C$_{ar}$), 137.5 (s, 2C, C$_{quat}$), 141.0 (s, 2C, C$_{quat}$), 143.4 (br s, 1C, C$_{HC=N}$), 146.5 (s, 2C, C$_{quat}$) 147.5 (s, 2C, C$_{quat}$);

$^{103}$Rh-NMR (15.8 MHz, [D$_8$]-THF, 25 °C): $\delta = 1129.$

Na[Ir(trop$_2$DAD)] (64b)

A small piece of sodium was added to a solution of [Ir(trop$_2$DAD)]OTf (10 mg, 12.8 $\mu$mol) in 0.5 mL [D$_8$]-THF in a NMR tube. The reaction mixture was kept in the ultrasonic bath for approximately 55 min; this procedure gave the symmetric complex sym-63b. Longer reaction times in the ultrasonic bath led to the formation of the asymmetric compound asym-64b. The monitoring of the reaction was crucial as deviation in the reaction time led to mixtures of sym-63b and asym-64b.

Symmetric Complex (sym-63b)

$^1$H NMR (500 MHz, [D$_8$]-THF, rt): $\delta = 3.07$ (s, 4H, H$_{ol}$), 5.43 (s, 2H, H$_{bz}$), 6.23 (s, 2H, H$_{HC=N}$), 6.68 (t, $^3J_{HH} = 7.5$ Hz, 4H, H$_{ar}$), 6.85 (t, $^3J_{HH} = 7.5$ Hz, 4H, H$_{ar}$), 6.97 (d, $^3J_{HH} = 7.5$ Hz, 4H, H$_{ar}$), 7.31 (d, $^3J_{HH} = 7.5$ Hz, 4H, H$_{ar}$);

$^{13}$C NMR (126 MHz, [D$_8$]-THF, rt): $\delta = 49.1$ (s, 4C, C$_{ol}$), 74.2 (s, 2C, C$_{bz}$), 120.1 (s, 2C, C$_{HC=N}$), 121.3 (s, 4C, C$_{ar}$), 125.0 (s, 4C, C$_{ar}$), 125.5 (s, 4C, C$_{ar}$), 126.8 (s, 4C, C$_{ar}$), 144.8 (s, 4C, C$_{quat}$), 146.7 (s, 4C, C$_{quat}$).

Asymmetric Complex (asym-64b)

$^1$H NMR (500 MHz, [D$_8$]-THF, rt): $\delta = 2.56$ (s, 2H, H$_{ol}$), 2.69 (s, 2H, H$_{ol}$), 4.12 (s, 1H, H$_{bz}$), 5.28 (s, 1H, H$_{bz}$), 5.39 (t, $^3J_{HH} = 7.0$ Hz, 2H, H$_{ar}$), 5.97 (d, $^3J_{HH} = 7.0$ Hz, 2H, H$_{ar}$), 6.17 (t, $^3J_{HH} = 7.0$ Hz, 2H, H$_{ar}$), 6.54 (dt, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 1.0$ Hz, 2H, H$_{ar}$), 6.73 (d, $^3J_{HH} = 7.0$ Hz, 2H, H$_{ar}$), 6.77 (dt, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 1.0$ Hz, 2H, H$_{ar}$), 6.85 (s, 1H, H$_{HC=N}$), 6.91 (dd, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 1.0$ Hz, 2H, H$_{ar}$), 7.19 (dd, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 1.0$ Hz, 2H, H$_{ar}$), 7.60 (s, 1H, H$_{HC=N}$);

$^{13}$C NMR (126 MHz, [D$_8$]-THF, rt): $\delta = 44.7$ (s, 2C, C$_{ol}$), 46.7 (s, 2C, C$_{ol}$), 76.0 (s, 1C, C$_{ol}$), 77.8 (s, 1C, C$_{ol}$), 108.9 (s, 2C, C$_{ol}$), 119.5 (s, 2C, C$_{ol}$), 121.7 (s, 2C, C$_{ol}$), 122.0 (s, 2C, C$_{ol}$), 125.2 (s, 4C, C$_{ar}$), 125.8 (s, 2C, C$_{ar}$), 126.8 (s, 4C, C$_{ar}$), 144.8 (s, 4C, C$_{quat}$), 146.7 (s, 4C, C$_{quat}$).
Section

$^{13}C$ NMR (75 MHz, CDCl$_3$, rt): $\delta = 33.1$ (d, $^2J_{PC} = 12.0$ Hz, 1C, CH$_2$P), 39.4 (d, $^1J_{PC} = 20.0$ Hz, 1C, CH$_3$N), 128.4 (s, 2C, C$_{ar}$), 128.5 (s, 2C, C$_{ar}$), 128.6 (s, 2C, C$_{ar}$), 132.7 (d, $^2J_{PC} = 18.5$ Hz, 4C, C$_{ar}$), 138.4 (d, $^1J_{PC} = 12.0$ Hz, 2C, C$_{quart}$);

$^{31}P$ NMR (121 MHz, CDCl$_3$, rt): $\delta = -21.7$ (s, 1P);

ATR IR (v in cm$^{-1}$): 3366w (N-H st), 3051w, 2931w (C-H st), 2860w (C-H st), 2512w, 2160w, 1971w, 1584w, 1480w, 1433m, 1306w, 1261w, 1156w, 1094w, 1062w, 1026w, 999w, 978w, 827m (P-C st), 736s, 693s, 652w;

$\text{C$_{ar}$}$, 128.5 (s, 2C, C$_{ar}$), 129.9 (s, 1C, C$_{HC=CH}$), 137.2 (s, 2C, C$_{quart}$), 139.2 (s, 2C, C$_{quart}$), 144.3 (s, 1C, C$_{HC=CH}$), 
146.4 (s, 2C, C$_{quart}$), 148.7 (s, 2C, C$_{ar}$).

5.2 Synthesis of a Diazadiene-Phosphano Ligand and its Complexes

2-(Diphenylphosphino)ethanamine (70)

\[
\text{C$_{14}$H$_{16}$NP} \quad M_w: 229.10 \text{ g/mol}
\]

Colourless liquid

The preparation was based on a literature method.\textsuperscript{[214]} Diphenylphosphane (2.0 g, 10.7 mmol, 1.9 mL) was added to a solution of potassium tert-butoxide (3.2 g, 28.4 mmol) in 40 mL THF. The mixture changed its colour to red and was stirred for 1 h at room temperature. Subsequently, dry 2-chloroethanamine hydrochloride (1.2 g, 10.5 mmol) was added and the reaction mixture was refluxed for 24 h. The colour changed from red to light yellow. The workup was performed under argon and only degassed solvents were used. The solvent was removed under reduced pressure and the crude product was diluted in 30 mL 10% hydrochloric acid. The aqueous phase was washed with 20 mL toluene, after which 35 mL of 10% sodium hydroxide was added and the aqueous solution was extracted three times with 35 mL toluene. The combined organic phase was washed with 40 mL brine, dried over Na$_2$SO$_4$ and the solvent was removed under reduced pressure to give a colourless oil (2.1 g, 9.2 mmol, 87%).

$^1$H NMR (300 MHz, CDCl$_3$, rt): $\delta = 1.51$ (br s, 2H, NH$_2$), 2.26 (t, $^3J_{HH} = 7.5$ Hz, 2H, CH$_2$P), 2.86 (m, 2H, CH$_2$N), 7.33-7.43 (m, 10H, H$_{ar}$);

$^{13}C$ NMR (75 MHz, CDCl$_3$, rt): $\delta = 33.1$ (d, $^2J_{PC} = 12.0$ Hz, 1C, CH$_2$P), 39.4 (d, $^1J_{PC} = 20.0$ Hz, 1C, CH$_3$N), 128.4 (s, 2C, C$_{ar}$), 128.5 (s, 2C, C$_{ar}$), 128.6 (s, 2C, C$_{ar}$), 132.7 (d, $^2J_{PC} = 18.5$ Hz, 4C, C$_{ar}$), 138.4 (d, $^1J_{PC} = 12.0$ Hz, 2C, C$_{quart}$);

$^{31}P$ NMR (121 MHz, CDCl$_3$, rt): $\delta = -21.7$ (s, 1P);
El-MS (70 eV, m/z, %): 229 (21, [M⁺]), 199 (28, [M⁺-CH₃N]), 186 (42, [M⁺-C₂H₆N]), 121 (66, [M⁺-C₆H₃]), 108 (100, [M⁺-C₆H₁₁N]), 91 (72), 77 (92), 65 (30), 51 (70).

**N,N’-(Butane-2,3-diylidene)bis(2-(diphenylphosphino)ethanamine) (71)**

![Structural formula](image)

C₃₂H₃₄N₂P₂

Mₜ: 508.22 g/mol

Colourless solid

Mᵣ: 144 °C

The preparation was based on a literature method.²⁰⁶ 2,3-Butandione (112 mg, 1.30 mmol) and 2-diphenylphosphinoethylamine (600 mg, 2.62 mmol) were stirred in substance for 3 h. Stirring became difficult when sufficient solid had formed and therefore 8 mL ethanol was added. The reaction mixture was stirred at room temperature for another 36 h. The solution over the formed solid was then decanted and the crude product was washed four times with 8 mL ethanol. The product was dried under reduced pressure to give a colourless solid (300 mg, 0.59 mmol, 45%).

¹H NMR (300 MHz, [D₆]-THF, rt): δ = 1.89 (s, 6H, CH₃), 2.47 (t, J₁HH = 7.5 Hz, 4H, CH₂P), 2.86 (m, 4H, CH₂N), 7.29-7.52 (m, 20H, Hₘ);

¹³C NMR (75 MHz, [D₆]-THF, rt): δ = 11.3 (s, 2C, CH₃), 29.7 (d, J₁PC = 12.5 Hz, 2C, CH₂P), 49.3 (d, J₁PC = 21.5 Hz, 2C, CH₂N), 128.0 (s, 4C, C₆H₆), 128.1 (s, 8C, C₆H₆), 132.6 (d, J₁PC = 19.0 Hz, 8C, C₆H₆), 139.3 (d, J₁PC = 14.5 Hz, 4C, C₆H₆), 167.3 (s, 1C, C₆H₆);

³¹P NMR (121 MHz, [D₆]-THF, rt): δ = -18.6 (s, 2P);

ATR IR (ν in cm⁻¹): 3056w, 2941w (C-H st), 2907w, 1882w 1819w, 1695m, 1622m (C=N st), 1583m, 1478m, 1431m, 1408m, 1366m, 1342m, 1313m, 1134m, 1096m, 1072m, 1058m, 1026m, 995m, 934m, 922m (P-C st), 864w, 746s, 733s, 702s, 632m, 619w;

El-MS (70 eV, m/z, %): 508 (9, [M⁺]), 480 (20), 321 (10, [M⁺-C₁₂H₁₀P]), 308 (16), 295 (18), 267 (24), 200 (14, [M⁺-C₁₆H₂₂P]), 183 (100, [M⁺-C₂₀H₂₄N₂P]), 152 (26), 121 (50), 108 (82), 95 (20), 77 (20), 68 (11).
**Experimental Section**

**Rhodium(I) Complex (72)**

\[
\begin{align*}
\text{C}_{32}\text{H}_{34}\text{F}_6\text{N}_2\text{P}_3\text{Rh} \\
M_w: 756.09 \text{ g/mol} \hspace{1cm} \text{Red solid}
\end{align*}
\]

2,3-Butanedione-bis(2-diphenylphosphinoethylimine) (13.0 mg, 25.6 µmol) and thallium(I) hexafluorophosphate (9.0 mg, 25.6 µmol) were added to a solution of \([\text{Rh}_2(\mu-\text{Cl})_2(\text{C}_2\text{H}_4)_4]\) (5.0 mg, 12.8 µmol) in 1 mL THF. The reaction mixture was stirred for 1 h at room temperature. The solvent was then evaporated; the crude product was resolved in dichloromethane and (1 mL) filtered over Celite. The solvent was removed under reduced pressure to yield a dark red solid (11.8 mg, 94%).

Two different complexes, 72 and 73, were observed and characterized by NMR spectroscopy. The initial ratio was 82 : 18 (72 : 73). After refluxing the complex for 1 d, the ratio changed to 38 : 62 (72 : 73). Longer refluxing had no influence on the product distribution.

\[1^1\text{H NMR} (700 \text{ MHz}, [D_8]-\text{THF}, \text{rt}): \delta = 2.102 (s, 6\text{H}, \text{CH}_3), 3.01 (m, 4\text{H}, \text{CH}_2\text{P}), 3.95 (s, 4\text{H}, \text{CH}_2\text{N}), 7.20-7.60 (m, 20\text{H}, \text{H}_{ar});\]

\[^{13}\text{C-NMR} (176 \text{ MHz}, [D_8]-\text{THF}, \text{rt}): \delta = 17.0 (s, 2\text{C}, \text{CH}_3), 34.8 (m, 2\text{C}, \text{CH}_2\text{P}), 51.2 (s, 2\text{C}, \text{CH}_2\text{N}), 128.4 (br s, 12\text{C}, \text{C}_{ar}), 130.0 (br s, 4\text{C}, \text{C}_{quart}), 132.9 (br s, 8\text{C}, \text{C}_{ar}), 172.5 (s, 2\text{C}, \text{C}_{MeC=\text{N}});\]

\[^{31}\text{P-NMR} (283 \text{ MHz}, [D_8]-\text{THF}, \text{rt}): \delta = 51.3 (d, ^1J_{RhP} = 166 \text{ Hz}, 2\text{P})\]

\[^{103}\text{Rh-NMR} (15.8 \text{ MHz}, [D_8]-\text{THF}, 25 ^\circ\text{C}): \delta = 227.\]
Experimental Section

Rhodium(I) Complex (73)

\[
\begin{align*}
\text{HNMR (700 MHz, [D}8\text{-THF, rt): } & \delta = 1.67 (d, ^3J_{HH} = 7.0 \text{ Hz, } 3H, \text{ CH}_2), 2.19 (s, 3H, \text{ CH}_3), 2.85 (m, 2H, \text{ CH}_2P), 3.56 (m, 1H, \text{ CH}_2N), 3.69 (m, 1H, \text{ CH}_2P), 3.78 (m, 1H, \text{ CH}_2N), 3.83 (m, 1H, \text{ CH}_2P), 5.20 (m, 1H, CH), 7.20-7.60 (m, 20H, H-ar); 8.41 (m, 1H, H-\text{HC=N}); \\
\text{13C NMR (176 MHz, [D}8\text{-THF, rt): } & \delta = 15.6 (s, 1C, \text{ CH}_3), 19.5 (s, 1C, \text{ CH}_3), 36.3 (dd, ^1J_{PC} = 13.0 \text{ Hz, } ^1J_{PC} = 21.0 \text{ Hz, } ^1J_{PC} = 9.0 \text{ Hz, } 1C, \text{ CH}_2P), 50.0 (s, 1C, \text{ CH}_2N), 76.5 (s, 1C, CH), 128.2 (brs, 4C, C-ar), 128.3 (brs, 4C, C-ar), 128.4 (brs, 2C, C-ar), 129.6 (s, 2C, C-ar), 129.8 (d, ^1J_{PC} = 4.0 \text{ Hz, } 2C, \text{ C-quat}), 129.9 (s, 2C, C-ar), 131.9 (d, ^2J_{PC} = 11.0 \text{ Hz, } 2C, \text{ C-ar}), 132.6 (d, ^2J_{PC} = 11.0 \text{ Hz, } 2C, \text{ C-ar}), 133.0 (d, ^1J_{PC} = 4.0 \text{ Hz, } 2C, \text{ C-quat}), 133.1 (s, 2C, C-ar), 170.7 (s, 1C, C-\text{HC=N}), 183.2 (s, 1C, C-MeC=N); \\
\text{31P NMR (283 MHz, [D}8\text{-THF, rt): } & \delta = 54.8 (dd, ^1J_{Rhp} = 166 \text{ Hz, } ^2J_{PP} = 33 \text{ Hz, } 1P), 54.9 (dd, ^1J_{Rhp} = 166 \text{ Hz, } ^2J_{PP} = 33 \text{ Hz, } 1P); \\
\text{103Rh-NMR (15.8 MHz, [D}8\text{-THF, 25 ºC): } & \delta = 139.
\end{align*}
\]

The rhodium(I) complex 73 was prepared according to procedure of 72.

\[
\begin{align*}
\text{C}_{32}\text{H}_{34}\text{F}_6\text{N}_2\text{P}_3\text{Rh} \\
M_w: 756.09 \text{ g/mol} \\
\text{Red solid}
\end{align*}
\]
5.3 Reductive Hydrogenation of the Diazadiene-Olefin Iridium(I) Complex

Procedure B1
Ethanol (0.6 g, 12.85 mmol) was added to a solution of [Ir(trop₂DAD)]OTf (0.1 g, 128.5 μmol) in 3 mL THF. The reaction mixture was refluxed for 24h. For the work-up, the solvent was removed under reduced pressure. The product was obtained as a red powder (93 mg, 119.0 μmol, 93%).

Procedure B2
Dihydrogen (1 bar) was pressed onto a frozen solution of [Ir(trop₂DAD)]OTf (6 mg, 7.7 μmol) in 1 mL THF. Afterwards, the reaction mixture was allowed to warm to room temperature and was stirred for 1h until a light red solution was formed. The solvent was then removed under reduced pressure and the product was analyzed by NMR-spectroscopy.
VIII. Appendix
1 List of Abbreviations

Å Angström (1 Å = 10\(^{-10}\) m)
° Degree
°C Degree Celsius
ACAC Acetoacetate
ar Aromatic
asy Asymmetrical
ATR Attenuated Total Reflectance
br Broad
bz Benzylic
cat. Catalytic
cht Cycloheptatrienyl
COD 1,5-Cyclooctadiene
COE Cyclooctene
COSY Homo-Nuclear Shift Correlation Spectroscopy
cr Centroid
CV Cyclic Voltametry
CW Continuous Wave
DACH Diaminocyclohexane
DAD 1,4-Diazabuta-1,3-diene
DAE Diaminoethane
DCM Dichloromethane
DICH 1,2-Diimino-cyclohexane
DMSO Dimethylsulfoxide
dr Diastereomeric Ratio
EI Electron Ionization
ENDOR Electron Nuclear Double Resonance
EPR Electron Paramagnetic Resonance
ESI Electron Spray Ionization
ETM Electron Transfer Mediator
EtOAc Ethylacetate
FC Flash chromatography
Appendix

<table>
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<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>Fc</td>
<td>Ferrocene</td>
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<tr>
<td>Fc&lt;sup&gt;+&lt;/sup&gt;</td>
<td>Ferrocenium Ion</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>GOase</td>
<td>Galactose Oxidase</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
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<td>HRMS</td>
<td>High Resolution Mass Spectroscopy</td>
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<tr>
<td>HYSCORE</td>
<td>Hyperfine Sublevel Correlation</td>
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<td>Hz</td>
<td>Hertz</td>
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<td>IR</td>
<td>Infra Red</td>
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<td>J</td>
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</tr>
<tr>
<td>mg</td>
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<td>min</td>
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<td>NMR</td>
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<td>NOESY</td>
<td>Nuclear Overhauser Effect Spectroscopy</td>
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<tr>
<td>ol</td>
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<tr>
<td>OTf</td>
<td>Triflate</td>
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<tr>
<td>ppm</td>
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<tr>
<td>R&lt;sub&gt;f&lt;/sub&gt;</td>
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<td>rt</td>
<td>Room Temperature</td>
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<tr>
<td>s</td>
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<td>sat.</td>
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<td>st</td>
<td>Stretching</td>
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<td>Description</td>
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<td>sy</td>
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<td>TEMPO</td>
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<td>tert</td>
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<td>THF</td>
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<td>TLC</td>
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<td>TMS</td>
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<tr>
<td>TPAP</td>
<td>Tetra-n-propylammonium Perruthenate</td>
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<tr>
<td>Trop</td>
<td>Dibenzotropylidene</td>
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<tr>
<td>TTC</td>
<td>Trichloroisocyanuric Acid</td>
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<tr>
<td>UV/Vis</td>
<td>Ultraviolet/visible</td>
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<td>λ</td>
<td>Wave Length</td>
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## 2 Crystallographic Data

**Crystallographic Data of [Ir(trop$_2$DAD)]OTf 18b**

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<th>Value</th>
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## Crystallographic Data of tropOEt 32

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### Crystallographic Data of [Rh(tropOH)$_2$]OTf 33

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<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P21/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>11.6297(6) Å</td>
</tr>
<tr>
<td>α</td>
<td>90°</td>
</tr>
<tr>
<td>b</td>
<td>23.9141(13) Å</td>
</tr>
<tr>
<td>β</td>
<td>102.458(4)°</td>
</tr>
<tr>
<td>c</td>
<td>10.1306(4) Å</td>
</tr>
<tr>
<td>γ</td>
<td>90°</td>
</tr>
<tr>
<td>Volume</td>
<td>2751.1(5) Å$^3$</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.648 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.592 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>1413</td>
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<tr>
<td>Crystal size</td>
<td>0.08 x 0.05 x 0.10 mm$^3$</td>
</tr>
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<td>Theta range for data collection</td>
<td>2.57 to 34.78°</td>
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<tr>
<td>Index ranges</td>
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<td>Reflections collected</td>
<td>40463</td>
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<tr>
<td>Independent reflections</td>
<td>11293 [R(int) = 0.109]</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Multi-scan</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>1.00000 and 0.97955</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
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<tr>
<td>Data / restraints / parameters</td>
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<td>Goodness-of-fit on F$^2$</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0450, wR2 = 0.0534</td>
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<td>R indices (all data)</td>
<td>R1 = 0.1576, wR2 = 0.0639</td>
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<td>Largest diff. peak and hole</td>
<td>0.682 and 0.009 e.Å$^{-3}$</td>
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### Crystallographic Data of [Rh(tropOEt)₂]PF₆

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<tr>
<th>Identification code</th>
<th>[Rh(tropOEt)₂]PF₆</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C₃₄H₃₂F₆O₂PRh</td>
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<tr>
<td>Formula weight</td>
<td>720.48</td>
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<tr>
<td>Temperature</td>
<td>296(2) 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>
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<td>Unit cell dimensions</td>
<td>a = 11.9046(11) Å , α = 90°</td>
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<tr>
<td></td>
<td>b = 14.2864(13) Å , β = 104.214(2)°</td>
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<tr>
<td></td>
<td>c = 18.6300(17) Å , γ = 90°</td>
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<tr>
<td>Volume</td>
<td>3071.5(5) Å₃</td>
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<td>Z</td>
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<tr>
<td>Density (calculated)</td>
<td>1.558 Mg/m³</td>
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<tr>
<td>Absorption coefficient</td>
<td>0.675 mm⁻¹</td>
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<td>F(000)</td>
<td>1464</td>
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<td>Crystal size</td>
<td>0.21 x 0.12 x 0.10 mm³</td>
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<tr>
<td>Theta range for data collection</td>
<td>1.76 to 27.34°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-12&lt;=h&lt;=15, -18&lt;=k&lt;=17, -21&lt;=l&lt;=24</td>
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<tr>
<td>Reflections collected</td>
<td>18818</td>
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<tr>
<td>Independent reflections</td>
<td>6754 [R(int) = 0.0468]</td>
</tr>
<tr>
<td>Completeness to theta = 27.34°</td>
<td>97.3 %</td>
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<tr>
<td>Absorption correction</td>
<td>Empirical</td>
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<tr>
<td>Max. and min. transmission</td>
<td>0.9355 and 0.8712</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>6754 / 0 / 397</td>
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<td>Goodness-of-fit on F²</td>
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<td>R1 = 0.0494, wR2 = 0.1151</td>
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<td>R indices (all data)</td>
<td>R1 = 0.0824, wR2 = 0.1293</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.776 and -0.672 e.Å³</td>
</tr>
</tbody>
</table>
Crystallographic Data of rac-/meso-[Rh(trop$_2$DAE)]PF$_6$ 40a

Identification code [Rh(trop$_2$DAE)]PF$_6$

Empirical formula C$_{32}$H$_{46}$F$_6$N$_2$PRh

Formula weight 738.59

Temperature 200(2) K

Wavelength 0.71073 Å

Crystal system Monoclinic

Space group P2$_1$/n

Unit cell dimensions

<table>
<thead>
<tr>
<th>a</th>
<th>13.0019(6) Å</th>
<th>α = 90°</th>
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</thead>
<tbody>
<tr>
<td>b</td>
<td>19.4050(9) Å</td>
<td>β = 104.415(2)°</td>
</tr>
<tr>
<td>c</td>
<td>15.9165(8) Å</td>
<td>γ = 90°</td>
</tr>
</tbody>
</table>

Volume 3889.3(3) Å$^3$

Z 5

Density (calculated) 1.463 Mg/m$^3$

Absorption coefficient 0.670 mm$^{-1}$

F(000) 1760

Crystal size 0.20 x 0.18 x 0.08 mm$^3$

Theta range for data collection 1.82 to 28.35°

Index ranges -17≤h≤17, -25≤k≤25, -21≤l≤21

Reflections collected 74290

Independent reflections 9690 [R(int) = 0.1039]

Completeness to theta = 28.35° 99.7 %

Refinement method Full-matrix least-squares on F$^2$

Data / restraints / parameters 9690 / 0 / 516

Goodness-of-fit on F$^2$ 1.040

Final R indices [I>2sigma(I)] R1 = 0.0509, wR2 = 0.1326

R indices (all data) R1 = 0.0703, wR2 = 0.1413

Largest diff. peak and hole 1.404 and -1.589 e.Å$^{-3}$
### Crystallographic Data of [Ir(trop2DAE)]OTf • CH2Cl2 40b

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Identification code</td>
<td>[Ir(trop2DAE)]OTf</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C33H30Cl2F6IrN2P</td>
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<tr>
<td>Formula weight</td>
<td>1725.32</td>
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<tr>
<td>Temperature</td>
<td>100(2) 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>P 21/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 9.3971(6) Å, α = 90°, b = 32.791(2) Å, β = 111.535(2)°, c = 10.7345(6) Å, γ = 90°</td>
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<tr>
<td>Volume</td>
<td>3076.8(3) Å3</td>
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<tr>
<td>Z</td>
<td>2</td>
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<tr>
<td>Density (calculated)</td>
<td>1.862 Mg/m³</td>
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<tr>
<td>Absorption coefficient</td>
<td>4.630 mm⁻¹</td>
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<tr>
<td>F(000)</td>
<td>1688</td>
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<tr>
<td>Crystal size</td>
<td>0.27 x 0.20 x 0.05 mm³</td>
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<tr>
<td>Theta range for data collection</td>
<td>2.13 to 44.89°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-18&lt;=h&lt;=18, -64&lt;=k&lt;=65, -21&lt;=l&lt;=20</td>
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<td>Reflections collected</td>
<td>98428</td>
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<tr>
<td>Independent reflections</td>
<td>24873 [R(int) = 0.0416]</td>
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<td>Completeness to theta = 44.89°</td>
<td>98.5 %</td>
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<tr>
<td>Absorption correction</td>
<td>Empirical</td>
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<tr>
<td>Max. and min. transmission</td>
<td>0.8015 and 0.3679</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>24873 / 0 / 518</td>
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<td>Goodness-of-fit on F²</td>
<td>1.131</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0492, wR2 = 0.1176</td>
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<td>R indices (all data)</td>
<td>R1 = 0.0591, wR2 = 0.1219</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>9.126 and -6.245 e.Å⁻³</td>
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**Appendix**

**Crystallographic Data of [Rh(trop₂EEA)]PF₆ • 2 THF • Dioxan 47a**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Identification code</td>
<td>[Rh(trop₂EEA)]PF₆</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₄₄H₅₁F₆NO₅PRh</td>
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<tr>
<td>Formula weight</td>
<td>1677.08</td>
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<tr>
<td>Temperature</td>
<td>100(2) K</td>
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<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>C 2/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
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</tr>
<tr>
<td>a</td>
<td>20.7878(13) Å</td>
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<tr>
<td>α</td>
<td>90°</td>
</tr>
<tr>
<td>b</td>
<td>15.9671(9) Å</td>
</tr>
<tr>
<td>β</td>
<td>102.016(2)°</td>
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<tr>
<td>c</td>
<td>21.9826(13) Å</td>
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<tr>
<td>γ</td>
<td>90°</td>
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<tr>
<td>Volume</td>
<td>7136.6(7) Å³</td>
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<tr>
<td>Z</td>
<td>4</td>
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<tr>
<td>Density (calculated)</td>
<td>1.561 Mg/m³</td>
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<tr>
<td>Absorption coefficient</td>
<td>0.598 mm⁻¹</td>
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<td>F(000)</td>
<td>3396</td>
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<tr>
<td>Crystal size</td>
<td>0.15 x 0.09 x 0.06 mm³</td>
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<tr>
<td>Theta range for data collection</td>
<td>1.62 to 36.38°</td>
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<tr>
<td>Index ranges</td>
<td>-34&lt;=h&lt;=34, -26&lt;=k&lt;=26, -36&lt;=l&lt;=36</td>
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<td>Reflections collected</td>
<td>89557</td>
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<tr>
<td>Independent reflections</td>
<td>17313 [R(int) = 0.0677]</td>
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<tr>
<td>Completeness to theta = 36.38°</td>
<td>99.5 %</td>
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<tr>
<td>Absorption correction</td>
<td>Empirical</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>17313 / 0 / 505</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.034</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0634, wR2 = 0.1806</td>
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<td>R1 = 0.0802, wR2 = 0.1913</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>2.510 and -1.334 e.Å³</td>
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**Crystallographic Data of [Ir(trop$_2$EEA)]PF$_6$ \cdot 3$THF$ 47b**

<table>
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<th>Property</th>
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<tr>
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<td>C$<em>{44}$H$</em>{51}$F$_6$IrNO$_4$P</td>
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<tr>
<td>Formula weight</td>
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<tr>
<td>Temperature</td>
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<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>C 1 2 / c1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 20.9043(14) Å, α = 90°</td>
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<tr>
<td></td>
<td>b = 15.8353(10) Å, β = 101.8420(10)°</td>
</tr>
<tr>
<td></td>
<td>c = 22.0295(14) Å, γ = 90°</td>
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<tr>
<td>Volume</td>
<td>7137.1(8) Å$^3$</td>
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<td>Z</td>
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<tr>
<td>Density (calculated)</td>
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<td>0.29 x 0.20 x 0.18 mm$^3$</td>
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<td>1.63 to 28.33°</td>
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<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
<td>8895 [R(int) = 0.0308]</td>
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<tr>
<td>Completeness to theta = 28.33°</td>
<td>99.7%</td>
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<tr>
<td>Max. and min. transmission</td>
<td>0.5433 and 0.4006</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
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<tr>
<td>Data / restraints / parameters</td>
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<td>Goodness-of-fit on F$^2$</td>
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<td>2.200 and -1.488 e.Å$^3$</td>
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## Crystallographic Data of [Ir(trop₂MIMA)]OTf • 1.5 CH₂Cl₂ S3b

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<td>C₃₄.₅H₂₉Cl₁F₃IrN₂O₂S</td>
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<tr>
<td>Temperature</td>
<td>100(2) K</td>
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<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>P 21/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
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<tr>
<td>a = 11.8025(9) Å</td>
<td>α = 90°</td>
</tr>
<tr>
<td>b = 24.2388(18) Å</td>
<td>β = 97.167(2)°</td>
</tr>
<tr>
<td>c = 23.5036(18) Å</td>
<td>γ = 90°</td>
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<tr>
<td>Volume</td>
<td>6671.3(9) Å³</td>
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<td>Z</td>
<td>8</td>
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<tr>
<td>Density (calculated)</td>
<td>1.806 Mg/m³</td>
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<td>Absorption coefficient</td>
<td>4.362 mm⁻¹</td>
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<td>F(000)</td>
<td>3560</td>
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<tr>
<td>Crystal size</td>
<td>0.23 x 0.20 x 0.14 mm³</td>
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<tr>
<td>Theta range for data collection</td>
<td>1.68 to 28.35°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-15 ≤ h ≤ 15, -31 ≤ k ≤ 31, -31 ≤ l ≤ 31</td>
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<tr>
<td>Reflections collected</td>
<td>685311</td>
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<tr>
<td>Independent reflections</td>
<td>16615 [R(int) = 0.0429]</td>
</tr>
<tr>
<td>Completeness to theta = 28.35°</td>
<td>99.7 %</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.5803 and 0.4336</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<td>Data / restraints / parameters</td>
<td>16615 / 0 / 891</td>
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<tr>
<td>Goodness-of-fit on F²</td>
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<tr>
<td>Final R indices [&gt;2sigma(I)]</td>
<td>R₁ = 0.0474, wR₂ = 0.1123</td>
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<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0611, wR₂ = 0.1198</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>5.850 and -1.994 e.Å⁻³</td>
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**Crystal data for CoCp\(^*\)\(_2\)[Ir(trop\(_2\)DAD)] - 2 THF 63b**

<table>
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<tr>
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<th>Value</th>
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<tbody>
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<td>Identification code</td>
<td>CoCp(^*)(_2)[Ir(trop(_2)DAD)]</td>
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<td>Empirical formula</td>
<td>C(<em>{60})H(</em>{72})CoIrN(_2)O(_2)</td>
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<tr>
<td>Formula weight</td>
<td>1104.46</td>
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<tr>
<td>Temperature</td>
<td>100(2) 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/n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 13.2268(12) Å, (\alpha = 90^\circ)</td>
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<td></td>
<td>b = 16.1856(15) Å, (\beta = 101.799(2)^\circ)</td>
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<tr>
<td></td>
<td>c = 23.122(2) Å, (\gamma = 90^\circ)</td>
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<tr>
<td>Volume</td>
<td>4845.5(8) Å(^3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.511 Mg/m(^3)</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>3.133 mm(^{-1})</td>
</tr>
<tr>
<td>F(000)</td>
<td>2256</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.30 x 0.10 x 0.10 mm(^3)</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.55 to 28.39(^\circ)</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-17(\leq)h(\leq)17, -21(\leq)k(\leq)21, -30(\leq)l(\leq)30</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>12117</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>12117 [R(int) = 0.0645]</td>
</tr>
<tr>
<td>Completeness to theta = 28.39(^\circ)</td>
<td>99.7 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Empirical</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.7447 and 0.4533</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on (F^2)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>12117 / 0 / 605</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.134</td>
</tr>
<tr>
<td>Final R indices [I&gt;2\text{sigma}(I)]</td>
<td>R1 = 0.0566, wR2 = 0.1410</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0701, wR2 = 0.1478</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>6.194 and -2.610 e.Å(^3)</td>
</tr>
</tbody>
</table>
3 Curriculum Vitae

Name: Friederike Tewes
Born: November 11th 1980
Nationality: German

Education

08/2000 – 06/2006
Phillips-University Marburg, Marburg, Germany
Master in Chemistry (Dipl. Chem.)

09/2003 – 08/2004
University Paris Sud XI, Orsay, France
Erasmus Exchange Program
Research project in the group of Prof. Kouklovsy

Phillips-University Marburg, Marburg, Deutschland
Diploma thesis in the group of Prof. Glorius
Synthesis of New Chirale Oxazoline-Olefin and N-Heterocyclic Carben Ligands

Swiss Federal Institute of Technology Zürich, Zürich, Switzerland
PhD thesis in the group of Prof. Grützmacher
Iridium-Catalyzed Dehydrogenation of Alcohols

Publications


IX. Literature
Literature

Literature

[214] C. Böhler, Dissertation ETH 14420 (Zürich), **2001**.


[221] S. Stoll, Dissertation ETH 15059 (Zürich), **2003**.

