The Coordination and Catalytic Chemistry of some Ru(Cp*) Complexes

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Publications


Abstract

An investigation into the slow kinetics of allylation reactions when a complex of the type \([\text{Ru}(\text{Cp}^*)(\text{N,N})(\text{CH}_3\text{CN})](\text{PF}_6)\), where N,N is a bipyridine derived chelating ligand, is the catalyst precursor led to the discovery of a series of compounds with an unexpected ‘tucked-in’ structure.

\[
\begin{array}{c}
\text{Ru} \\
\text{PF}_6 \\
\text{N} \quad \text{N} \\
\end{array}
\]

The formation of these complexes, by addition of an allyl carbonate substrate to \([\text{Ru}(\text{Cp}^*)(\text{N,N})(\text{CH}_3\text{CN})](\text{PF}_6)\), is thought to be the first example of an intramolecular allylation of a Ru(Cp*) methyl group.

To determine whether this chemistry could be extended to complexes containing phosphorus rather than nitrogen in the coordination sphere of ruthenium, a number of Ru(II) Cp* species with phosphine ligands were prepared. It was found that reaction of \([\text{Ru}(\text{Cp}^*)(\text{CH}_3\text{CN})_3](\text{PF}_6)\) with \(\text{P(o-tolyl)}_3\) resulted in the formation of an unexpected sandwich complex where the phosphine ligand is coordinated to the ruthenium through its arene electrons rather than through the lone pair of electrons on the P atom.

\[
\begin{array}{c}
\text{Ru} \\
\text{PF}_6 \\
\text{P} \\
\end{array}
\]

Since Ru(II) Cp complexes containing phosphine ligands have been shown to be good catalysts for the isomerisation of allyl alcohols to their corresponding carbonyl compounds, the sandwich complex \([\text{Ru}(\text{Cp}^*)(\eta^3\text{-o-tolyl})\text{P(o-tolyl)}_2](\text{PF}_6)\) and a number of other Cp* complexes of both Ru(II) and Ru(IV) were tested as catalysts for the isomerisation of 3-butene-2-ol to the industrially important methyl ethyl ketone. The best results were achieved when the catalyst precursor complex was the Ru(IV) species \([\text{RuCp}^*(\eta^3\text{-CH}_2\text{CHCH}_2)\)
(CH$_3$CN)$_2$](PF$_6$)$_2$. This complex was subsequently investigated as a catalyst for the isomerisation of a number of other allyl alcohols.

[RuCp*($\eta^3$-CH$_2$CHCH$_2$)(CH$_3$CN)$_2$](PF$_6$)$_2$ has also been shown to catalyse allylic phenolation reactions, albeit very slowly. The rate of allylation reactions was improved markedly on moving from phenols to thiophenols as the nucleophile. The allylic phenylsulfenylation reactions were found to be faster in the presence of excess $p$-toluene sulfonic acid. To explore this observation, the sandwich complex [RuCp*($\eta^6$-$p$-Me-C$_6$H$_4$SO$_3$H)](PF$_6$), where $p$-toluene sulfonic acid coordinates to a Ru(II) Cp* fragment through its arene electrons, was synthesised and itself used as the catalytic precursor complex in an allylic phenylsulfenylation reaction.
Zusammenfassung


Bei der Erforschung der langsamen Kinetik in Allylierungsreaktionen unter Verwendung von \([\text{Ru(Cp}^*(N,N)(\text{CH}_3\text{CN})](\text{PF}_6)](\text{PF}_6)\) als Katalysatorvorläufer, wobei N,N für \(N,N'-\text{Bipyridin}-\text{Derivate}\) steht, wurde eine Reihe neuartiger Ruthenium(II)-Komplexe isoliert und NMR-spektroskopisch charakterisiert. Die Bildung der Komplexe kann durch eine intramolekulare Allylierung einer Methylgruppe im Cp*-Ring, bei der Reaktion eines Allyl-Carbonats mit dem Katalysatorvorläufer \([\text{Ru(Cp}^*(N,N)(\text{CH}_3\text{CN})](\text{PF}_6)](\text{PF}_6)\), verstanden werden.

\[
\text{[Ru(Cp}^*(\text{CH}_3\text{CN})_3](\text{PF}_6) \text{ reagiert mit P(\text{o-tolyl})_3 unter Verdrängung der substitutionslabilen Acetonitril-Liganden zu einem unerwarteten Sandwich-Komplex [Ru(Cp}^*{\eta^6-\text{o-tolyl})P(\text{o-tolyl})_2](\text{PF}_6). Dabei koordiniert der Phosphanligand über das \pi-\text{System einer Aryleinheit und fungiert somit als 6-Elektronen-Donor.}
\]

Ru(II)Cp Komplexe mit Phosphanliganden sind bekannt, die Isomerisierung einer Vielzahl von Allylalkoholen zu den entsprechenden gesättigten Carbonylderivaten effizient zu katalysieren. Infolgedessen wurden der Komplex \([\text{Ru(Cp}^*{\eta^6-\text{o-tolyl})P(\text{o-tolyl})_2}(\text{PF}_6)]\) und eine Reihe weiterer RuCp*-Komplexe als Katalysatorvorläufer für die Isomerisierung von 3-Buten-2-ol zu Methyllethylketon (MEK) untersucht, wobei das beste Ergebnis mit dem Ru(IV)
Komplex [RuCp*($\eta^3$-CH$_2$CHCH$_2$)(CH$_3$CN)$_2$](PF$_6$)$_2$ erzielt wurde. Folglich wurde die Aktivität dieses Komplexes auch auf andere Allylalkohole überprüft.

Des Weiteren fungiert [RuCp*($\eta^3$-CH$_2$CHCH$_2$)(CH$_3$CN)$_2$](PF$_6$)$_2$ als Katalysator für die allylische Phenolierung, obwohl diese Reaktionen nur sehr langsam ablaufen. Die Reaktionsgeschwindigkeit wurde erhöht, indem anstatt Phenole Thiophenole als Nucleophile eingesetzt wurden. Die allylischen Phenylsulfenylierungen verlaufen deutlich schneller in Gegenwart eines Überschusses an $p$-Toluolsulfonsäure. Um diesen Effekt weiter aufzuklären, wurde der Sandwich-Komplex [RuCp*($\eta^6$-p-Me-C$_6$H$_4$SO$_3$H)](PF$_6$) dargestellt, in dem $p$-Toluolsulfonsäure über das $\pi$-System an das Ru(II)Cp* Fragment koordiniert, und als Katalysatorvorläufer für die allylische Phenylsulfenylierung verwendet.
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1 Introduction
1.1 Introduction

Chapters 2 and 3 of this thesis are concerned with the synthesis and characterization of some Ru(II) complexes with unexpected coordination chemistry. In Chapters 4 and 5 two types of ruthenium catalysed reaction, isomerisation of allyl alcohols and allylic phenylsulphenylations, are investigated. In this brief introduction the general coordination chemistry of ruthenium is reviewed and some examples of reactions catalysed by ruthenium complexes are given.

1.2 Selected Coordination Chemistry of Ruthenium

Ruthenium complexes are known with oxidation states ranging from -2, e.g. [Ru(CO)\textsubscript{4}]\textsuperscript{2-}, to +8, e.g. RuO\textsubscript{4}. The low oxidation states are stabilized by π–acceptors such as NO\textsuperscript{+}, PR\textsubscript{3} and CO, the high oxidation states by π–donors such as F\textsuperscript{-}, O\textsuperscript{2-} and N\textsubscript{3-}.

The ruthenium complexes involved in the research presented in this thesis have oxidation states of +2 to +4. In these oxidation states octahedral coordination is favoured. When polyhapto Cp or Cp\textsuperscript{*} ligands are coordinated to ruthenium a piano stool structure is usually adopted.

1.2.1 Halide Ligands

The octahedral ruthenium(IV) anions [RuX\textsubscript{6}]\textsuperscript{2-} (X = F, Cl, Br) are readily reduced to ruthenium (III) species.\textsuperscript{1} All trihalides of Ru(III) are known but only Ru(III)Cl\textsubscript{3} had been well characterized.\textsuperscript{1} Ruthenium trichloride is bought commercially as RuCl\textsubscript{3}.3H\textsubscript{2}O and in aqueous solution the octahedral Ru(III)(H\textsubscript{2}O)\textsubscript{6} species is present along with chloride coordinated species. In Chapters 2-4 of this thesis RuCl\textsubscript{3} hydrate was the starting point for the synthesis of a number of (Cp\textsuperscript{*}) ruthenium complexes via the polymer [Ru\textsuperscript{II}(Cp\textsuperscript{*})Cl\textsubscript{2}]\textsubscript{n}.\textsuperscript{2} I, or the tetramer [Ru\textsuperscript{III}(Cp\textsuperscript{*})(\mu\textsuperscript{3}-Cl)]\textsubscript{4}.\textsuperscript{3} 2.

Triphenylphosphine undergoes direct redox reaction with RuCl\textsubscript{3} hydrate to yield [Ru\textsuperscript{II}Cl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3}] and [Ru\textsuperscript{III}Cl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3}].\textsuperscript{4} The former complex has an octahedral structure, the latter a square pyramidal structure with the vacant octahedral site being effectively blocked by a phenyl ring. The analogous bromide complexes have also been prepared by first shaking a methanolic RuCl\textsubscript{3} hydrate solution with a large excess of LiBr for 24 hrs before addition of the phosphine ligand.
1.2.2 Nitrogen Ligands

1.2.2.1 Monodentate

The combination of ruthenium(II) with acetonitrile ligands is a useful one. In the experiments described in this thesis, the lability of CH$_3$CN was an important factor in selecting suitable starting materials. For example, the readily available salts [Ru$^{II}$((Cp or Cp*) (CH$_3$CN)$_3$)(PF$_6$)$_5$] are used in the synthesis of a number of half sandwich complexes and these salts often find application as catalytic precursors in a number of ruthenium catalysed reactions.$^6$-$^9$

Acetonitrile containing Ru(IV) species may be intermediates in such reactions and can themselves be used as catalytic precursors.$^{10}$-$^{17}$

Reaction of [Ru$^{II}$((Cp*)(CH$_3$CN)$_3$)(OTf)] with pyridine produces either the mono- or trisubstituted product depending on the concentration of the ligand. When [Ru$^{II}$((Cp*)(η$^1$-pyridine)(CH$_3$CN)$_2$)(OTf)], 3, is heated to 80 °C under vacuum the complex [Ru$^{II}$((Cp*)(η$^6$-pyridine))(OTf)], 4, is formed where the pyridine ligand is no longer coordinated through the nitrogen atom but through the π-electrons (Equation 1).$^{18}$

$$\text{Equation 1}$$
1.2.2.2 Bidentate

A number of Ru(IV) complexes are known which contain deprotonated ethylenediamine ligands.\textsuperscript{19} For example, $[\text{Ru}^{\text{IV}}(\text{tmen-H})_2(\text{tmen})]^{2+}$, 5, is an octahedral complex with the two relatively short Ru-N amide bonds cis to one another.\textsuperscript{20}

The Ru(III) species, 6,\textsuperscript{21} which contains one bidentate bisoxazoline ligand, is a useful precursor to a range of mixed ligand ruthenium(III) complexes.

[\text{Ru(bipy)}]^{3+}$ is a powerful oxidising agent.\textsuperscript{22} Its redox partner, [Ru(bipy)]$^{2+}$, although thermally stable, can be photochemically oxidised.

In Ru(II) chemistry the most important class of bidentate nitrogen ligands are bipyridines and bipyridine derivatives. As well as the trisbipyridine complex mentioned above, a number of mixed ligand species exist. Complexes of the type $[\text{Ru}(\text{Cp}^*)(\text{N,N})(\text{CH}_3\text{CN})](\text{PF}_6)$,\textsuperscript{23-30} where N,N is a bipyridine derivative, are the starting point for the generation of the new tucked-in complexes presented in Chapter 2.

Ru(II)Cp* species with other bidentate nitrogen ligands such as α-diimines\textsuperscript{31} and bisoxazolines\textsuperscript{32} have been prepared. A remarkably stable unsaturated Ru(II) complex, 7, has been characterized which contains one Cp* ligand and one bidentate TMEDA ligand.\textsuperscript{33} This 16e' complex has $C_2$ symmetry and the angle between the planes of the Cp* ring and the N-Ru-N bonds is 89.3°.
An important class of Ru(II) complexes with chelating nitrogen ligands are the chiral arene-N-tosylethylenediamine complexes for asymmetric hydrogenation developed by Noyori and coworkers. For example, the chiral $\eta^6$-arene Ts-dpen ruthenium complex, 8, is an enantioselective catalyst for the hydrogenation of acetophenone.$^{34}$

1.2.3 Phospine Ligands

In complexes of ruthenium with coordinating phosphorus ligands, it is much more likely that the ruthenium centre will be in the +2 oxidation state than in the +3 or +4 oxidation states.$^{22}$ In Ru(IV) chemistry, phosphines are found as coligands in oxo complexes.$^{19}$ There are few complexes of Ru(III) with phosphine ligands.$^{22}$ One that has been characterised is [PMePh$_3$] [trans-RuCl$_4$(PPh$_3$)$_2$].$^{35}$ Ru(II) complexes with phosphorus ligands have been well established and some examples of species with both mono- and bidentate phosphorus ligands are given below.

1.2.3.1 Monodentate

$\text{Cis-[Ru(PMe}_3\text{)}\text{H}_2$, 9, has a distorted octahedral geometry with the $\text{cis}-\text{P-Ru-P}$ angles considerably larger than $90^\circ$.$^{36}$ The $\text{trans}-\text{P-Ru-P}$ angle is much smaller than $180^\circ$ with these axial phosphines bent in towards the hydride ligands. This deviation from octahedral
geometry is due to steric repulsions between the methyl substituents on the phosphorus atoms \textit{cis} to each other.

As well as the triphenylphosphine containing chloride complexes mentioned in section 1.1.1, PPh\textsubscript{3} and related ligands are also found in a number of Ru(II)Cp complexes such as [RuCp(PPh\textsubscript{3})(CH\textsubscript{3}CN)\textsubscript{2}](PF\textsubscript{6}), 10.\textsuperscript{37}

Chapter 3 looks at some interesting coordination chemistry when P(o-tolyl)\textsubscript{3} ligands are combined with Cp* containing complexes of Ru(II) and Ru(IV).

\textbf{1.2.3.2 Bidentate}

Common bidentate phosphorus ligands found in complexes of Ru(II) are 1,2-bis(diphenylphosphino)methane,-ethane,-propane and –butane (dpdm, dppe, dppp and dppb respectively). Crystal structures of \textit{trans}-[RuCl(CO)(dppe)\textsubscript{2}]\textsuperscript{+} and \textit{trans}-[RuCl(CO)(dppm)\textsubscript{2}]\textsuperscript{+} have been obtained.\textsuperscript{38}

The catalytic activity of complexes [RuClCp(L\textsubscript{2})] in isomerisation reactions has been shown to increase in the order L\textsubscript{2} = dpdm<dppe<dppp<dppb.\textsuperscript{39}

Of particular interest are chiral bidentate phosphorus ligands due to their potential use in enantioselective catalysis. Diop, 11, binap, 12, and chiraphos, 13, to name just a few, have all been combined with Ru(II) chloride species for use in catalytic systems.\textsuperscript{40,41}
1.2.4 $\eta^6$-Arene Ligands

The synthesis of the presumably polymeric complex $\text{RuCl}_2(\eta^6$-$\text{C}_6\text{H}_6$)$^{42}$ was reported in 1962. At this time little research had been carried out on the reactions of arene rings coordinated to metals in oxidation states higher than +1.$^{43}$ It was found that reaction of this complex with KCN led to formation of a species with an $\eta^5$-coordinated benzene ring and the CN substituted at the sixth, non-coordinated carbon.$^{44}$ $\text{RuCl}_2(\eta^6$-$\text{C}_6\text{H}_6$) was also shown to undergo reaction with several phosphine ligands to make new species of the type $\text{RuCl}_2\text{PR}_3(\eta^6$-$\text{C}_6\text{H}_6$)$^{45}$ [Ru$^{II}$(Cp or Cp*)($\eta^6$-arene)]$^+$ complexes are of particular interest because they can act as catalytic precursors in ruthenium catalysed organic transformations where new C-C bonds are formed,$^{46}$ for example in allylic alkylation reactions.

In Chapter 5, RuCp*($\eta^6$-arene) complexes are reported where a benzenesulfonic acid derivative coordinates to the ruthenium in an $\eta^6$ manner. The complex [RuCp*($\eta^6$-$p\text{Me-C}_6\text{H}_4\text{SO}_3\text{H}$)](PF$_6$) is shown to be a suitable catalyst for the alkylation of indole and of thiophenol.

1.3 Selected Ruthenium Catalysed Reactions

1.3.1 Allylation Reactions

Cp or Cp* complexes of Ru(II) catalyse a number of allylation reactions.$^{47-49}$
These transformations are thought to proceed via a Ru(IV)(η³-allyl) intermediate. Such intermediates can be formed by oxidative addition of the allyl substrate to ruthenium(II). Subsequent attack by a nucleophile on the allyl ligand forms the alkene coordinated product which can then dissociate from the metal centre (Scheme 1).

Allylation reactions mediated by ruthenium catalysts are of interest because the branched product is regioselectively formed. This has been shown to be due to electronic effects. The more substituted terminal allyl carbon has more positive charge and a more suitable LUMO than the less substituted terminal carbon and it is therefore the preferred site of nucleophilic attack.

A range of C, O and N nucleophiles can be used in allylation reactions providing a convenient route to products with new C-C, C-O and C-N bonds. For example, the reaction of PhCH(OOC₂tBu)CH=CH₂ with phenol in the presence of [RuCp*(η⁻⁻⁻¹-CH₂CHCHPh)(DMF)₂]₂(PF₆)₂, produces the product of a Friedel-Crafts reaction with the new C-C bond being formed predominantly to the para phenol carbon. However, the same reaction in the presence of [RuCp*(OC(OtBu)O)(η²⁻⁻⁻⁻⁻¹-CH₂CHCHPh)](PF₆)₂, leads to new
C-O bonds being formed between the phenol oxygen and predominantly the more substituted allyl carbon. The latter catalyst also facilitates the reaction of PhCH(OOC<sub>2</sub>FBu)CH=CH<sub>2</sub> with various amines to form new C-N bonds. When triethylamine is the nucleophile only the linear product is observed. These transformations are summarised in Scheme 2.

The fact that a slight modification of the Ru(IV) catalyst can completely redirect the nature of organic products formed illustrates the flexibility of ruthenium complexes in allylation reactions.

In Chapter 5 some ruthenium catalysed allylations of phenols and thiophenols are presented.

### 1.3.2 Isomerisation

Ruthenium catalysts play a central role in the isomerisation of allylic alcohols into their corresponding aldehydes and ketones. For example, RuCl<sub>3</sub>.3H<sub>2</sub>O catalyses the
transformation of $\text{CH}_2=\text{C(CH}_3\text{)}\text{CH}_2\text{OH}$ into $\text{CH}(\text{CH}_3)_2\text{CH}=\text{O}$.\textsuperscript{71, 72} Three mechanisms proposed for such transformations are detailed in the introduction to Chapter 4. Ruthenium catalysed isomerisation reactions are not limited to allyl alcohols. Propargylic alcohols can also be isomerised to the corresponding $\alpha,\beta$-unsaturated carbonyl compounds. Scheme 3 shows the proposed mechanism of such a transformation with a ruthenium indenyl catalyst.\textsuperscript{73} After coordination of the substrate to the ruthenium centre, an apparent intramolecular 1,2-hydride migration takes place to form the vinyl ruthenium species. This reaction is highly chemoselective and tolerates the presence of carbonyl, hydroxy, alkyne and alkene groups.

![Scheme 3](image)

**1.3.3 Metathesis**

In organic syntheses, olefin metathesis with alkylidene complexes provides a widely used method of creating new C-C bonds.\textsuperscript{74, 75} In recent years, Grubbs and co-workers have developed a variety of ruthenium alkylidene complexes containing phosphine and N-heterocyclic carbene ligands which function as catalysts in metathesis reactions.\textsuperscript{76} Complex 16\textsuperscript{77, 78} is a popular ring closing and cross metathesis catalyst. Although it tolerates a number
of different functional groups, its application is limited to electron rich alkene substrates. Complex 17\textsuperscript{70,81} however, can catalyse metathesis of alkenes with electron withdrawing groups such as fluorinated alkenes and α,β-unsaturated carbonyl substrates. It has the same functional group tolerance as 16 but works at reduced catalyst loadings and reaction times are faster.\textsuperscript{82}

The Chauvin mechanism for olefin metathesis is shown in Scheme 4.\textsuperscript{83} The ruthenium carbene species forms a metallocyclobutane complex with the alkene substrate. This intermediate then collapses so to form a new ruthenium carbene species and an alkene which retains one of its original substituents and takes a CHR group from the starting ruthenium complex.

Scheme 4
1.3.4 Hydrogenation

Hydrogenation of functionalised alkenes, aldehydes, ketones and nitro compounds can be catalysed by a number of ruthenium complexes. However, in the case of functionalised alkenes, ruthenium complexes generally make less active hydrogenation catalysts than rhodium, iridium and cobalt complexes.\(^84,\,85\) This milder reactivity of ruthenium complexes can be used to advantage in chemoselective hydrogenation of polyalkenes. For example, RuHCl(PPh\(_3\))\(_3\) selectively reduces the least substituted alkene in terminal conjugated dienes (Equation 2).\(^86\)

\[
\text{RuHCl(PPh}_3\text{)}_3 \xrightarrow{\text{H}_2 \text{ (1 atm)}} \text{benzene-ethanol} \quad \text{RuHCl(PPh}_3\text{)}_3 \xrightarrow{\text{H}_2 \text{ (1 atm)}} \text{benzene-ethanol}
\]

Equation 2

The mechanism for the hydrogenation of alkenes with RuHCl(PPh\(_3\))\(_3\) is shown in Scheme 5. The first step is dissociation of a phosphine ligand to make room for alkene coordination. The next step is reversible hydride migration. Hydrogen addition occurs followed by reductive elimination of the alkane.

Scheme 5
Low valent ruthenium complexes are good catalysts for the reduction of carbonyl compounds and nitro compounds. Two examples of such chemoselective reductions effected with \( \text{RuCl}_2(\text{PPh}_3)_3 \) are shown in Scheme 6.

\[
\begin{align*}
\text{O} & \quad \text{RuCl}_2(\text{PPh}_3)_3 \\
\text{H}_2 \text{ (12 atm)} & \quad 180 \degree \text{C} \\
\text{CO}_2 \text{H} & \quad \text{O} \\
\end{align*}
\]

Scheme 6

Ruthenium catalysts can also be employed in enantioselective hydrogenations. One example of an enantioselective hydrogenation catalyst is complex 8, whose structure is given in section 1.2.2.2. This species is a transfer hydrogenation catalyst which utilises isopropanol to hydrogenise ketones (Scheme 7).

Ruthenium binap catalysts can also be used to reduce a wide range of functionalised ketones with high enantioselectivities. An example is shown in Scheme 8.
Scheme 7

Scheme 8

\[
\text{Acetaldehyde} \xrightarrow{\text{RuCl}_2[(R)\text{-binap}]} \text{OH} \quad (92\% \text{ ee})
\]
More recently, a ruthenium binap hydrido amindo complex, 18, was developed by Morris and coworkers, which is an active catalyst for the hydrogenation of acetophenone.\textsuperscript{90}

![Species 18](image)

Species 18 behaves like the Noyori Ru(II) complexes with diamine ligands. One unique feature, however, is that the rate of reactions catalysed by 18 have a dependence on product concentration. The reaction rate increases as product builds up.

### 1.4 Concluding Remarks

The examples shown here give only a brief overview of the role ruthenium complexes play as catalysts in organic transformations. Later in this thesis, the use of ruthenium to catalyse the isomerisation of allylic alcohols and the formation of new C-O and C-S bonds will be investigated in more detail.

The coordination chemistry of ruthenium with a variety of different ligands has been described. In the next chapter the synthesis of some new complexes of ruthenium (II) are reported which, due to their large, strongly bonded bidentate nitrogen ligands, adopt an unexpected tucked-in structure.
1.5 References

47. Morisaki, Y.; Kondo, T.; Mitsudo, T, Organometallics, 1999, 18, 4742-4746
Intramolecular Allylation of a Ru(Cp*) Methyl Group
2.1 Introduction

As indicated in Chapter 1, an increasingly large number of ruthenium complexes are finding applications in homogeneous catalysis.\(^1\)\(^-\)\(^3\) Amongst the most popular Ru-derivatives are those containing Cp or Cp* ligands.\(^4\) Although complexes of Ru(II) are still the most prevalent, there is an increasing interest in the use of Ru(IV) salts as starting materials for selected catalytic transformations.\(^5\)

A number of Ru(Cp*) allylation catalysts are known, for example 1-5, which are regioselective and afford high branched to linear ratios in the products.\(^4\)\(^-\)\(^6\) In some cases, e.g., using 4 and 5, the catalysis has been found to be relatively slow.\(^4\) There is no immediately obvious reason for this, since oxidative addition of the branched compound PhCH(X)CH=CH\(_2\), where X is a suitable halogen or carbonate leaving group, to Trost’s catalyst,\(^7\) [Ru(CH\(_3\)CN)\(_3\)(Cp*)]PF\(_6\), 1, is complete within several minutes at room temperature and affords high yields of isolable Ru(IV) allyl complexes.\(^8\)

![Chemical structures](image-url)

The chelating nitrogen salts [Ru(Cp*)(N,N)(CH\(_3\)CN)]PF\(_6\), \(^6\)\(^,\)\(^9\) where N,N is a bipyridyl derivative, are relatively slow catalysts for regioselective allylic substitution reactions taking 16 hours at room temperature to catalyse the reaction of a cinnamyl carbonate, PhCH=CHCH\(_2\)OCO\(_2\)Et with various C-, O- and N-nucleophiles.\(^9\)

In order to investigate these slow reaction kinetics, the relative rates of oxidative addition of allyl substrates to complexes 6a-c were followed by \(^1\)H NMR and are reported in this chapter.
The unexpected formation of a new series of complexes, thought to result from intramolecular allylation of a Cp* methyl group is also described.

\[
\begin{align*}
\text{N} & \text{Ru} \quad \text{N} \quad \text{NCCH}_3 \\
\text{PF}_6 & \\
\text{N} = & \begin{array}{c}
\text{N} \\
\text{a}
\end{array} \\
\text{N} & \begin{array}{c}
\text{b}
\end{array} \\
\text{N} & \begin{array}{c}
\text{c}
\end{array}
\end{align*}
\]
2.2 Results and Discussion

2.2.1 Addition of PhCH=CHCH$_2$Cl (Cinnamyl Chloride) to [RuCp*(N,N)(CH$_3$CN)](PF$_6$) Complexes

The complexes [RuCp*(N,N)(CH$_3$CN)](PF$_6$), where N,N = 2,2’-bipyridine, 6a, 4,4’-dimethyl-2,2’-bipyridine, 6b, 1,10-phenanthroline, 6c, and 2,2’-biquinoline, 6d, were prepared according to the literature procedure.$^9$ Oxidative addition of cinnamyl chloride, PhCH=CH-CH$_2$Cl, to these complexes leads to the formation of the known dicationic species [RuCp*(N,N)(η$_3$-CH$_2$CHCHPh)]$^{2+}$, 7, where the bipyridine derived chelating ligand is strongly coordinated to the ruthenium centre and only the labile CH$_3$CN ligand is lost (Equation 1).

$$
\text{[RuCp*(N,N)(CH$_3$CN)](PF$_6$)} + \text{PhCH=CHCH}_2\text{Cl} \rightarrow \text{[RuCp*(N,N)(η$_3$-CH$_2$CHCHPh)](PF$_6$) Cl}$

Equation 1

The relative kinetics of these reactions at room temperature were followed by $^1$H NMR (Table 1) and were found to be significantly slower than the analogous oxidative addition to [RuCp*(CH$_3$CN)$_3$(PF$_6$)] where greater than 80 % conversion to [RuCp*Cl(η$_3$-CH$_2$CHCHPh)](CH$_3$CN)](PF$_6$) occurs in less than three minutes.$^8$

Table 1: Conditions: 0.015 mmol Ru complex, 0.015 mmol cinnamyl chloride, 0.5 ml CD$_3$CN, room temperature.

<table>
<thead>
<tr>
<th>Complex</th>
<th>4 mins</th>
<th>Conversion (%)</th>
<th>10 mins</th>
<th>20 mins</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>32</td>
<td>45</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>6b</td>
<td>66</td>
<td>79</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>6c</td>
<td>49</td>
<td>63</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>6d</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

The nature of the bipyridine derived ligand has an influence on the rate of oxidative addition. Conversion was fastest with 4,4’-dimethyl-2,2’-bipyridine as the bidentate nitrogen ligand.
This is thought to be due to electronic effects. No oxidative addition was observed on addition of cinnamyl chloride to \([\text{RuCp}^*(\eta^2\text{-}2,2'-\text{biquinoline})(\text{CH}_3\text{CN})](\text{PF}_6)\), presumably due to steric hindrance from the bulky chelating ligand. For complexes 6a-c, maximum conversion was achieved after 20 minutes and in no case did full conversion to products occur, perhaps because the Cl' set free reacts to afford a less active chloro-complex.

2.2.2 Addition of Phenyl Allyl Carbonates to [RuCp*(N,N)(CH₃CN)](PF₆) Complexes

To avoid the strongly coordinating Cl' ligand, the rates of reaction of complexes 6a-d with allyl carbonates were investigated. However, the addition of allyl carbonates to [RuCp*(N,N)(CH₃CN)](PF₆) complexes did not produce the expected \(\eta^3\)-allyl products of oxidative addition. Instead, the allyl substrate formed a new bond to the coordinated Cp* resulting in a new ligand of type 8.

The resulting novel complexes, 9, can be rationalised as arising from oxidative addition of the allyl carbonate followed by deprotonation of one Cp* methyl group by the carbonate or corresponding alkoxide anion and then rapid attack of the CH₂⁻ on the substituted terminal allyl carbon (Scheme 1).
Although Castro et al.\textsuperscript{10} have reported a related structure using a dinuclear tetramethylfulvene as starting material (Equation 2), this is believed to be the first reported intramolecular allylation reaction of a Cp* methyl group. The observation of the branched product is consistent with calculations\textsuperscript{8a} which suggest an orbital controlled product.

The relative kinetics of addition of both branched and linear phenyl allyl carbonate substrates to 6a and 6b were followed by $^1$H NMR (Table 2).
Table 2: Conditions: 0.015 mmol Ru complex, 0.015 mmol allyl carbonate, 0.5 ml CD$_3$CN, room temperature.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Carbonate</th>
<th>10% Conversion</th>
<th>20% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>OCO$_2$Bu</td>
<td>1 hr 50 mins</td>
<td>4 hrs</td>
</tr>
<tr>
<td>6a</td>
<td>OCO$_2$Bu</td>
<td>3 hrs</td>
<td>6 hrs</td>
</tr>
<tr>
<td>6b</td>
<td>OCO$_2$Bu</td>
<td>20 mins</td>
<td>50 mins</td>
</tr>
<tr>
<td>6b</td>
<td>OCO$_2$Bu</td>
<td>1 hr</td>
<td>1 hr 40 mins</td>
</tr>
</tbody>
</table>

As seen previously when cinnamyl chloride was reacted with 6a and 6b, reaction is faster when the bipyridine ligand contains para methyl groups. No reaction occurred on addition of the allyl carbonate substrates to 6d. Formation of the products [Ru(1-(CH$_2$CHPhCH=CH$_2$)-2,3,4,5-tetramethylcyclopentadiene)(2,2’-bipyridine)](PF$_6$), 9a, and [Ru(1-(CH$_2$CHPhCH=CH$_2$)-2,3,4,5-tetramethylcyclopentadiene)(4,4’-dimethyl-2,2’-bipyridine)](PF$_6$), 9b, was significantly faster with the branched substrate as the starting material. It was observed that the branched carbonate isomerises to the linear carbonate in ca 30 minutes (Equation 3). The linear carbonate also undergoes some isomerisation to the branched isomer but this process was found to be much slower.

![Equation 3](image)

The complexes 9a, 9b and [Ru(1-(CH$_2$CHPhCH=CH$_2$)-2,3,4,5-tetramethylcyclopentadiene)(1,10-phenanthroline)](PF$_6$), 9c, were prepared in high yield from the reaction of PhCH=CH-CH$_2$OOC$_2$Et with the corresponding [RuCp*(N,N)(CH$_3$CN)](PF$_6$) complexes. The relatively slow reaction kinetics could be accelerated by addition of 2 equivalents of carbonate and by increasing the reaction temperature to 60 °C.
Related tucked-in complexes could also be synthesised from carbonates with substituted aryl groups, e.g. 4-MeO-C₆H₄-CH(OCO₂tBu)-CH=CH₂, 10, and C₁₀H₇-CH(OCO₂tBu)-CH=CH₂, 11.

Whereas the reaction of [RuCp*(4,4’-dimethyl-2,2’-bipyridine)(CH₃CN)](PF₆) with 10 led to the expected tucked-in complex [Ru{1-(CH₂-CH(C₆H₄OMe)-CH=CH₂)-2,3,4,5-tetramethylcyclopentadiene}(4,4’-dimethyl-2,2’-dipyridyl)](PF₆), 12, reaction with substrate 11 led to an almost 1:1 mixture of [Ru{1-(CH₂-CH(naphthalene)-CH=CH₂)-2,3,4,5-tetramethylcyclopentadiene}(4,4’-dimethyl-2,2’-dipyridyl)](PF₆), 13, and another species thought to be its isomer, [Ru{1-(CH₂-CH₂-CH=CH(naphthalene))-2,3,4,5-tetramethylcyclopentadiene}(4,4’-dimethyl-2,2’-dipyridyl)](PF₆), 14.

The presence of an aryl moiety in the starting carbonate was shown not to be a prerequisite for the formation of tucked-in complexes. The products [Ru{1-(CH₂-CH₂-CH=CH₂)-2,3,4,5-tetramethylcyclopentadiene}(2,2’-dipyridyl)](PF₆), 15a, and [Ru{1-(CH₂-CH₂-CH=CH₂)-2,3,4,5-tetramethylcyclopentadiene}(4,4’-dimethyl-2,2’-dipyridyl)](PF₆), 15b, were formed readily from CH₂=CH-CH₂OCO₂tBu and the corresponding [RuCp*(N,N)(CH₃CN)](PF₆) complexes.
### 2.2.3 NMR Data Supporting the Proposed Structures of the Tucked-in Complexes

The tucked-in complexes described above were characterised by $^1$H, $^{13}$C, COSY, HMQC, HMBC and NOESY NMR experiments. The carbon and proton assignments are listed in the appendix.

Based on the absence of the relatively complicated (but typical) multiplet for the central allyl $^1$H resonance which often appears between 5 and 7 ppm,

$^{5,8,11}$ it was clear that complexes 9 and 12-15 were not routine Ru(IV) allyl salts.
Both the $^1$H and $^{13}$C spectra for 9, 12 and 15 revealed four non-equivalent Cp methyl groups, instead of the usual sharp singlet for the equivalent five methyl groups of the complexed Cp* ligand (Fig. 1). For the mixture of isomers 13 and 14, eight Cp methyl signals can be seen (Fig. 2).

![Figure 1: Section of the $^{13}$C NMR spectrum of 12 showing the four non-equivalent remaining methyl groups of the Cp moiety (500 MHz, CD$_3$CN).](image1)

![Figure 2: Section of the $^{13}$C NMR spectrum of the almost 1:1 mixture of complexes 13 and 14 showing two sets of four non-equivalent Cp methyl groups (500 MHz, CD$_3$CN).](image2)

The four carbons of the tucked-in segment could be identified by a series of two-dimensional proton and carbon correlation spectra which indicated the presence of two CH and two CH$_2$ groups, all at relatively low frequencies. The complexed olefin $^{13}$C data for the tucked-in complexes are fairly typical and reveal the CH$_2$ and CH-olefinic carbons at 52.0 ppm and 87.0 ppm, respectively (Fig. 3).
The relative position of the coordinated double bond was determined via 2-D NOESY spectroscopy (Fig. 4).

Selective cross-peaks from a) one of the two non-equivalent *ortho* pyridine protons to the two CH$_2$ protons at the unsubstituted end of the complexed double bond and b) from the second *ortho* pyridine proton to the aliphatic and olefinic CH protons, can be seen. Further, each of the two *ortho* pyridine protons shows selective cross-peaks to the two proximate methyl groups of the tetramethyl Cp ligand. This indicates that the olefin is ca parallel to the Cp* moiety which is in agreement with literature solid-state results for Ru(Cp-type) olefin complexes.
complexes.\textsuperscript{10,12,13}

Summarizing, the complexes 6a-c only transiently oxidatively add the allyl starting material as rapidly as e.g., [RuCp*(CH$_3$CN)$_3$](PF$_6$). In the absence of added nucleophile, the carbonate (or alkoxide) base, formed via the oxidative addition reaction generates a carbon anion which attacks the Ru(IV) allyl to form the new olefin complexes. While tucked-in Cp$^*$ complexes, for example of Zr\textsuperscript{14}, Ta\textsuperscript{15} and Sc\textsuperscript{16}, as well as a number of tethered Cp derivatives,\textsuperscript{17-23} are well known in the literature, this Ru-mediated intramolecular allylation is unprecedented.
2.3 Experimental

All reactions and manipulations were performed under an N\textsubscript{2} atmosphere using standard Schlenk techniques. The solvents and reagents were dried and distilled using standard procedures and stored under nitrogen. NMR spectra were normally recorded with Bruker DPX-400 and 500 MHz spectrometers. Chemical shifts are given in ppm; coupling constants (\textit{J}) in Hertz. Elemental analysis and mass spectroscopic studies were performed at ETHZ.

[Ru(8a)(2,2’-bipyridine)]PF\textsubscript{6}, \textit{9a}. A solution of PhCH=CH-CH\textsubscript{2}OCO\textsubscript{2}Et (34.3 mg, 0.166 mmol) in 2 mL acetonitrile was added to a brown solution of 6a (48.1 mg, 0.083 mmol) in 2 mL acetonitrile. The reaction mixture was stirred for 16 h at 60 °C then the solvent was reduced under vacuum and ether was added to precipitate a brown solid. The solid was collected, washed three times with ether then dried under vacuum. Yield: 49.9 mg (92%).

Elemental Analysis (%) calculated for C\textsubscript{29}H\textsubscript{31}N\textsubscript{2}F\textsubscript{6}PRu: C 53.29, H 4.78, N 4.29; found: C 53.44, H 4.88, N 4.95. Mass Spectrometry: \textit{m/z} 509 [\textit{M}^+]. \textit{1}H NMR (500 MHz, CD\textsubscript{3}CN) δ: 1.36 (s); 1.38 (s); 1.95 (s); 2.22 (s) (4 Cp* Me), 2.24; 2.40 (dd, \textit{J} = 14.1 Hz, 7.7 Hz) (CH\textsubscript{2}), 2.24; 3.56 (d, \textit{J} = 3.56 Hz) (=CH\textsubscript{2}), 3.86 (m) (CH=CH\textsubscript{2}), 4.49 (m) (CHPh), 7.26 (Ph \textit{para}), 7.36 (Ph \textit{meta}), 7.52 (Ph \textit{ortho}), 7.62; 7.69; 8.01; 8.09; 8.32; 8.35; 9.08; 9.32 (8 bipy protons). 

\textit{13}C\{\textit{1}H\}NMR (125 MHz, CD\textsubscript{3}CN) δ: 7.2; 7.8; 8.3; 8.7 (4 Cp* Me), 27.3 (CH\textsubscript{2}), 52.0 (=CH\textsubscript{2}), 55.8 (CHPh), 81.7 (CCH\textsubscript{2}), 84.4 (CCH\textsubscript{3}), 87.0 (CH=CH\textsubscript{2}), 99.4 (CCH\textsubscript{3}), 100.9 (CCH\textsubscript{3}), 106.6 (CCH\textsubscript{3}), 123.3, 123.5, 126.1, 126.4, 127.0 (Ph \textit{para}), 127.5 (Ph \textit{ortho}), 128.8 (Ph \textit{meta}), 137.1, 137.9, 144.7 (Ph ipso), 153.8, 154.6.

[Ru(8a)(4,4’-dimethyl-2,2’-dipyridyl)]PF\textsubscript{6}, \textit{9b}. A solution of PhCH=CH-CH\textsubscript{2}OCO\textsubscript{2}Et (30.7 mg, 0.149 mmol) in 2 mL acetonitrile was added to an orange solution of 6b (73.0 mg, 0.120 mmol) in 2 mL acetonitrile. The reaction mixture was stirred for 2.5 h at 60 °C then the solvent was reduced under vacuum and ether was added to precipitate a brown solid. The solid was collected, washed three times with ether then dried under vacuum. Yield: 66.9 mg.

\textit{1}H NMR of this brown solid showed that approximately 10 % of the material was unreacted complex 6b. The brown solid was dissolved in 2 mL of acetonitrile and a further 3.4 mg (0.016 mmol) of PhCH=CH-CH\textsubscript{2}CO\textsubscript{2}Et in 2 mL acetonitrile was added. The solution was stirred for 5 h at 60 °C then a brown solid was isolated as described above. Yield: 058.4 mg.
Elemental Analysis (%) calcd for C₃₁H₃₁N₂F₆PRu.H₂O: C 53.17, H 5.29, N 4.00; found: C 53.22, H 5.26, N 4.65. Mass Spectrometry: m/z 537 [M⁺].

1H NMR (500 MHz, CD₃CN) δ: 1.35 (s); 1.38 (s); 1.93 (s); 2.20 (s) (4 Cp* Me), 2.22; 2.39 (dd, J = 14.4 Hz, 7.7 Hz) (CH₂), 2.14 (d, J = 8.2 Hz); 3.52 (d, J = 12.5 Hz) (=CH₂), 2.57 (s); 2.61 (s) (2 bipy Me), 3.79 (m) (CH=CH₂), 2.14 (d, J = 8.2 Hz); 3.52 (d, J = 12.5 Hz) (=CH₂), 2.57 (s); 2.61 (s) (2 bipy Me), 3.79 (m) (CH=CH₂), 2.57 (s); 2.61 (s) (2 bipy Me), 3.79 (m) (CH=CH₂), 2.57 (s); 2.61 (s) (2 bipy Me), 3.79 (m) (CH=CH₂), 2.57 (s); 2.61 (s) (2 bipy Me), 3.79 (m) (CH=CH₂), 2.57 (s); 2.61 (s) (2 bipy Me), 3.79 (m) (CH=CH₂), 2.57 (s); 2.61 (s) (2 bipy Me), 3.79 (m) (CH=CH₂), 2.57 (s); 2.61 (s) (2 bipy Me), 3.79 (m) (CH=CH₂).

13C{¹H} NMR (125 MHz, CD₃CN) δ: 7.2; 7.8; 8.4; 8.8 (4 Cp* Me), 20.4; 20.6 (2 bipy Me), 27.4 (CH₂), 51.5 (C(CH₃)), 55.8 (C(CHPh)), 81.5 (CCH₃), 83.9 (CCH₃), 86.2 (CH=CH₂), 99.2 (CCH₃), 100.5 (CCH₃), 106.3 (CCH₃), 123.8, 124.0, 127.0 (Ph para), 127.5 (Ph ortho), 127.6, 128.8, 128.8 (Ph meta), 144.8 (Ph ipso), 149.6, 150.4, 153.0, 153.9 154.1, 152.2.

[Ru(8a)(1,10-phenanthroline)]PF₆, 9c. A solution of PhCH=CH-CH₂OCO₂Et (39.6 mg, 0.192 mmol) in 2 mL acetonitrile was added to an orange solution of 6c (57.9 mg, 0.096 mmol) in 2 mL acetonitrile. The reaction mixture was stirred for 16 h at 60 °C then the solvent was reduced under vacuum and ether was added to precipitate an orange solid. The solid was collected, washed three times with ether then dried under vacuum. Yield: 63.3 mg (97%). Elemental Analysis (%) calcd for C₃₁H₃₁N₂F₆PRu: C 54.95, H 4.61, N 4.13; found: C 55.13, H 4.82, N 4.14. Mass Spectrometry: m/z 533 [M⁺].

1H NMR (500 MHz, CD₃CN) δ: 1.36 (s); 1.38 (s); 2.05 (s); 2.34 (s) (4 Cp* Me), 2.31 (m); 2.45 (dd, J = 14.4 Hz, 7.7 Hz) (CH₂), 2.19 (d, J = 8.1 Hz); 3.65 (d, J = 12.5 Hz) (=CH₂), 3.95 (m) (CH=CH₂), 4.59 (m) (CHPh), 7.21 (Ph para), 7.34 (Ph meta), 7.52 (Ph ortho), 7.96; 8.04; 8.05; 8.12; 8.56; 8.64; 9.42; 9.63 (8 phenanthroline protons). 13C{¹H} NMR (125 MHz, CD₃CN) δ: 7.4; 7.9; 8.4; 9.0 (4 Cp* Me), 27.5 (CH₂), 51.9 (C(CH₃)), 55.7 (CHPh), 81.2 (CCH₃), 83.9 (CCH₃), 86.9 (CH=CH₂), 99.8 (CCH₃), 100.8 (CCH₃), 125.3, 125.5, 127.0 (Ph para), 127.5 (Ph ortho), 127.6, 127.7, 128.8 (Ph meta), 130.7, 130.9, 135.8, 136.5, 146.0, 146.2, 144.7 (Ph ipso), 153.9, 154.9.

[Ru(8b)(4,4'-dimethyl-2,2'-dipyridyl)]PF₆, 12. A solution of 4-MeO-C₆H₄-CH(OCO₂tBu)-CH=CH₂ (50.2 mg, 0.190 mmol) in 2 mL acetonitrile was added to an orange solution of 6b (57.6 mg, 0.095 mmol) in 2 mL acetonitrile. The reaction mixture was stirred for 16 h at 60 °C then the solvent was reduced under vacuum and ether was added to precipitate an ochre solid. The solid was collected, washed three times with ether then dried under vacuum. Yield: 64.4 mg (95%). Elemental Analysis (%) calcd for C₃₂H₃₂N₂OF₆PRu: C 54.01, H 5.24, N 3.94;
found: C 53.61, H 5.32, N 4.09. Mass Spectrometry: m/z 567 [M⁺]. ¹H NMR (500 MHz, CD₃CN) δ: 1.35 (s); 1.37 (s); 1.93 (s); 2.18 (s) (4 Cp* Me), 2.17 (d, J = 8.1 Hz); 2.35 (dd, J = 14.5 Hz, 7.7 Hz) (CH₂), 2.13; 3.50 (d, J = 12.1 Hz) (=CH₂), 2.57 (s); 2.61 (s) (2 bipy Me), 3.79 (CH=CH₂), 3.79 (s) (OMe), 4.41 (m) (CH₂Ph), 6.90 (Ph ortho), 7.42 (Ph meta), 7.44; 7.52; 8.17; 8.19; 8.87; 9.09; (6 bipy protons). ¹³C{¹H}NMR (125 MHz, CD₃CN) δ: 7.2; 7.8; 8.4; 8.8 (4 Cp* Me), 20.5; 20.6 (2 bipy Me), 51.5 (=CH₂), 55.8 (CHnaphthalene), 81.5 (CCH₃), 84.1 (CH₂Ph), 85.9 (CH=CH₂), 99.2 (CCH₃), 100.6 (CCH₃), 106.4 (CCH₃), 124.0, 153.0, 153.8 (bipy).

[Ru(8c)(4,4′-dimethyl-2,2′-dipyridyl)]PF₆₄, 13, and 14. A solution of (naphthalene)CH(OCON₃Bu)-CH=CH₂ (45.6 mg, 0.160 mmol) in 2 mL acetonitrile was added to an orange solution of 6b (48.6 mg, 0.080 mmol) in 2 mL acetonitrile. The reaction mixture was stirred for 16 h at 60 °C then the solvent was reduced under vacuum and ether was added to precipitate an ochre solid. The solid was collected, washed three times with ether then dried under vacuum. Yield: 53.9 mg (92%). ¹H NMR (500 MHz, CD₃CN) δ: 1.35 (s); 1.38 (s); 1.95 (s); 2.23 (s) (4 Cp* Me), 2.19; 3.59 (=CH₂), 3.86 (CH=CH₂), 4.63 (m) (CHnaphthalene), 7.52; 8.17; 8.19; 8.89; 9.09; 9.13 (bipy protons). ¹³C{¹H}NMR (125 MHz, CD₃CN) δ: 7.2; 7.8; 8.4; 8.8 (4 Cp* Me), 20.5; 20.6 (2 bipy Me), 51.5 (=CH₂), 55.8 (CHnaphthalene), 81.5 (CCH₃), 84.1 (CCH₃), 85.9 (CH=CH₂), 99.2 (CCH₃), 100.6 (CCH₃), 106.4 (CCH₃), 124.0, 153.0, 153.8 (bipy).

[Ru(8d)(2,2′-dipyridyl)]PF₆₄, 15a. A solution of CH₂=CH-CH₂OCO₂tBu (27.5 mg, 0.173 mmol) in 2 mL acetonitrile was added to a solution of 6b (50.3 mg, 0.087 mmol) in 2 mL acetonitrile. The reaction mixture was stirred for 16 h at 60 °C then the solvent was removed under vacuum and the residue washed several times with ether. The resulting red brown solid was then dried under vacuum. Yield: 42.7 mg (85%). Mass Spectrometry: m/z 433 [M⁺]. ¹H NMR (500 MHz, CD₃CN) δ: 1.32 (s); 1.34 (s); 1.92 (s); 2.12 (s) (4 Cp* Me), 2.05 (d, J = 8.6 Hz); 3.43 (d, J = 12.5 Hz) (=CH₂), 2.10; 2.12 (CH₂), 2.72; 3.05 (m) (CH₂), 3.87 (m) (CH=CH₂), 7.60, 7.68, 8.00, 8.07, 8.31, 8.33, 9.06, 9.20 (8 bipy protons). ¹³C{¹H}NMR (125 MHz, CD₃CN) δ: 7.3, 7.7, 8.2, 8.7 (4 Cp* Me), 21.2 (CH₂), 39.3 (CH₂), 54.7 (=CH₂), 80.7
[Ru(8d)(4,4'-dimethyl-2,2'-dipyridyl)]PF₆, 15b. A solution of CH₂=CH-CH₂OCO₂Bu (13.7 mg, 0.087 mmol) in 2 mL acetonitrile was added to a solution of 6b (26.3 mg, 0.043 mmol) in 1.5 mL acetonitrile. The reaction mixture was stirred for 16 h at 60 °C then the solvent was reduced under vacuum and ether was added to precipitate an ochre solid. The solid was collected, washed three times with ether then dried under vacuum. Yield 13.7 mg (52 %). Elemental Analysis (%) caled for C₂₅H₃₁N₂F₆PRu.H₂O: C 48.11, H 5.29, N 4.49; found: C 48.39, H 5.43, N 5.26. Mass Spectrometry: m/z 461 [M⁺].

1H NMR (400 MHz, CD₂Cl₂, δ): 1.35 (s); 1.37 (s); 1.90 (s); 2.11 (s) (4 Cp* Me), 2.00; 3.39 (d, J = 12.1 Hz) (CH₂), 2.08 (d, J = 8.1 Hz) ; 2.12 (CH₂), 2.61 (s); 2.65 (s) (2 bipy Me), 2.77 (m); 3.05 (m) (CH₂), 3.80 (m) (CH=CH₂), 7.40, 7.46, 8.05, 8.08, 8.82, 8.93 (6 bipy protons). 13C{¹H}NMR (100 MHz, CD₂Cl₂, δ: 7.9; 8.4; 8.9, 9.4 (4 Cp* Me), 21.2; 21.3 (2 bipy Me), 21.4 (CH₂), 39.5 (CH₂), 54.8 (=CH₂), 80.4 (CCH₃), 82.6 (CCH₃), 84.9 (CH=CH₂), 98.1 (CCH₃), 104.3 (CCH₃), 108.7 (CCH₃), 123.7, 124.0, 127.2, 127.5, 149.6, 150.4, 152.1, 153.3, 153.9, 154.0.
2.4 References


Reactions of Ru(Cp*) Complexes with P(o-tolyl)$_3$
3.1 Introduction

In Chapter 2 it was shown that ruthenium complexes containing chelating nitrogen ligands react with allyl carbonates to form complexes with an unexpected tucked-in structure. Based on these results, it was of interest to determine whether similar tucked-in complexes could be generated by reaction of allyl carbonates with ruthenium complexes containing phosphorus ligands. Although the Ru(II) phosphorus complexes reported in this chapter did not react with allyl carbonates, their coordination chemistry was found to be interesting in its own right and is discussed here.

The ease with which \([\text{Ru}((\text{Cp or Cp}^*)\text{(CH}_3\text{CN})_3](\text{PF}_6)]\) forms coordinatively unsaturated complexes, and subsequently reacts with organic arenes, has lead to the observation of a relatively large number of cationic \([\text{Ru}((\text{Cp or Cp}^*)(\text{\eta}^6\text{-arene})](\text{anion})\) salts, where the arene might be a solvent molecule or an organic reagent. For example, the monocationic species \([\text{Ru}((\text{Cp}^*)(\text{\eta}^6\text{-C}_6\text{H}_6})]^+, 1\), which is isoelectronic with ruthenocene, was first reported by Zelonka and Baird in 1972.\(^1\) This sandwich complex is a convenient precursor to the versatile \([\text{Ru}(\text{Cp})\text{(CH}_3\text{CN})_3](\text{PF}_6)\) (Equation 1).\(^2\)

![Equation 1](image)

Complexes 2-4\(^3\) were synthesised by reaction of \([\text{RuCp}^*(\text{CH}_3\text{CN})_3](\text{PF}_6)\) with three equivalents of the corresponding linear arylcarbonate in acetone.

![Complexes 2-4](image)
These \([\text{RuCp}^*(\eta^6\text{-arene})](\text{PF}_6)\) salts were subsequently tested for catalytic activity in allylic alkylation reactions with dimethyl malonate as the nucleophile and the arylcarbonate corresponding to the complexed arene as the substrate (Equation 2). In all three cases the organic products were formed, albeit relatively slowly on a timescale of 4-10 hours. The observation that a catalytically active species is generated when an \([\text{RuCp}^*(\eta^6\text{-arene})](\text{PF}_6)\) salt is used as the catalyst precursor suggests that such sandwich complexes may be involved in the catalytic cycle when the catalyst precursor is \([\text{RuCp}^*(\text{CH}_3\text{CN})_3](\text{PF}_6)\) or \([\text{RuCp}^*(\eta^3\text{-PhCH-CH-CH}_2)(\text{OC(OrBu)O})](\text{PF}_6)\).^3,4

\[
\text{ArOCO}_2(t\text{Bu/Et}) + \text{MeO'CO'COOMe} \rightarrow \text{MeO'COOMe} + \text{ArOC} = \text{O}
\]

Equation 2: **Conditions:** 0.07 mmol carbonate, 0.217 mmol dimethyl malonate, 0.213 mmol NaH, 0.002 mmol catalyst (3 mol %), 0.5 mL DMF-\(d_7\)

Most commonly when a phosphine ligand is allowed to react with a Ru(Cp or Cp*) species the resulting product is a monosubstituted phosphine complex. The complexes 5-7, reported by Kirchner and co-workers, were readily prepared by the reaction of one equivalent of the corresponding phosphine with \([\text{Ru(Cp)}(\text{CH}_3\text{CN})_3](\text{PF}_6)\) in dichloromethane.\(^5\)
In principle, for reactions involving EAr₃ ligands, with E = P, As, Sb or Bi, an aryl moiety on the E-atom can compete with the electron pair on the E-atom for bonding to the ruthenium centre. Whereas PPh₃, AsPh₃ and SbPh₃ react stoichiometrically with [RuCp(CH₂CN)₃](PF₆) to form the expected monosubstituted product [RuCp(EPh₃)(CH₂CN)₂](PF₆), the analogous reaction with BiPh₃ was found to give a mixture of two compounds, 8 and 9, where a phenyl ring of the BiPh₃ ligand was η⁶-coordinated to the ruthenium (Equation 3).

![Equation 3](image)

In a rare example (not involving a Cp ring), one aromatic ring of Binap has been shown to be capable of an η⁶-bonding mode. The unexpected complex, 10, in which Binap acts as an 8e arene-mono-phosphine donor to Ru(II), was synthesised by reaction of the cationic hydride complex [RuH(η⁶-benzene)(Binap)](CF₃SO₃) with PPh₃ at 80 °C in 1,2-dichloroethane.

![Equation 3](image)

In this chapter an unexpected sandwich complex is reported where a P(tolyl)₃ type ligand coordinates to a Ru(Cp*) species through the arene electrons rather than through the lone pair...
of electrons on the phosphorus atom. Detailed NMR studies and a crystal structure are presented.
3.2 Results and Discussion

3.2.1 The Reaction of a Ru(II) Cp* Complex with P(o-tolyl)3

Reaction of $[\text{Ru(Cp*)(CH_3CN)_3}(\text{PF}_6)]$ with two equivalents of P(o-tolyl)$_3$ led to formation of the sandwich complex $[\text{Ru(Cp*)}$(η$_6$-o-tolyl)P(o-tolyl)$_2$](PF$_6$), 11, plus one equivalent of unreacted phosphine rather than the expected bis-phosphine complex. Complex 11 could be isolated in good yield (Equation 4) from the reaction mixture as a yellow powder and crystals suitable for X-ray diffraction were obtained by layering a dichloromethane solution of 11 with diethyl ether.

![Equation 4]

The $^{31}$P NMR spectrum of 11 reveals a singlet at $\delta = -36.7$. This chemical shift appears at an unusually low frequency, and provides an indication of the formation of the unexpected product. If the ligand were coordinated to ruthenium via the lone pair of electrons on the phosphorus, we would expect to see a singlet at around 40 ppm. Figure 1 shows this $^{31}$P signal (as an inset) as well as the four well-resolved proton resonances of the complexed o-tolyl group ($\delta = 5.40, 5.69, 5.74$ and 5.84).

Figure 2 shows sections of the one-bond (left) and $^{13}$C, $^1$H long-range (right) correlations, from which one can assign the four $^{13}$CH and the two fully substituted carbon signals of the complexed arene moiety at $\delta > 100$ ppm. These $^1$H and $^{13}$C absorptions were all shifted to relatively low frequency, in keeping with the literature. There were three non-equivalent methyl resonances in both the $^1$H and $^{13}$C spectra and these can be assigned using Overhauser methods.
Figure 1: The complete $^1$H NMR (500 MHz, CD$_2$Cl$_2$) spectrum for 11, bottom trace, showing the three non-equivalent o-tolyl methyl groups and, top left, the expansion of the region containing the arene protons 3-6. The $^{31}$P (202 MHz, CD$_2$Cl$_2$) signal is shown top right. Once the arene ring is complexed, the $^{31}$P spin-spin coupling to the ring protons is reduced in magnitude and often not resolved.

Figure 2: One bond correlation (left) showing the four $^{13}$C chemical shifts for the CH resonances in the complexed arene and long-range correlation (right) indicating the positions of the two arene ipso-carbons for salt 4, close to 102 ppm (500 MHz, CD$_2$Cl$_2$).
The unexpected structure of 11 was confirmed by X-Ray crystallography. Figure 3 shows two views of the cation and a selection of bond lengths and bond angles is given in the caption to the figure. The immediate coordination sphere of the metal contains the Cp* and one η⁶-o-tolyl group. One of the remaining two o-tolyl groups is situated away from the metal, below the plane of the complexed arene moiety thereby minimizing possible steric effects between the P(o-tolyl)₂ group and the Cp*. As expected, the Ru-C(η⁶-o-tolyl) separations for C11, C12 and C16 are somewhat longer than for C13-C15, presumably due to the steric effects associated with the P(o-tolyl)₂ group. Nevertheless, all six Ru-C bond lengths are in the region expected for Ru-arene complexes.⁹-¹⁹ The five Ru-C(Cp*) separations are all normal and not significantly different from values given in the literature for similar compounds.

![Figure 3: ORTEP views of the cation of salt 11 showing 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Ru–C(1) 2.172(6), Ru–C(2) 2.188(5), Ru–C(3) 2.180(6), Ru–C(4) 2.174(6), Ru–C(5) 2.184(7), Ru–C(11) 2.254(5), Ru–C(12) 2.222(6), Ru–C(13) 2.207(5), Ru–C(14) 2.204(6), Ru–C(15) 2.199(6), Ru–C(16) 2.216(6), Ru–centre of the Cp* 1.819(6), Ru–centre of the complexed arene 1.705(6), P(1)–C(1)–P(31) 1.846(5), P(1)–C(2)–P(31) 1.844(7); C(21)–P(1)–C(31) 99.2(3), C(21)–P(1)–C(11) 101.5(3), C(31)–P(1)–C(11) 101.9(3).](image)

The analogous reaction with two equivalents of the meta-tolyl phosphine, gave the expected bis-phosphine product, 12, δ³¹P = 42.7. Reaction with the para-tolyl phosphine, gave mostly 13, δ³¹P = 41.2 as expected but also a small amount (ca 4%) of the (η⁶-p-tolyl) salt, 14, δ³¹P = 25.9 (Scheme 1).
Evidence for the formation of the small amount of $\eta^6$-p-tolyl phosphine complex comes from both the $^1$H (Fig. 4) and $^{13}$C NMR spectra where the characteristic low frequency chemical shifts of the complexed arene, 14 are observed. The difference in stability between 13 and 14 is not so large as to prevent the formation of a readily detectable amount of the somewhat surprising arene complex.
3.2.2 The Reaction of a Ru(II) Cp* Complex with Other Bulky Phosphorus Ligands

To investigate whether other bulky PR$_3$ donors might also choose to avoid P-complexation, the related reactions using the phosphite ligands, 15 and 16 were studied. Reaction of [Ru(Cp*)(CH$_3$CN)$_3$](PF$_6$) with 2.1 equivalents of tris ortho-xenyl phosphite, 15, leads to predominantly the mono-phosphite product, Ru(Cp*)(15)(CH$_3$CN)$_2$(PF$_6$), 17. However, a series of weak signals in the $^1$H spectrum in the region between 5.4 ppm and 6.2 ppm suggest the presence of a small proportion, less than 5%, of arene complexed species. Product 17
could be isolated by layering an acetone solution of the crude product with diethyl ether and cooling to -40 °C.

Reaction of [Ru(Cp*)(CH$_3$CN)$_3$](PF$_6$) with 1.1 equivalents of the phosphite 16 resulted in the mono-phosphite complex, 18, with no trace of arene complexed species observable in the $^1$H NMR spectrum (Figure 5). Presumably the oxygen atoms of these phosphite ligands provide enough flexibility such that the three P-substituents can be comfortably placed in a position remote from the Cp* ring.

![Image](image_url)

Figure 5: $^1$H NMR spectrum (300 MHz, acetone-$d_6$) of 18, left, with an expansion of the region between 1.5 and 1.8 ppm showing that the Cp* signal is a doublet with $J_{PH} = 2.7$ Hz. $^{31}$P NMR spectrum (121 MHz, acetone-$d_6$), right, showing the phosphorus resonance of the bound phosphite ligand at 133.6 ppm.

It is interesting that the most intense set of peaks in the MALDI mass spectra of 17 and 18 correspond to Ru(Cp*)(15), and Ru(Cp*)(16), respectively, i.e., the loss of the two acetonitrile molecules. For 18, these were more or less the only signals between m/e 600-900. Moreover, the strongest signals in the mass spectra of the isomeric bis-phosphine salts 12 and 13, correspond to the cation of 14, i.e., “Ru(Cp*)(phosphine)”. Although these mass spectra do not prove structure, it seems likely that these were the 18e $\eta^6$-arene cations. All of the NMR and mass spectral observations support the idea that P-coordination will not always result in the most stable species.
3.2.3 The Reaction of a Ru(IV) Cp* Complex with P(o-tolyl)$_3$

The Ru(IV) dicationic allyl complex 19 was recently prepared in the group. This salt is an interesting catalytic precursor in a Friedel-Crafts type coupling reaction.$^{20}$

![Diagram](image)

Given the ease with which the DMF molecules can be replaced, the salt 19 was allowed to react with two equivalents of P(o-tolyl)$_3$ in acetone solution at room temperature. The crude isolated solid product, which was washed with ether to remove excess unreacted phosphine, proved to be a mixture of two components, 20 and 21, in a ratio of ca two to one.

![Diagram](image)

The two phosphorus chemical shifts were found at $\delta = 26.1$ and $\delta = 24.2$ (Fig. 6) for 20 and 21, respectively. In the $^1$H-NMR spectrum, the four protons of the allyl fragment in the major species, 20, appear as three resonances at a) $\delta = 7.05$ (Ph-CH=) with $^3J_{HH} = 15.4$ Hz and $^3J_{PH} = 4.3$ Hz, b) $\delta = 6.02$ ppm ($=CHCH_2$, as a complex multiplet strongly overlapped with the complexed arene resonances of 21) and c) $\delta = 4.77$ (PCH$_2$) with $^3J_{PH} = 14.0$ Hz and $^3J_{HH} = 7.5$ Hz. The first two chemical shifts plus the 15.4 Hz $^3J_{HH}$ coupling were in agreement with a trans olefin fragment. The presence of the 14 Hz $^3P$ coupling to the $\alpha$-protons (Fig. 6) was proven by a $^{31}P$, $^1$H correlation.

The analogous proton allyl signals for the minor product, 21, were found at a) $\delta = 6.92$ (Ph-CH= $^3J_{HH} = 14.9$ Hz and $^4J_{PH} = 4.0$ Hz), b) $\delta = 6.30$ ($=CHCH_2$ $^3J_{HH} = 14.9$, $^3J_{HH} = 7.3$ and $^3J_{PH} = 4.0$ Hz) and c) $\delta = 4.92$ (PCH$_2$ $^3J_{PH} = 14.1$ Hz and $^3J_{HH} = 7.3$ Hz). Once again the presence of
$^{31}$P coupling was shown by a $^{31}$P,$^1$H correlation, and the two relatively high frequency proton chemical shifts plus the 14.9 Hz $^3$J$_{HH}$ coupling were in agreement with a trans olefin fragment.

Figure 6: A section of the $^1$H NMR spectrum (500 MHz, CD$_2$Cl$_2$), left, showing the two aliphatic PCH$_2$ resonances for 20 and 21. The observed doublet of doublets stems from $^3$J$_{PH}$ and $^3$J$_{HH}$. The two $^{31}$P (202 MHz, CD$_2$Cl$_2$) resonances are shown on the right.

In the $^1$H NMR spectrum one finds a strongly second order group of multiplets between 5.6 ppm and 5.9 ppm, which were assigned as the $\eta^6$-arene proton signals belonging to 21. The Ph protons of the allyl fragment in 20 were found at routine positions.

The PCH$_2$ proton resonances in both 20 and 21 can be correlated to aliphatic $^{13}$CH$_2$ signals at $\delta = 29.3$ and $\delta = 29.2$, for the major and minor products, respectively. Both $^{13}$C resonances show relatively large $^1$J$_{PC}$ values of ca 52 Hz which were typical for sp$^3$ hybridized carbons attached to a quaternary P-atom.$^{21,22}$ The coupling constants $^1$J$_{PC}$ in the known phosphonium salt, [Ph$_3$PCH$_2$CH=CH$_2$]$^+$, at 49.7 Hz and $^2$J$_{PH}$ at 14.9 Hz were in excellent agreement with our measured values.
Strong evidence in support of the (η⁶-C₆H₅) ligand in 21 comes from the ¹³C NMR results. One finds three ¹³C NMR CH signals for the complexed arene of 21 at the expected low frequencies: δ = 85.1 (ortho) δ = 87.3 (meta) and at δ = 87.12 (para) in the ratio 2:2:1 respectively. The olefinic carbons of the trans double bonds in both 20 and 21 were found in a typical region for such sp² carbons. For both 20 and 21 one observes three equivalent methyl resonances in both the ¹H and ¹³C spectra.

Whether inter- or intramolecular, the mechanism for the formation of species 20 and 21 seems to involve initial nucleophilic attack by the lone pair of phosphorus electrons on the least substituted allylic carbon (Scheme 2). Although molecular orbital calculations suggest that attack in the more substituted position should be preferred, in this case steric effects due to the bulky P(o-tolyl)₃ ligand must be dominating. The resulting alkene complex dissociates to give the major product, phosphonium salt 20, and a Ru(Cp*) fragment with three coordinated solvent molecules. Coordination of 20 to the Ru(Cp*) fragment affords the minor product, the η⁶-arene complex 21.

Scheme 2
The nucleophilic attack of a group 15 atom on a coordinated allyl is not unprecedented and there is a report in the literature of a complexed ammonium ion, \( \text{CH}_2=\text{CHCH}_2\text{NEt}_3^+ \), derived from the attack of triethylamine, as a nucleophile, on a Ru(IV) allyl complex.\(^5\)

3.2.4 The Reaction of a Ru(II) Cp Complex with P(o-tolyl)\(_3\)

Based on the observation that P(o-tolyl)\(_3\) is too sterically crowded to coordinate to the Ru(Cp*) fragment through the lone pair of electrons on the P-atom, we were interested in finding out if P-complexation would be possible if the Cp* group was replaced by the smaller Cp ligand. Reaction of one equivalent of P(o-tolyl)\(_3\) with \([\text{Ru}(\text{Cp})(\text{CH}_3\text{CN})_3](\text{PF}_6)\) afforded the complex \([\text{Ru}(\text{Cp})(\text{P(o-tolyl)O})_3(\text{CH}_3\text{CN})_2](\text{PF}_6)\), \(\text{22}\), where the phosphine ligand is coordinated to the ruthenium through the lone pair of electrons on the P atom. With Cp rather than Cp* as a ligand there is less steric hindrance and the bulky phosphine ligand is not forced to coordinate through its arene electrons as with \(\text{11}\).

Nevertheless, rotation around the P-C bond is restricted and at room temperature broad signals in the 'H NMR spectrum were seen due to slow exchange of the o-tolyl methyl groups. At 243 K rotation around the P-C bond is slow on an NMR timescale and the signals from the o-tolyl protons and methyl groups are resolved into sharp lines (Fig. 7).

Six singlets can be seen in the 'H spectrum at 243 K in the region between 1.5 and 2.5 ppm. The signal at 2.40 ppm, which remains sharp at all temperatures, corresponds to the three equivalent acetonitrile ligands of a small amount, ca 10 \%, of unreacted \([\text{Ru}(\text{Cp})(\text{CH}_3\text{CN})_3](\text{PF}_6)\).
Figure 7: The $^1$H NMR spectra of $\text{[Ru(Cp)(P(o-tolyl)$_3$)(CH$_3$CN)$_2$](PF}_6 )$ (400 MHZ, CD$_2$Cl$_2$) at 298 K, 273 K and 243 K).

CH correlation NMR spectroscopy (Fig. 8) was used to assign the remaining five signals to the three non equivalent methyl groups of the coordinated P(o-tolyl)$_3$ ligand (1.51, 1.77 and 2.42 ppm) and to the two non equivalent acetonitrile ligands in 22 (1.81 and 2.36 ppm). In the $^{13}$C NMR spectrum of 22 the P(o-tolyl)$_3$ methyl carbons come in the range 22-25 ppm and can be identified due to their coupling with phosphorus which causes them to appear as doublets.
To conclude, it seems that the bulky P(o-tolyl)$_3$ fragment is not readily compatible with the Ru(Cp$^*$) fragment in either the +2 or +4 oxidation state and tends to avoid coordination to the ruthenium centre through the lone pair of electrons on the P-atom. The Cp ligand is sufficiently small that P(o-tolyl)$_3$ will react with the Ru(II)(Cp) fragment to form a new Ru-P bond.
3.3 Experimental

All reactions and manipulations were performed under an N₂ atmosphere using standard Schlenk techniques. The solvents and reagents were dried and distilled using standard procedures and stored under nitrogen. NMR spectra were normally recorded with Bruker DPX-250, 300 and 500 MHz spectrometers. In some cases the spectra were measured at 273 K to avoid decomposition. Chemical shifts are given in ppm; coupling constants (J) in Hertz. Elemental analysis and mass spectroscopic studies were performed at ETHZ.

The ³¹P resonance for the PF₆⁻ anion, although not noted in the preparative sections, was found for each salt at δ = -144.4 as a sharp septet.

[RuCp*(η⁶-o-tol)P(o-tol)]PF₆, 11. A solution of P(o-tol)_3 (157.3 mg, 0.517 mmol) in 3 mL acetone was added to a solution of [RuCp*(CH₃CN)_3]PF₆ (108.6 mg, 0.215 mmol) in 3 mL acetone. After stirring for two hours the solvent was removed under vacuum. The remaining pale yellow solid was washed with diethyl ether. Yield 125.6 mg (85%). Crystals were obtained by layering a dichloromethane solution of the crude product with diethyl ether.

¹H NMR (500 MHz, CD₂Cl₂, 273 K) δ (ppm): 1.95 (s, 15H, C₅Me₅), 2.10 (s, 3H, Me₇), 2.39 (s, 3H, Me₇'), 2.74 (s, 3H, Me₇''), 5.40 (d, J = 5.8 Hz, 1H, H₆), 5.69 (t, J = 5.8 Hz, 1H, H₅), 5.74 (d, J = 5.4 Hz, 1H, H₃), 5.84 (t, J = 5.4 Hz, 1H, H₄), 6.90 (dd, J = 7.23, 3.65 Hz, 1H, H₆'), 7.16 (m, 1H, H₃'), 7.21 (m, 1H, H₄'), 7.26 (m, 1H, H₆''), 7.29 (m, 1H, H₄''), 7.38 (m, 1H, H₅''), 7.41 (m, 1H, H₃'''), 7.42 (m, 1H, H₅'''). ¹³C{¹H}NMR (125 MHz, CD₂Cl₂, 273 K) δ (ppm): 10.6 (C₅Me₅), 18.8 (Me₇), 21.4 (Me₇'), 22.2 (Me₇''), 86.8 (C₅), 88.2 (C₃), 88.3 (C₆), 89.3 (C₄), 96.7 (C₅Me₅), 102.0 (C₂), 102.6 (C₁), 126.9 (C₃'), 127.4 (C₆''), 129.9 (C₄'), 130.0 (C₂''), 131.2 (C₅'), 131.5 (C₃''), 137.8 (C₄''), 142.3 (C₁'), 148.0 (C₁''). ³¹P{¹H}NMR (202 MHz, CD₂Cl₂, 273 K) δ (ppm): -36.7. Elemental Analysis (%) calculated for C₃₁H₃₆F₆P₂Ru: C 54.31, H 5.29; found: C 53.55, H 5.34. Mass Spectrometry: m/z: 541.1 [M⁺].
A solution of P(m-tol)₃ (97.0 mg, 0.319 mmol) in 2 mL acetone was added to a solution of [RuCp*(CH₃CN)₃]PF₆ (80.0 mg, 0.159 mmol) in 3 mL acetone. The yellow reaction mixture was stirred for 2 h at room temperature after which time the solvent was removed under vacuum. The resulting crude product was washed with diethyl ether to afford a yellow solid. Yield: 76.5 mg (47%).

[**RuCp*(P(m-tol))₃CH₃CN]**PF₆, 12. A solution of P(m-tol)₃ (97.0 mg, 0.319 mmol) in 2 mL acetone was added to a solution of [RuCp*(CH₃CN)₃]PF₆ (80.0 mg, 0.159 mmol) in 3 mL acetone. The yellow reaction mixture was stirred for 2 h at room temperature after which time the solvent was removed under vacuum. The resulting crude product was washed with diethyl ether to afford a yellow solid. Yield: 76.5 mg (47%).

[**RuCp*(P(m-tol))₃CH₃CN]**PF₆, 12. A solution of P(m-tol)₃ (97.0 mg, 0.319 mmol) in 2 mL acetone was added to a solution of [RuCp*(CH₃CN)₃]PF₆ (80.0 mg, 0.159 mmol) in 3 mL acetone. The yellow reaction mixture was stirred for 2 h at room temperature after which time the solvent was removed under vacuum. The resulting crude product was washed with diethyl ether to afford a yellow solid. Yield: 76.5 mg (47%).

[**RuCp*(P(m-tol))₃CH₃CN]**PF₆, 12. A solution of P(m-tol)₃ (97.0 mg, 0.319 mmol) in 2 mL acetone was added to a solution of [RuCp*(CH₃CN)₃]PF₆ (80.0 mg, 0.159 mmol) in 3 mL acetone. The yellow reaction mixture was stirred for 2 h at room temperature after which time the solvent was removed under vacuum. The resulting crude product was washed with diethyl ether to afford a yellow solid. Yield: 76.5 mg (47%).

[**RuCp*(P(m-tol))₃CH₃CN]**PF₆, 12. A solution of P(m-tol)₃ (97.0 mg, 0.319 mmol) in 2 mL acetone was added to a solution of [RuCp*(CH₃CN)₃]PF₆ (80.0 mg, 0.159 mmol) in 3 mL acetone. The yellow reaction mixture was stirred for 2 h at room temperature after which time the solvent was removed under vacuum. The resulting crude product was washed with diethyl ether to afford a yellow solid. Yield: 76.5 mg (47%).

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6.7 Hz, $J = 6.4$ Hz, 2H, H2, 7), 7.02 (m, 12H, H3, 13), 7.06 (m, 12H, H2, 13). $^{13}$C{$^1$H}NMR (125 MHz, CD$_2$Cl$_2$, 273 K) δ (ppm): 5.6 (MeCN, 13), 9.6 (C$_{5}$Me$_{5}$, 13), 10.9 (C$_{5}$Mes, 14), 18.4 (Me, C5, 7), 21.3 (6Me, 13), 87.9 (C2, 14), 88.3 (C3, 14), 92.8 (C$_{5}$Mes), 102.0 (C4, 14), 128.8 (C3, 13), 129.5 (MeCN, 13), 132.3 (C1, 13), 134.1 (C2, 13), 140.6 (C4, 13).

$^{31}$P{$^1$H}NMR (202 MHz, CD$_2$Cl$_2$, 273 K) δ (ppm): 41.2 (13), 25.9 (14). Elemental Analysis (%) calculated for $96 \%$ C$_{54}$H$_{60}$NF$_6$P$_3$Ru and 4 % C$_{31}$H$_{36}$F$_6$P$_2$Ru: C 62.58, H 5.83; found: C 61.94, H 6.06. Mass Spectrometry: m/z: 305 [P(p-tol)]$_3$, 541 [M$^+$ - CH$_3$CN - P(p-tol)$_3$] 13 and [M$^+$] 14, 845 [M$^+$ - CH$_3$CN] 13.

[RuCp*(15)(CH$_3$CN)$_2$]PF$_6$, 17. A solution of tris ortho xenyl phosphite (233.2 mg, 0.433 mmol) in 3 mL acetone was added to a solution of [RuCp*(CH$_3$CN)$_3$]PF$_6$ (104.0 mg, 0.206 mmol) in 4 mL acetone. The yellow reaction mixture was stirred for 2 h at room temperature after which time the solvent was removed under vacuum. The resulting crude product was washed with diethyl ether to afford 124.6 mg of a yellow solid. Crystals of the pure monosubstituted phosphite complex were obtained by dissolving 50 mg of the yellow solid in acetone, layering with diethyl ether and cooling to -40 °C. %). $^1$H NMR (250 MHz, acetone-d$_6$, room temperature) δ (ppm): 1.21 (d, $J_{PC} = 2.3$ Hz, 15H, C$_{5}$Me$_{5}$, 15H, 2MeCN), 2.38 (s, 6H, 2MeCN), 7.07 – 7.70 (m, 27H, tris ortho xenyl phosphite protons). $^{31}$P{$^1$H}NMR (101 MHz, acetone-d$_6$, room temperature) δ (ppm): 136.4. Elemental Analysis (%) calculated for C$_{50}$H$_{48}$N$_2$O$_3$F$_6$P$_2$Ru: C 59.94, H 4.83, N 2.80; found: C 60.13, H 5.00, N 2.53. Mass Spectrometry: m/z: 775 [M$^+$ - 2CH$_3$CN], 857 [M$^+$], 1313 [M$^+$ - 2CH$_3$CN + tris ortho xenyl phosphite].

[RuCp*(16)(CH$_3$CN)$_2$]PF$_6$, 18. A solution of tris(2,4-di-tert-butylphenyl)phosphite (149.5 mg, 0.231 mmol) in 3 mL acetone was added to a solution of [RuCp*(CH$_3$CN)$_3$]PF$_6$ (106.0 mg, 0.210 mmol) in 3 mL acetone. The yellow reaction mixture was stirred for 2 h at room temperature after which the solvent was removed under vacuum. The crude product was washed with hexane and dried under vacuum to yield the yellow monosubstituted phosphite complex. Yield: 50.0mg (21%). $^1$H NMR (300 MHz, acetone-d$_6$, room temperature) δ (ppm): 1.28 (s, 27H, tBu), 1.40 (s, 27H, tBu), 1.63 (d, $J_{PC} = 2.7$ Hz, 15H, C$_{5}$Me$_{5}$, 15H, 2MeCN), 7.16 (dd, $J = 8.7$, 2.4 Hz, 3H), 7.47 (d, $J = 2.1$ Hz, 3H), 7.64 (dd, $J = 8.7$, 1.7 Hz, 3H). $^{31}$P{$^1$H}NMR (121 MHz, acetone-d$_6$, room temperature) δ (ppm): 133.6. Elemental Analysis (%) calculated for C$_{56}$H$_{84}$N$_2$O$_3$F$_6$P$_2$Ru: C 60.58, H 7.63, N 2.52; found: C 60.47, H 7.57, N 2.52. Mass Spectrometry: m/z: 883.5 [M$^+$ - 2CH$_3$CN].
A solution of P(o-tol)₃ (34.9 mg, 0.115 mmol) in 1 mL acetone was added to a solution of [RuCp*(DMF)₂(η₃-phenylallyl)][PF₆]₂ (52.5 mg, 0.057 mmol) in 1 mL acetone. The reaction mixture was stirred for 2 h at room temperature after which time the solution was concentrated under vacuum to precipitate a dark yellow powder. The solid was collected and washed with diethyl ether. It was found to be a mixture of 20 and 21. Yield: 53.5 mg.

1H NMR (500 MHz, acetone-d₆, 273 K) δ (ppm): 1.94 (s, C₅Me₅), 2.39 (s, tolyl Me), 4.77 (dd, JₚH = 14.1, J = 7.5 Hz, Hα'), 4.92 (dd, J = 14.9, 7.3, JₚH = 4.0 Hz, Hβ'), 6.02 (m, Hβ'), 6.30 (ddd, J = 14.9, 7.3, JₚH = 4.0 Hz, Hγ), 6.92 (dd, J = 14.9, JₚH = 4.0 Hz, Hγ').

1H NMR (500 MHz, CD₂Cl₂, 0 °C) δ (ppm): 5.64 (m, H₃), 5.74 (m, H₄), 5.83 (m, H₂), 7.18 (m, H₂'), 7.30 (m, H₄').

13C{¹H}NMR (125 MHz, CD₂Cl₂, 273 K) δ (ppm): 10.7 (C₅Me₅), 23.1 (d, JCP = 17.2 Hz, tolyl methyl groups), 23.2 (d, JCP = 16.2 Hz, tolyl methyl groups, 20), 29.2 (d, JPC = 52.5 Hz, Cp), 29.3 (d, JPC = 52.5 Hz, Cβ), 85.1 (C2), 87.2 (C4), 87.3 (C3), 97.1 (C1), 97.7 (C₅Me₅).

31P{¹H}NMR (202 MHz, acetone-d₆, 273 K) δ (ppm): 25.3, 26.1.

Mass Spectrometry: m/z: 421 [M⁺], 541 [RuCp*P(o-tol)]⁺, 657 [RuCp*(P(o-tol))₃(CH₂-CH-CH-Ph)]⁺, 803 [M’] 21. RuCp*(P(p-tol))₃(CH₂-CH-CH-Ph)](PF₆)⁺

A solution of P(o-tol)₃ (33.6 mg, 0.111 mmol) in 1 mL CH₂Cl₂ was added to a solution of [RuCp(CH₃CN)]PF₆ (48.0 mg, 0.111 mmol) in 1 mL CH₂Cl₂. After stirring for 2 h at room temperature the solution was concentrated under vacuum then diethyl ether was added to precipitate a brown solid. This solid was collected then washed three times with ether. Yield: 64.8 mg which was shown by NMR to be a 1:10 mixture of unreacted [Ru(Cp)(CH₃CN)](PF₆) and the product. 1H NMR (400 MHz, CD₂Cl₂, -243 K) δ (ppm): 1.51 (s, 3H, p-tolyl Me), 1.77 (s, 3H, p-tolyl Me), 1.81 (s, 3H, CH₃CN), 2.36 (s, 3H, CH₃CN), 2.42 (s, 3H, p-tolyl Me), 4.22 (s, 5H, Cp), 6.8-8.4 (m, 12H, p-tolyl protons).

13C{¹H}NMR (100 MHz, CD₂Cl₂, 243 K) δ (ppm): 3.9 (CH₃CN), 5.1 (CH₃CN), 22.3 (d, JCP = 6.7 Hz, p-tolyl Me), 23.8 (d, JCP = 1.2 Hz, p-tolyl Me), 25.0 (d, JCP = 5.9 Hz, p-tolyl Me), 77.8
(d, $J_{CP} = 2$ Hz, Cp), 125-144 ($p$-tolyl carbons). $^{31}$P{$^{1}$H}NMR (101 MHz, CD$_2$Cl$_2$) $\delta$ (ppm): 46.4.
3.4 References


4 Isomerisation of Allylic Alcohols to Carbonyl Compounds Catalysed by Ru(Cp) and Ru(Cp*) Complexes
4.1 Introduction

Given the activity of various Ru complexes as catalysts for the isomerisation of allyl alcohols, some of the Ru(II)Cp* complexes with nitrogen and phosphorus ligands described in Chapters 2 and 3 were tested for their suitability as catalysts for the isomerisation of 3-buten-2-ol to Methyl Ethyl Ketone (MEK).

MEK is used as a solvent for coatings, in adhesives, printing inks, for manufacturing textiles and plastics, as a catalyst for some polymerisation reactions and as a chemical intermediate e.g., in the synthesis of MEK peroxide. As such it is produced on a large industrial scale, most commonly by a three step method starting with 1-butene and involving sequential reduction and oxidation reactions. A one pot catalytic transformation starting from 3-butene-2-ol would be desirable because it would be atom economical and could avoid the use of toxic and expensive reagents.\textsuperscript{1,2}

Three general mechanisms have been suggested for the transition metal catalysed isomerisation of allylic alcohols to carbonyl compounds.\textsuperscript{1-3} The Alkyl Mechanism (Scheme 1) involves a metal hydride that can be present in the precursor complex or generated in situ.

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

\textbf{Scheme 1: The Alkyl Mechanism for the Transition Metal Catalysed Isomerisation of Allylic Alcohols into Carbonyl Compounds}
A second mechanistic proposal is the π-Allyl Mechanism which proceeds via a metal allyl intermediate (Scheme 2). The metal must have two vacant coordination sites and have the ability to increase its oxidation number by 2.

Scheme 2: The π-Allyl Mechanism for the Transition Metal Catalysed Isomerisation of Allylic Alcohols into Carbonyl Compounds

A third alternative mechanism, the Alkoxide mechanism (Scheme 3), was suggested to account for the fact that some transition metal catalysts isomerise allylic alcohols much faster than unfunctionalised alkenes. This mechanism goes via an alkoxide intermediate in which there is a metal-oxygen bond.
Many complexes of ruthenium have been shown to be suitable catalysts for the isomerisation of allylic alcohols to carbonyl compounds.\textsuperscript{4-11} Ru(acac)\textsubscript{3}, for example, rapidly isomerises 3-butene-2-ol to MEK at 100 °C.\textsuperscript{12}

\begin{equation}
\begin{aligned}
\text{OH} & \quad \text{Ru(acac)}_3 \\
\text{100 °C, 15 mins} & \quad \text{O} \\
\text{86 %}
\end{aligned}
\end{equation}

Equation 1

There is a precedence in the literature for ruthenium complexes with phosphine ligands as isomerisation catalysts. RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3} in the presence of 3 equivalents of K\textsubscript{2}CO\textsubscript{3} converts 1-octene-3-ol to the corresponding ketone in 20 minutes with a TON of 94.\textsuperscript{13}

\begin{equation}
\begin{aligned}
\text{OH} & \quad [\text{RuCl}_2(\text{PPh}_3)_3] \\
\text{65 °C} & \quad \text{O} \\
\end{aligned}
\end{equation}

Equation 2
The related catalyst RuHCl(PPh$_3$)$_3$ converts 3-butene-2-ol to MEK with a TON of 450 after 1 hr at 110 °C.  
Ru(Cp) and Ru(Cp*) complexes with phosphine ligands are also known to be active as isomerisation catalysts. For example, RuCpCl(PPh$_3$)$_2$ has been shown to isomerise allylic alcohols to ketones and aldehydes. Since this complex is substitutionally inert, high reaction temperatures and high concentrations of both the catalyst and a chloride scavenger are required.

![Equation 3](image)

Subsequently a more substitutionally labile group of complexes of the type [RuCp(PR$_3$)(CH$_3$CN)$_2$]PF$_6$ was developed which exhibit improved catalytic activity. These monosubstituted phosphine complexes typically achieve > 98 % conversion of 3-butene-2-ol to MEK after 3-5 minutes and at lower temperatures than the related bisphosphine complexes (Table 1).

![Equation 4](image)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time (min)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RuCp(PPh$_3$)(CH$_3$CN)$_2$]PF$_6$</td>
<td>3</td>
<td>&gt; 98</td>
</tr>
<tr>
<td>[RuCp(PMe$_3$)(CH$_3$CN)$_2$]PF$_6$</td>
<td>5</td>
<td>&gt; 98</td>
</tr>
<tr>
<td>[RuCp(PCy$_3$)(CH$_3$CN)$_2$]PF$_6$</td>
<td>3</td>
<td>&gt; 98</td>
</tr>
</tbody>
</table>

The use of Ru(Cp) complexes with bidentate phosphine ligands as catalysts for allylic alcohol isomerisation has also been investigated. Even with a low concentration (0.018 mol %) of such catalysts the conversion of 3-butene-2-ol to MEK proceeds at a high rate. For example,
with RuCpCl(dppm) as the catalyst a TOF of 530 h\(^{-1}\) is observed after 2 mins. Increasing the chain length of the didentate ligand increases the catalytic activity, presumably because it is easier for one arm of the chelating ligand to dissociate from the metal to open up another coordination site.

\[
\text{TOF} = 530 \text{ h}^{-1} \quad 1675 \text{ h}^{-1} \quad 5500 \text{ h}^{-1} \quad 18000 \text{ h}^{-1}
\]

In this chapter, the activities of a number of Ru(Cp/Cp*) complexes with phosphorus, nitrogen and allyl ligands as catalysts for the isomerisation of 3-butene-2-ol are investigated. Although the literature is dominated with Ru(II) and Ru(III) as catalytic precursors for such transformations, the best results obtained here were with the Ru(IV) species \(\text{RuCp}^*(\eta^3-\text{CH}_2\text{CHCH}_2)(\text{CH}_3\text{CN})_2)(\text{PF}_6)_2\) as the precursor complex. Subsequently, this complex was tested as a catalyst for the isomerisation of other allylic alcohols.

The complex \([\text{RuCp}^*(\text{PPh}_3)_2(\text{CH}_3\text{CN})](\text{PF}_6)\) was found to be less catalytically active than its Cp analogue due to a competing side reaction resulting in the formation of a new species which is discussed in section 4.2.4.
4.2 Results and Discussion

4.2.1 [RuCp*(η^3-CH₂CHCH₂)(CH₃CN)₂]PF₆₂ as a Catalyst for Isomerisation

The rate of isomerisation of 3-butene-2-ol to MEK at 100 °C with a variety of Ru(Cp/Cp*) catalysts was followed by ¹H NMR (Table 2).

![Equation 5](image)

Table 2: Conditions: 0.004 mmol catalyst, 22.5 mmol alcohol, 100 °C, 30 mins.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RuCp(PPh₃)₂Cl + 1.2 eq AgOTs</td>
<td>39 %</td>
</tr>
<tr>
<td>2</td>
<td><a href="PF%E2%82%86">RuCp*(PPh₃)₂CH₃CN</a></td>
<td>4 %</td>
</tr>
<tr>
<td>3</td>
<td><a href="PF%E2%82%86">RuCp*(CH₃CN)₃</a></td>
<td>7 %</td>
</tr>
<tr>
<td>4</td>
<td><a href="PF%E2%82%86">RuCp*(η^3-CH₂CHCH₂)(CH₃CN)₂</a>₂</td>
<td>59 %</td>
</tr>
</tbody>
</table>

By far the best result was achieved with the Ru(IV) species [RuCp*(η^3-CH₂CHCH₂)(CH₃CN)₂](PF₆)₂, 1, (entry 4) where 59 % conversion to MEK was observed after 30 minutes. Using this catalyst at room temperature, no conversion to MEK was observed after six hours.

Complex 1 was found to catalyse the isomerisation of other allylic alcohols (Table 3) but was limited to those with a terminal double bond. This may reflect the difficulty in coordinating
the C=C bond to ruthenium due to steric hindrance when the double bond is substituted at both ends.

Propionaldehyde, produced when allyl alcohol (entry 5) is isomerised, undergoes a condensation reaction with the starting alcohol to give a hemiacetal. In the case of the branched phenyl allyl alcohol (entry 9), no ketone isomerisation product was observed. Instead it appeared that ca 26 % of the starting alcohol had isomerised to form its linear analogue. This is consistent with results presented in Chapter 2 where it was shown that a series of Ru(II) Cp* complexes with chelating bipyridine ligands could isomerise branched phenyl allyl carbonate to its linear isomer in ca 30 mins. This branched to linear isomerisation is thought to proceed via a ruthenium allyl intermediate.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Allyl Alcohol</th>
<th>Products</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>(\text{O} \quad \text{H} \quad \text{O} \quad \text{H} \quad \text{O} \quad + \quad \text{OH} )</td>
<td>(\text{H} \quad \text{O} \quad \text{OH} )</td>
<td>21 %</td>
</tr>
<tr>
<td>6</td>
<td>(\text{O} \quad \text{H} \quad \text{O} )</td>
<td>(\text{O} \quad \text{K} )</td>
<td>98%</td>
</tr>
<tr>
<td>7</td>
<td>(\text{O} \quad \text{H} \quad \text{O} )</td>
<td>(\text{O} \quad \text{K} )</td>
<td>59 %</td>
</tr>
<tr>
<td>8</td>
<td>(\text{O} \quad \text{H} \quad \text{O} )</td>
<td>(\text{O} \quad \text{K} )</td>
<td>&gt; 99 %</td>
</tr>
<tr>
<td>9</td>
<td>(\text{O} \quad \text{Ph} \quad \text{H} \quad \text{O} )</td>
<td>(\text{Ph} \quad \text{O} )</td>
<td>26 %</td>
</tr>
<tr>
<td>10</td>
<td>(\text{O} \quad \text{H} \quad \text{O} )</td>
<td>No conversion</td>
<td>No conversion</td>
</tr>
<tr>
<td>11</td>
<td>(\text{Ph} \quad \text{O} \quad \text{H} )</td>
<td>No conversion</td>
<td>No conversion</td>
</tr>
</tbody>
</table>
Table 3: Conditions: 0.004 mmol RuCp*(η^{3}-CH_{2}CHCH_{2})(CH_{3}CN)_{2}(PF_{6})_{2}, 22.5 mmol alcohol, 100 °C, 6 hrs.

4.2.2 Effect of added Acid or Base

The rate of isomerisation of 3-buten-2-ol to MEK with 1 as the catalyst precursor was attempted in the presence of an acid and of a base. With 1 eq of camphor sulfonic acid it took 2 hrs to reach 55 % conversion. Almost the same conversion is achieved by the catalyst alone in 30 mins. The isomerisation is not catalysed by camphor sulfonic acid alone.

With 1 eq of diisopropylethylamine there was no conversion after 1 hr but 19 % conversion after 3 hrs. With 1 eq of proton sponge there was no conversion to MEK even after 3 hrs.

It seems the isomerisation reaction is faster without added acid or base.

4.2.3 Comparison with other Ru(Cp*/Cp) Catalysts containing P, N and Allyl Ligands

A number of other Ru(Cp/Cp*) complexes were then tested for their ability to isomerise 3-buten-2-ol to MEK under the optimised conditions developed for 1: 6 hrs at 100 °C (Table 4). No superior catalyst could be identified.

Table 4: Conditions: 0.004 mmol catalyst, 22.5 mmol 3-butene-2-ol, 100 °C, 6 hrs

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td><img src="image1" alt="Catalyst 12" /></td>
<td>57 %</td>
</tr>
<tr>
<td>13</td>
<td><img src="image2" alt="Catalyst 13" /></td>
<td>No conversion</td>
</tr>
<tr>
<td>14</td>
<td><img src="image3" alt="Catalyst 14" /></td>
<td>28 %</td>
</tr>
</tbody>
</table>
Under these conditions it appears that [RuCp*(CH$_3$CN)$_3$](PF$_6$) (entry 12) is a better catalyst for the isomerisation of 3-butene-2-ol than its Ru(Cp) analogue (entry 19).

No conversion to MEK was observed with either [RuCp*(tris ortho xenyl phosphite) (CH$_3$CN)$_2$]PF$_6$ (entry 13) or [RuCp*(2,2’-dipyridyl)(CH$_3$CN)](PF$_6$) (entry 16) as the catalyst precursor. This may be because coordination of the allylic alcohol substrate to the ruthenium metal centre is hindered by the bulky phosphite and bipyridine ligands. The complex with the
bipyridine ligand has only one coordination site available to the substrate which may further disfavour the isomerisation reaction.

Similarly, [RuCp*(p-tolyl-binap)(CH$_3$CN)](PF$_6$) (entry 15) and RuCp*(η$^3$-CH$_3$CHPh)(CH$_3$CN)Cl](PF$_6$)$_2$ (entry 17), each with only one free coordination site available, are poor catalysts for the isomerisation of 3-butene-2-ol under these conditions achieving only 10 and 20% conversion to MEK respectively.

The stable sandwich complex [Ru(Cp*){(η$^6$-o-tolyl)P(o-tolyl)$_2$](PF$_6$) (entry 14), which was characterised in Chapter 3, was able to convert 28 % of the 3-butene-2-ol to MEK. At 100 °C, the reaction temperature, there is enough energy to remove the η$^6$-arene moiety from the ruthenium metal centre. It cannot be that all molecules of [Ru(Cp*){(η$^6$-o-tolyl)P(o-tolyl)$_2$]}(PF$_6$) dissociate completely to leave the bare Ru(Cp*) fragment otherwise we would expect reactivity similar to that of [RuCp*(CH$_3$CN)$_3$](PF$_6$) (entry 12).

4.2.4 Isomerisation with [RuCp*(PPh$_3$)$_2$(CH$_3$CN)](PF$_6$) and an Unexpected Side Product

During initial experiments to determine suitable reaction conditions for these isomerisation reactions, an unusual temperature dependence was observed with [RuCp*(PPh$_3$)$_2$(CH$_3$CN)](PF$_6$) as the catalyst precursor. At 60 °C, 20% conversion to MEK was achieved after 2 hrs. At 100 °C only 5% conversion to MEK was achieved after 2 hrs.

The organic material from the reaction carried out at 60 °C was removed under vacuum leaving a pale yellow solution and a white precipitate. On washing with ether only the white solid remained. The $^{31}$P NMR spectrum of this white solid revealed one singlet at 27.2 ppm plus the distinctive PF$_6$ septet at -144.4 ppm, reminiscent of the $^{31}$P spectra of the phosphonium salt species discussed in Chapter 3. The mass spectrum of this white solid gave
\[ [M^+] = 317.1 \] which corresponds to a species containing one \( \text{PPh}_3 \) group, four carbons and seven protons. The \( ^{13} \text{C} \) NMR spectrum (Fig. 1) suggests the following structure:

![Structure](image)

The three intense signals at 130.9 ppm, 134.5 ppm and 135.8 ppm, which have phosphorus carbon coupling constants of 12.5 Hz, 9.9 Hz and 2.9 Hz respectively, belong to the ortho, meta and para carbons of the phenyl groups. The doublet at 154.8 ppm is assigned to the β sp\(^3\) carbon and has \( J_{\text{PC}} = 10.3 \) Hz. The two overlapping doublets at 117.2 ppm (\( J_{\text{PC}} = 81.0 \) Hz) and 117.6 ppm (\( J_{\text{PC}} = 88.2 \) Hz) can be assigned to the α carbon and the ipso phenyl carbon. Finally the two methyl carbons are found at 15.5 ppm and 16.6 ppm with coupling constants of 11.5 Hz and 16.8 Hz respectively.

![Figure 1](image)

Figure 1: \( ^{13} \text{C} \) NMR spectrum (100 MHz, CD\(_2\)Cl\(_2\)) of the phosphonium salt isolated from the reaction mixture after 22.5 mmol of 3-butene-2-ol were heated to 60 °C in the presence of 0.004 mmol of [RuCp*\((\text{PPh}_3)_2(\text{CH}_3\text{CN})]\)(PF\(_6\)) for 2 hrs.

There is no obvious explanation as to the mechanism of formation of this phosphonium salt. It seems likely that the initial step is intra- or intermolecular nucleophilic attack of the triphenylphosphine (P\((o\text{-tolyl})_3\) has been shown to act as a nucleophile in chapter 3) on a ruthenium coordinated allyl to give either the branched or linear allyl phosphonium salts:
It may be possible for such species to undergo a ruthenium mediated isomerisation to the observed product.

If nucleophilic attack is faster at higher temperatures, this would explain why the conversion to MEK is much less at 100 °C. The competing reaction to form the phosphonium salt renders the catalyst inactive.

4.2.5 Isomerisation with \([\text{RuCp}(\text{PPh}_3)(\text{CH}_3\text{CN})_2](\text{PF}_6)\)

As mentioned in the introduction to this chapter, \([\text{RuCp}(\text{PPh}_3)(\text{CH}_3\text{CN})_2](\text{PF}_6), 2,\) has already been reported to be an efficient catalyst for the isomerisation of 3-butene-2-ol to MEK at 57 °C in chloroform.\textsuperscript{17}

We found that the related complex \([\text{RuCp}(\text{P(o-tolyl)}_3)(\text{CH}_3\text{CN})_2](\text{PF}_6), 3,\) (characterised in Chapter 3) was a less active isomerisation catalyst than its triphenylphosphine analogue under these conditions (Table 5). The Ru(IV) species 1 is not effective as an isomerisation catalyst under these conditions and produces only a small amount of MEK, 31 % after 2 hrs, plus a number of other organic products which could not be identified by \(^1\text{H}\) or \(^{13}\text{C}\) NMR.

Table 5: **Conditions:** 0.0056 mmol catalyst (1 mol %), 0.56 mmol 3-butene-2-ol, 0.5 ml CDCl\(_3\), 57 °C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time</th>
<th>Conversion to MEK</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1</td>
<td>2 hrs</td>
<td>31 % *</td>
</tr>
<tr>
<td>21</td>
<td>2</td>
<td>10 mins</td>
<td>&gt;98 %</td>
</tr>
<tr>
<td>22</td>
<td>3</td>
<td>2 hrs</td>
<td>76 %</td>
</tr>
</tbody>
</table>
In this Chapter, a variety of Ru(Cp/Cp*) complexes with both nitrogen and phosphorus ligands were compared as catalysts for the isomerisation of 3-butene-2-ol to MEK. The best results were achieved when the catalyst precursor complex was [RuCp*(η^3-CH_2CHCH_2)(CH_3CN)_2](PF_6)_2, 1. At 100 °C, low concentrations (0.004 mmol) of this species facilitated 98% conversion to MEK after 6 hrs. Complex 1 was subsequently shown to isomerise a number of other allyl alcohols under these conditions to their corresponding aldehydes and ketones, provided that the double bond was in the terminal position. 1 was not a good isomerisation catalyst for 3-butene-2-ol under milder conditions (57 °C in CDCl_3).
4.3 Experimental

4.3.1 Isomerisation Reactions

In a typical reaction the allylic alcohol (22.5 mmol) was transferred by syringe into a round bottom flask then the solid catalyst (0.004 mmol, 0.018 mol %) was added. The flask was attached to a reflux condenser and lowered into an oil bath heated to 100 °C. At regular intervals a probe from the reaction mixture was taken with a pasteur pipette and diluted with 0.5 ml of CDCl₃ to measure the conversion to product by ¹H NMR. NMR spectra were normally recorded with Bruker DPX-250 and 300 MHz spectrometers. A typical spectrum is shown in Figure 2. The conversion was measured by comparing the integral of the methyl group of MEK at 1.01 ppm with that of the 3-butene-2-ol methyl at 1.23 ppm.

![OH](OH.png) → ![X](X.png)

Figure 6: The ¹H NMR spectrum (300 MHz, CDCl₃) of the isomerisation of 3-butene-2-ol to MEK using [RuCp*Cl(η¹-CH₃CHCHPh)(CH₃CN)](PF₆) as the catalyst precursor.

4.3.2 Synthesis of the Catalyst Precursor Complexes

All reactions and manipulations were performed under an N₂ atmosphere using standard Schlenk techniques. The solvents and reagents were dried and distilled using standard
procedures and stored under nitrogen. NMR spectra were normally recorded with Bruker DPX-250, 300 and 500 MHz spectrometers. Chemical shifts are given in ppm; coupling constants ($J$) in Hertz.

[RuCpCl(PPh$_3$)$_2$, [RuCp(CH$_3$CN)$_3$](PF$_6$) and [RuCp*(CH$_3$CN)$_3$](PF$_6$) are commercially available.

[RuCp*(η$^3$-CH$_2$CHCH$_2$)(CH$_3$CN)$_3$](PF$_6$)$_2$, [RuCp*Cl(η$^3$-CH$_2$CHCHPh)(CH$_3$CN)](PF$_6$)$_2$, [RuCp*(2,2’-dipyridyl)(CH$_3$CN)][(PF$_6$)$_2$ and [RuCp(PPh$_3$)(CH$_3$CN)$_2$](PF$_6$)$_2$ were synthesised according to the literature procedures.

The synthesis of [Ru(Cp*)(η$^6$-o-tolyl)P(o-tolyl)$_2$](PF$_6$) and [RuCp{P(o-tolyl)$_3$}(CH$_3$CN)](PF$_6$) are described in Chapter 3.

[RuCp*(PPh$_3$)$_2$](CH$_3$CN)]. A solution of PPh$_3$ (123.7 mg, 0.472 mmol) in 3 ml acetone was added to a yellow solution of [RuCp*(CH$_3$CN)$_3$](PF$_6$) (113.3 mg, 0.225 mmol) in 3 ml acetone. The reaction mixture turned immediately cloudy. After stirring for 2 hrs, the solvent was removed under vacuum to leave a yellow solid. This was washed 3 times with ether then dried under vacuum. Yield: 152.0 mg (71 %). $^1$H NMR (500 MHz, CD$_2$Cl$_2$) δ: 1.17 (s, 15H, Cp*), 2.66 (s, 3H, CH$_3$CN), 7.11-7.43 (m, 30H 2PPh$_3$).

$^{31}$P{$^1$H} NMR (202 MHz, CD$_2$Cl$_2$) δ: -143.2 (septet, PF$_6$), 43.4 (s, 2PPh$_3$).

[RuCp*(p-tolyl binap)(CH$_3$CN)](PF$_6$). A solution of p-tolyl binap (124.3 mg, 0.183 mmol) in 3 ml acetone was added to a yellow solution of [RuCp*(CH$_3$CN)$_3$](PF$_6$) (92.4 mg, 0.183 mmol) in 3 ml acetone. After stirring for 2 hrs, the solvent was removed under vacuum to leave a yellow solid. Yellow crystals could be obtained by layering a CH$_2$Cl$_2$ solution of the crude product with hexane. Yield: 171.0 mg (85 %). Elemental Analysis (%) calcd for C$_{60}$H$_{58}$NF$_6$P$_3$Ru: C 65.45, H 5.31, N 1.27; found: C 64.45, H 5.40, N 1.02. Mass Spectrometry: $m/z$ 915 [M$^+$-CH$_3$CN]. $^1$H NMR (300 MHz, acetone-d$_6$) δ: 1.26 (s, 15H, Cp*), 1.45 (s, 3H, Me), 2.10(s, 3H, CH$_3$CN), 2.16(s, 3H, Me), 2.46(s, 3H, Me), 2.48 (s, 3H, Me), 5.6-8-6 (m, 24H, p-tolyl and binap protons). $^{31}$P{$^1$H} NMR (121 MHz, acetone-d$_6$) δ: -144.2 (septet, PF$_6$), 43.1(d, $J_{PP}$ = 45.6 Hz), 51.4 (d, $J_{PP}$ = 45.6 Hz).

[RuCpCl(η$^3$-CH$_2$CHCH$_2$)(CH$_3$CN)](PF$_6$). CH$_2$=CH-CH$_2$Cl (0.02ml, 0.242 mmol) was added to a solution of [RuCp(CH$_3$CN)$_3$](PF$_6$) (100.0 mg, 0.230 mmol) in 4 ml of acetonitrile. The
reaction mixture was stirred for 1 hr then the solvent was removed under vacuum. After washing 3 times with ether an ochre solid was obtained which was dried under vacuum. Yield: 74.6 mg (76 %). $^1$H NMR (250 MHz, CD$_3$CN) $\delta$: 2.46 (s, 3H, CH$_3$CN), 3.99 (m, 1H, $\eta^3$-allyl), 4.29 (m, 2H, $\eta^3$-allyl), 4.50 (m, 1H, $\eta^3$-allyl), 5.15 (m, 1H, CH$_2$CHCH$_2$), 5.99 (s, 5H, Cp).
4.4 References

Allylic Phenolations and Phenylsulfenylations
5.1 Introduction

In Chapter 4 it was shown that the Ru(IV) complex \([\text{RuCp}^*(\eta^3-\text{CH}_2\text{CHCH}_2)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2\) was a suitable catalytic precursor for the isomerisation of a number of allyl alcohols to their corresponding aldehydes and ketones. In this chapter the range of transformations catalysed by this species will be extended to include allylic phenolation and phenylsulfonylation reactions.

Ru(IV) complexes containing Cp or Cp* ligands are finding applications in a number of catalytic transformations.\(^1\)\(^-\)\(^8\) Ruthenium catalytic precursors for allylation reactions are of particular interest because they can be regioselective and afford high branched to linear ratios in the products.\(^9\)\(^-\)\(^11\)

The ruthenium (IV) carbonate complex \([\text{RuCp}^*\{\text{OC}(\text{OrBu})\text{O}\}(\eta^3-\text{CH}_2\text{CHCHPh})](\text{PF}_6)_2\), 1, has been shown to catalyse allylic phenolation reactions.\(^12\)

![Image of Ru(IV) complex](image)

With 1 as the catalytic precursor, phenolation of the branched phenyl allyl carbonate, \(\text{PhCH}(...\text{Bu})\text{CH}=\text{CH}_2\) (Equation 1), is relatively fast with full conversion occurring after a couple of hours. Formation of the branched product is favoured and this regioselectivity has been shown to be due to electronic effects.\(^13\)

\[
\begin{align*}
\text{Ph} & \quad \text{OCO}_2\text{Bu} \\
\text{Ph} & \quad \text{OH} \\
& \quad \text{acetonitrile}
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{OCO}_2\text{Bu} \\
\text{Ph} & \quad \text{OH} \\
& \quad \text{acetonitrile}
\end{align*}
\]

Equation 1: Conditions: 0.07 mmol carbonate, 0.21 mmol phenol, 0.0021 mmol 1, 0.5 mL CD$_3$CN.

We were interested in finding out whether other Ru(IV)(Cp*) species with \(\eta^3\)-allyl ligands were catalytically active in allylic phenolation reactions. In this chapter, the relative kinetics of allylic phenolation reactions with catalytic amounts of \([\text{RuCp}^* (\eta^3-\text{CH}_2\text{CHCHPh}) \text{Cl}] (\text{PF}_6)_2\), 2, and \([\text{RuCp}^*(\eta^3-\text{CH}_2\text{CHCH}_2)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2\), 3, are presented. These
reactions were found to be significantly slower than those with 1 as the catalytic precursor. The very slow reaction kinetics when 3 was the catalytic precursor were further explored by carrying out allylic phenolation reactions in the presence of added acid and added base. Experiments using thiophenols instead of phenols as the nucleophile are also described.

![Chemical structures](image-url)
5.2 Results and Discussion

5.2.1 Allylic Phenolation Reactions

Reactions of PhCH(OCO$_2$tBu)CH=CH$_2$, 4, with various phenol derivatives (Equation 2) were carried out in the presence of catalytic amounts of either 1, 2 or 3 and followed by $^1$H NMR. The results are shown in Table 1.$^{14,15}$

\[
\text{PhCH(OCO$_2$tBu)CH=CH$_2$} + \text{PhOH} \rightarrow \text{PhCH(OCO$_2$tBu)CH=CHPh} + \text{PhCO$_2$tBu}
\]

Equation 2: X = H, Cl, I, Me, CO$_2$Me or NO$_2$

Table 1: **Conditions:** 0.07 mmol 4, 0.21 mmol nucleophile, 0.0021 mmol cat., 0.5 mL CD$_3$CN.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Nucleophile</th>
<th>Time</th>
<th>Conversion</th>
<th>b:l</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>phenol</td>
<td>146 mins</td>
<td>98</td>
<td>34:1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>p-Cl-phenol</td>
<td>93 mins</td>
<td>95</td>
<td>87:1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>p-I-phenol</td>
<td>125 mins</td>
<td>95</td>
<td>69:1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>p-Me-phenol</td>
<td>140 mins</td>
<td>97</td>
<td>30:1</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>p-CO$_2$Me-phenol</td>
<td>102 mins</td>
<td>97</td>
<td>55:1</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>p-NO$_2$-phenol</td>
<td>86 mins</td>
<td>96</td>
<td>17:1</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>p-Me-phenol</td>
<td>19 h</td>
<td>91</td>
<td>30:1</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>p-CO$_2$Me-phenol</td>
<td>27 h</td>
<td>96</td>
<td>60:1</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>p-NO$_2$-phenol</td>
<td>15 h</td>
<td>96</td>
<td>8:1</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>phenol</td>
<td>13 d</td>
<td>98</td>
<td>10:1</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>p-Cl-phenol</td>
<td>6d</td>
<td>97</td>
<td>10:1</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>p-I-phenol</td>
<td>4 d</td>
<td>96</td>
<td>62:1</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
<td>p-Me-phenol</td>
<td>10 d</td>
<td>98</td>
<td>17:1</td>
</tr>
<tr>
<td>14</td>
<td>3</td>
<td>p-CO$_2$Me-phenol</td>
<td>2 d</td>
<td>97</td>
<td>57:1</td>
</tr>
<tr>
<td>15</td>
<td>3</td>
<td>p-NO$_2$-phenol</td>
<td>21 h</td>
<td>95</td>
<td>30:1</td>
</tr>
</tbody>
</table>

In general the allylic phenolation reactions are fastest with an electron withdrawing group in the para phenol position. $p$-NO$_2$-phenol reacts most quickly with 4 regardless of which ruthenium complex is taken as the catalytic precursor.

With 1 as the catalytic precursor the allylic phenolation reactions typically take less than 3 hours. With 2 these reactions take 15-27 hours and with 3 they take several days. The very
slow reaction kinetics with 3 as the catalytic precursor are surprising. One might expect that allylic phenolation reactions should be faster with 3 than with 2 since the latter species has only one coordination site available to the substrate while the former has two (assuming that complexation is rate determining).

Furthermore, in the first catalytic cycle with 3 as the catalytic precursor (Scheme 1), the more catalytically active species 1 should be generated. One would therefore expect that allylic phenolation reactions with 3 should be almost as fast as those with 1 with a short incubation period to generate the more active species.

Scheme 1

The reaction of 4 with p-Me-phenol in the presence of catalytic amounts of 3 was repeated with added acid and with added base to find out if the very slow reaction kinetics could be accelerated. With 3 eq of diisopropylethylamine 30% conversion was achieved after 24 hours and the branched to linear ratio was 6.6:1. The same reaction without diisopropylethylamine takes 2 days to reach 30% conversion. The faster rate of reaction in the presence of a base could indicate that the effective nucleophile is the phenolate anion rather than phenol. Another possibility is that the base reacts with complex 3 to generate a more active catalytic species. This will be discussed in section 5.2.2.3.
On addition of 3 eq of \( p \)-toluene sulfonic acid the allyl carbonate substrate 4 rapidly decomposed and no reaction with \( p \)-Me-phenol was observed.

### 5.2.2 Allylic Phenylsulfenylation Reactions

Since allylic phenolations carried out in the presence of 3 are very slow, related reactions with thiophenols as the nucleophile were carried out to determine if changing the nucleophile from an O to an S atom would have an effect on the reaction rate.

These allylic phenylsulfenylation reactions were attempted using two different allyl carbonate substrates, 4 and \( \text{CH}_2=\text{CHCH}_2(\text{OCO}_2\text{tBu}) \), 5. Table 2 shows the results of these phenylsulfenylation reactions with 3 as the catalytic precursor.

![Scheme 2: X = H, Me, Cl, OMe](image)

Table 2: **Conditions:** 0.07 mmol carbonate, 0.21 mmol nucleophile, 0.0021 mmol 3, 0.5 mL CD_{3}CN.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Nucleophile</th>
<th>Time</th>
<th>Conversion (%)</th>
<th>b:l</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>4</td>
<td>thiophenol</td>
<td>50 mins</td>
<td>100</td>
<td>2.3:1</td>
</tr>
<tr>
<td>17</td>
<td>4</td>
<td>( p )-Me-thiophenol</td>
<td>95 mins</td>
<td>100</td>
<td>1.4:1</td>
</tr>
<tr>
<td>18</td>
<td>4</td>
<td>( p )-Cl-thiophenol</td>
<td>240 mins</td>
<td>95</td>
<td>1.7:1</td>
</tr>
<tr>
<td>19</td>
<td>4</td>
<td>( p )-OMe-thiophenol</td>
<td>45 mins</td>
<td>100</td>
<td>1.4:1</td>
</tr>
<tr>
<td>20</td>
<td>4</td>
<td>( p )-CN-thiophenol</td>
<td>25 mins</td>
<td>100</td>
<td>3:1</td>
</tr>
<tr>
<td>21</td>
<td>4</td>
<td>( p )-COMe-thiophenol</td>
<td>30 mins</td>
<td>100</td>
<td>1.3:1</td>
</tr>
<tr>
<td>22</td>
<td>5</td>
<td>thiophenol</td>
<td>30 mins</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>23</td>
<td>5</td>
<td>( p )-Me-thiophenol</td>
<td>30 mins</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>72 h</td>
<td>91</td>
<td>-</td>
</tr>
<tr>
<td>24</td>
<td>5</td>
<td>( p )-Cl-thiophenol</td>
<td>30 mins</td>
<td>26</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>72 h</td>
<td>71</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>5</td>
<td>( p )-OMe-thiophenol</td>
<td>17 mins</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>26</td>
<td>5</td>
<td>( p )-CN-thiophenol</td>
<td>55 mins</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>27</td>
<td>5</td>
<td>( p )-COMe-thiophenol</td>
<td>45 mins</td>
<td>100</td>
<td>-</td>
</tr>
</tbody>
</table>
Sulfur is a better nucleophile than oxygen\textsuperscript{16} and it is not surprising that the rate of reaction is significantly faster when thiophenols instead of phenols are the nucleophiles. The reaction of substrates 4 and 5 with thiophenol are relatively fast, going to completion in 50 and 30 minutes respectively (entries 16 and 22).

When the thiophenol nucleophile has a mesomerically electron withdrawing \textit{para} substituent such as CN or COMe, a change in the reaction rate is observed. Compared to unsubstituted thiophenol, these nucleophiles react faster with substrate 4 (entries 20 and 21) and slower with substrate 5 (entries 26 and 27).

When the nucleophile has the mesomerically electron donating OMe group in the \textit{para} position (entries 19 and 25), reaction with both 4 and 5 is faster than when unsubstituted thiophenol is the nucleophile.

While mesomerically electron donating or withdrawing \textit{para} substituents tend to increase reaction rates slightly, inductively electron donating or withdrawing \textit{para} substituents tend to decrease reaction rates. The slowest reaction rates are observed when the thiophenol has an inductively electron withdrawing chlorine group in the \textit{para} position. The reaction of \textit{p}-Cl-thiophenol with 4 takes 4 hours to reach 95 % conversion (entry 18) making it approximately five times slower than the analogous reaction with unsubstituted thiophenol. \textit{p}-Cl-thiophenol reacts slowly with substrate 5 producing only 26 % conversion after 30 mins (entry 24). After this time, the reaction rate drops off significantly and even after 72 hours, only 71% conversion to products has been achieved.

Reaction rates are also slow (compared to unsubstituted thiophenol) with an inductively electron donating methyl group in the \textit{para} thiophenol position. \textit{p}-Me-thiophenol, like its Cl substituted analogue, reacts very slowly with substrate 5. Although 50 % conversion to products is achieved after 30 minutes, it takes 72 hours to reach 91 % conversion.

In collaboration with Dr A. Zaitsev, the reaction of alcohols, rather than carbonates with thiophenol were studied. Complex 3 catalysed the reaction of thiophenol with PhCH(OH)CH=CH\textsubscript{2} to give full conversion to products after 20 minutes and with CH\textsubscript{2}(OH)CH=CH\textsubscript{2} to give full conversion after 30 minutes. It seems that catalyst 3 does not require a good leaving group such as carbonate or Cl on the allyl substrate to rapidly afford products. It is presumed that the allyl OH is protonated by the acidic thiophenol SH producing water as a leaving group.
An even better catalytic system for phenylsulfenylation of allyl alcohols is a 1:1 mixture of [Ru(Cp*)(CH$_3$CN)$_3$](PF$_6$) and p-toluenesulfonic acid. A selection of recent results is shown in Table 3.

Table 3: **Conditions:** 0.07 mmol carbonate, 0.07 mmol nucleophile, 0.0035 mmol [RuCp*(CH$_3$CN)$_3$](PF$_6$), 0.5 mL CD$_3$CN.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Nucleophile</th>
<th>Time</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>O-H</td>
<td>thiophenol</td>
<td>10 mins</td>
<td>100</td>
</tr>
<tr>
<td>29</td>
<td>O-H</td>
<td>p-Me-thiophenol</td>
<td>10 mins</td>
<td>100</td>
</tr>
<tr>
<td>30</td>
<td>O-H</td>
<td>p-Cl-thiophenol</td>
<td>6 mins</td>
<td>100</td>
</tr>
<tr>
<td>31</td>
<td>O-H</td>
<td>p-OMe-thiophenol</td>
<td>10 mins</td>
<td>100</td>
</tr>
<tr>
<td>32</td>
<td>O-H</td>
<td>p-CN-thiophenol</td>
<td>7 mins</td>
<td>100</td>
</tr>
<tr>
<td>33</td>
<td>O-H</td>
<td>p-COMe-thiophenol</td>
<td>5 mins</td>
<td>100</td>
</tr>
</tbody>
</table>

It is interesting that, in both Table 2 and Table 3, there seems to be a rather confusing rate dependence on the nature of the para-substituent for the thiophenol nucleophiles. Although the reaction conditions differ slightly (5 mol % catalyst rather than 3 mol % in Table 3 and only 1 equivalent of nucleophile), it is clear from both sets of results is that there is no time or yield advantage to be gained by wasting the carbonate atoms.

### 5.2.2.1 Isomerisation of the Products of Allylic Phenylsulfenylation Reactions

The allylic phenylsulfenylation reactions catalysed by 3 were followed by $^1$H NMR. For selected phenylsulfenylation reactions of substrate 4, the change in the ratio of branched to linear product as the reaction progresses is shown in Table 4. It was observed that the branched to linear ratio of the products decreases with time.

Table 4: **Conditions:** 0.07 mmol carbonate, 0.21 mmol $p$-X –thiophenol (X=H, Me, Cl), 0.0021 mmol 3, 0.5 mL CD$_3$CN.

<table>
<thead>
<tr>
<th>Nucleophile</th>
<th>Time</th>
<th>Conversion (%)</th>
<th>b:l Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>thiophenol</td>
<td>30 mins</td>
<td>89</td>
<td>2.5:1</td>
</tr>
<tr>
<td></td>
<td>50 mins</td>
<td>100</td>
<td>2.3:1</td>
</tr>
<tr>
<td>$p$-Me-thiophenol</td>
<td>60 mins</td>
<td>91</td>
<td>1.7:1</td>
</tr>
<tr>
<td></td>
<td>95 mins</td>
<td>100</td>
<td>1.4:1</td>
</tr>
<tr>
<td>$p$-Cl-thiophenol</td>
<td>160 mins</td>
<td>87</td>
<td>2.2:1</td>
</tr>
<tr>
<td></td>
<td>240 mins</td>
<td>95</td>
<td>1.7:1</td>
</tr>
<tr>
<td></td>
<td>300 mins</td>
<td>96</td>
<td>1.5:1</td>
</tr>
</tbody>
</table>
The tendency of the branched phenylsulfonylated allyls to rearrange to their linear isomers may explain why the allylic phenylsulfonylation reactions described in section 5.2.2 exhibit a poorer regioselectivity than the allylic phenolation reactions discussed in section 5.2.1. The branched phenolated allyls do not readily isomerise to their linear forms.

Indeed, the reaction of 4 with phenol, catalysed by \([\text{RuCp}^\ast(\text{CH}_3\text{CN})_3](\text{PF}_6)\) goes to completion in 50 minutes with a branched to linear ratio of products of 99:1.\(^{12}\) A similar reaction of substrate 4, also catalysed by \([\text{RuCp}^\ast(\text{CH}_3\text{CN})_3](\text{PF}_6)\) but this time with p-Me-thiophenol as the nucleophile, goes to completion in 60 minutes with a branched to linear ratio of 0.8:1 in the products. After 15 minutes, when 54 % conversion has been achieved, the branched to linear ratio is 1.6:1. This ratio decreases steadily as the reaction progresses.

Although it has been shown that branched to linear isomerisation of phenylsulfonylated allyls occurs readily, as yet no attempt has been made to understand the mechanism of this isomerisation.

### 5.2.2.2 Effect of Added Acid or Base on the Rate of Allylic Phenylsulfonylation

When p-Me-thiophenol was allowed to react with 4 in the presence of 3 and 3 eq of diisopropylethylamine, the rate of reaction decreased slightly. Full conversion to products was achieved after 140 mins whereas without added base, the same reaction goes to completion in 95 mins. The regioselectivity was better in the presences of diisopropylethylamine. The observed branched to linear ratio was 6.8:1.

Improved regioselectivity and a marginally faster reaction time was achieved by the addition of 3 eq of tributylamine to the reaction of p-Me-thiophenol with 4 in the presence of 3. The reaction went to completion in 85 minutes and the branched to linear ratio was 5:1.

With 3 eq of p-toluene sulfonic acid, the reaction of 4 with p-Me-thiophenol in the presence of 3 went to completion in 5 minutes. Without added acid, this same reaction takes 95 minutes. The branched to linear ratio in the presence of acid was poorer, only 1:1 compared with 1.4:1 when no acid is added.

Camphor sulfonic acid was also found to increase the reaction rate of p-Me-thiophenol with 4 in the presence of 3. Adding 3 eq of Camphor sulfonic acid was, however, not as effective as adding 3 eq of p-toluene sulfonic acid and the reaction time was slower, 25 minutes compared with 5, and the branched to linear ratio worse, 1:1.4 compared with 1:1.
It appears that the addition of a base primarily affects the regioselectivity of allylic phenylsulfenylation reactions catalysed by 3. Addition of an acid significantly increases the reaction kinetics and has only a small impact on the regioselectivity.

Table 5: **Conditions:** 0.07 mmol 4, 0.21 mmol p-Me-thiophenol, 0.0021 mmol 3 (3 mol %), 0.21 mmol acid or base, 0.5 mL CD$_3$CN.

<table>
<thead>
<tr>
<th>Acid/Base</th>
<th>Time</th>
<th>Conversion (%)</th>
<th>b:l</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>95 mins</td>
<td>100</td>
<td>1.4:1</td>
</tr>
<tr>
<td>diisopropylethylamine</td>
<td>140 mins</td>
<td>100</td>
<td>6.8:1</td>
</tr>
<tr>
<td>tributylamine</td>
<td>85 mins</td>
<td>100</td>
<td>5:1</td>
</tr>
<tr>
<td>p-toluene sulfonic acid</td>
<td>5 mins</td>
<td>100</td>
<td>1:1</td>
</tr>
<tr>
<td>camphor sulfonic acid</td>
<td>25 mins</td>
<td>100</td>
<td>1:1.4</td>
</tr>
</tbody>
</table>

Camphor sulfonic acid was found to catalyse the reaction of p-Me-thiophenol with 4, even without the presence of ruthenium species 3. The reaction of p-Me-thiophenol with 4 catalysed by 3 equivalents of camphor sulfonic acid was slow however, taking 120 mins to reach 20 % conversion and strongly favouring the linear product with a b:l ratio of 1:19. With 3 mol % of camphor sulfonic acid no reaction was observed between 4 and p-Me-thiophenol. The experiments involving camphor sulfonic acid are summarised in Table 6.

Table 6: **Conditions:** 0.07 mmol 4, 0.21 mmol p-Me-thiophenol, 0.5 mL CD$_3$CN.

<table>
<thead>
<tr>
<th>Camphor Sulfonic Acid</th>
<th>3</th>
<th>Time</th>
<th>Conversion (%)</th>
<th>b:l</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>0.0021 mmol</td>
<td>95 mins</td>
<td>100</td>
<td>1.4:1</td>
</tr>
<tr>
<td>0.21 mmol (3 eq)</td>
<td>0.0021 mmol</td>
<td>25 mins</td>
<td>100</td>
<td>1:1.4</td>
</tr>
<tr>
<td>0.21 mmol (3 eq)</td>
<td>none</td>
<td>120 mins</td>
<td>20</td>
<td>1:19</td>
</tr>
<tr>
<td>0.0021 mmol (3 mol%)</td>
<td>none</td>
<td>120 mins</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

5.2.2.3 The Generation of New Complexes in the Presence of a Diisopropylethylamine

An added acid or base may react with the catalyst 3 to generate a new species which itself is a better or worse catalyst for the allylic phenolation and phenylsulfenylation reactions. An NMR scale reaction of 3 with an excess of diisopropylethylamine in acetonitrile revealed proton signals in the $^1$H NMR spectrum (Fig. 1) belonging to a vinyl group and strongly shifted isopropyl and ethyl signals (as well as resonances from free diisopropylethylamine) suggesting the formation of species 6.
The $^{13}$C NMR spectrum of the reaction mixture shows olefinic carbon resonances at 125.7 and 127.4 ppm which indicates that the double bond of 6 is not coordinated to the ruthenium metal centre. One would expect ruthenium bonded $^{13}$C olefinic resonances to occur between 50 and 80 ppm.

The proposed mechanism for the formation of ammonium salt 6 (Scheme 3) is analogous to that proposed for the formation of the phosphonium salt 20 in Chapter 3. The first step is nucleophilic attack of the nitrogen on a terminal $\eta^3$-allyl carbon of 3 to generate an alkene complex. Since this alkene complex is not observed in either the $^1$H or $^{13}$C NMR spectra, it must rapidly dissociate to give the products.

![Scheme 3](image)

It seems likely that an alkene complex is an intermediate in the formation of 6 since in 1999 Kirchner and co-workers reported a similar reaction where triethylamine attacks the allyl
ligand of a Ru(Cp)(η^3-CH₂CHCH₂) complex to form a new species, 7, where the ammonium ion CH₂=CHCH₂NEt₃⁺ remains coordinated to the ruthenium through its π-alkene electrons.¹⁷

The larger size of the Cp* ligand compared with Cp may be responsible for the fact that 7 is a stable species while the alkene complex that dissociates to form 6 cannot be isolated.

The mechanism depicted in Scheme 3 indicates that a product of the reaction of 3 with diisopropylethylamine should be the Ru(Cp*) trisacetonitrile complex. Indeed, the large Cp* methyl signal at 1.62 ppm in the ^1H NMR spectrum (Fig. 1) corresponds to the species [RuCp*(CH₃CN)$_3$](PF₆). This complex is not, however, responsible for the observed regioselectivity of the reaction of p-Me-thiophenol with 4 in the presence of 3 and 3 eq of diisopropylethylamine (b:l = 6.8:1). As described in section 5.2.2.1, with [RuCp*(CH₃CN)$_3$] (PF₆) as the catalytic precursor, the linear product is favoured when 4 is allowed to react with p-Me-thiophenol (b:l = 0.8:1).
Figure 1: The $^1$H NMR spectrum (300 MHz) of the reaction of 3 with excess diisopropylethylamine in CD$_3$CN resulting in ammonium salt 6 and [RuCp*(CH$_3$CN)$_3$](PF$_6$).

To explore the possibility that the improved regioselectivity of the reaction of 4 with p-Me-thiophenol when base is added may be the result of a new complex being generated, the $^1$H NMR spectrum of a 1:1:1 mixture of [RuCp*(CH$_3$CN)$_3$](PF$_6$), diisopropylethylamine and p-Me-thiophenol was measured. Figure 2 shows this spectrum (top trace) with the spectrum of a 1:1 mixture of [RuCp*(CH$_3$CN)$_3$](PF$_6$) and p-Me-thiophenol (bottom trace) for comparison. It can be seen that on addition of diisopropylethylamine that a) the SH signal at 3.9 ppm disappears, b) the arene resonances shift from 7.17 to 7.27 ppm and c) the Cp* signal at 1.63 ppm belonging to [RuCp*(CH$_3$CN)$_3$](PF$_6$) becomes smaller in intensity while two new Cp* signals grow in at 1.44 and 1.45 ppm. This suggests that the p-Me-thiophenol has coordinated to the ruthenium metal centre.
Figure 2: The $^1$H NMR spectrum (250 MHz, CD$_3$CN) of a 1:1:1 mixture of [RuCp*(CH$_3$CN)$_3$](PF$_6$), diisopropylethylamine and p-Me-thiophenol (top trace) and a 1:1 mixture of [RuCp*(CH$_3$CN)$_3$](PF$_6$) and p-Me-thiophenol (bottom trace).

To characterise the new Ru(Cp*)(p-Me-thiophenol) complex, a larger scale reaction of [RuCp*(CH$_3$CN)$_3$](PF$_6$) with p-Me-thiophenol was carried out in the presence of an excess of diisopropylethylamine. A red crystalline solid was isolated and studied using a variety of 1D and 2D NMR measurements. It was found to be a mixture of two Ru(Cp*) complexes. Signals belonging to the major product (80%) were assigned to the species [RuCp*(p-Me-C$_6$H$_5$S)$_2$(CH$_3$CN)]($\text{HN}^+{\text{CHMe}_2})_2{\text{CH}_2}$CH$_3$), 8.
The $^1$H NMR arene signals and Cp* methyl signals (1.46 ppm) from species 8 correspond to the complex formed in the preceding NMR scale reaction. Integrating the signals in the $^1$H NMR spectrum reveals that the ratio of $p$-Me-thiophenol groups to Cp* and to protonated diisopropylethylamine is 2:1:1. A broad signal at ca. 6.2 ppm corresponds to the NH proton (Fig. 3). It is split into three peaks due to coupling to $^{14}$N (spin = 1). The coupling constant is 52.5 Hz which fits with reported values for one bond $^{15}$N-$^1$H coupling constants in alkylammonium ions. A correction factor must be applied to extrapolate from the $^{15}$N to the $^{14}$N nucleus. As expected, this signal shows no cross peaks in the CH correlation spectra (HMQC and HMBC).

Figure 3: Region of the $^1$H NMR spectrum (500 MHz, CD$_3$CN) showing the NH signal of the protonated diisopropylethylamine cation.

The reaction of 4 with $p$-Me-thiophenol was carried out in the presence of catalytic amounts of the crude solid containing species 8. No conversion to products occurred indicating that species 8 is not the source of the catalytic activity nor the regioselectivity when this reaction is carried out with 3 as the catalyst precursor complex and an excess of base.
5.2.2.4 The Generation of New Complexes in the Presence of \( p \)-Toluene Sulfonic Acid

When an \(^1\)H NMR spectrum was measured of a 1:1 mixture of 3 and \( p \)-toluene sulfonic acid in acetonitrile, no change in the chemical shifts of the \( \text{Cp}^* \) or allyl protons belonging to 3 was observed. Although complex 3 does not appear to react with \( p \)-toluene sulfonic acid, there is still the possibility that a sandwich complex of the type \([\text{RuCp}^*(\eta^6-p\text{Me-C}_6\text{H}_4\text{SO}_3\text{H})](\text{PF}_6)\) may be transiently formed during the allylic phenylsulfenylation reactions catalysed by 3 when excess \( p \)-toluene sulfonic acid is present.

To investigate this possibility, the complexes \([\text{RuCp}^*(\eta^6-C_6\text{H}_5\text{SO}_3\text{H})](\text{PF}_6), 9, [\text{RuCp}^*(\eta^6-p\text{Me-C}_6\text{H}_4\text{SO}_3\text{H})](\text{PF}_6), 10, and [\text{RuCp}^*(\eta^6-p\text{Cl-C}_6\text{H}_4\text{SO}_3\text{H})](\text{PF}_6), 11, were generated by allowing \([\text{RuCp}^*(\text{CH}_3\text{CN})_3](\text{PF}_6)\) to react with one equivalent of the corresponding arene sulfonic acid in acetone at room temperature.

\(^1\)H NMR spectra of the yellow solids obtained revealed signals around 6 ppm corresponding to the complexed \( \eta^6 \)-arene protons in species 9-11 plus signals between 7 and 8 ppm belonging to the free arene sulfonic acid species (Fig. 4).

With the electron withdrawing chlorine substituent in the \( para \) position, formation of the sandwich complex was not strongly favoured and the ratio of free \( p \)-chlorobenzene sulfonic acid to complexed was 1:2. The corresponding ratio for complex 9 was 1:10. With the electron donating methyl group in the \( para \) position, formation of the sandwich complex was somewhat more favoured and the ratio of free to complexed \( p \)-toluene sulfonic acid was 1:12 (Fig. 4). The more electron density in the arene ring, the greater the proportion of \( \eta^6 \)-arene complex formed.
To determine whether the η⁶-arene complex 10 is involved in the catalytic cycle when allylic phenylsulphenylations are catalysed by 3 and an excess of p-toluene sulfonic acid, the reaction of p-Me-thiophenol with 4 was carried out in the presence of catalytic amounts of 10. Since it was not possible to separate 10 from free p-toluene sulfonic acid, a quantity of the mixture was taken for the catalysis that was 3 mol % in ruthenium. After 3.5 hours, 92 % conversion was achieved and the branched to linear ratio of the products was 1.3:1. The same reaction was faster with 3 mol % of 3 alone, which goes to completion in 1 hour 35 mins (Table 2, Entry 17). This suggests that species 10 is not involved in the catalytic cycle for allylic phenylsulphenylation reactions when 3 is the catalytic precursor.

Subsequently, the catalytic activity of 10 in the allylation of indole was tested (Equation 3).
There have already been reports in the literature of the use of alcohols in the allylation of nitrogen heterocycles.\textsuperscript{20-23} These reactions are slow and frequently require the use of Lewis acid additives in substantial amounts.

The Ru(IV) complex 3 tolerates alcohols as substrates in acetonitrile solution and has been shown to catalyse the allylation of indole with allyl alcohol.\textsuperscript{24} A combination of [RuCp*(CH\textsubscript{3}CN)\textsubscript{3}](PF\textsubscript{6}) plus one equivalent of p-toluene sulfonic acid catalyses the reaction of $\alpha$-vinyl benzyl alcohol, 12, with indole (Equation 3). There is 100% conversion to products after 40 mins with a branched to linear ratio of 9.5:1.\textsuperscript{25}

The reaction of 12 with indole using 10 as the catalytic precursor, however, goes more slowly to completion (100% conversion after 2 h 45 mins) and the branched to linear ratio is poorer (1.6:1).

To summarise, complex 3 works effectively as a catalyst for the reaction of thiophenols and phenols with allyl carbonates. In these reactions, thiophenols react more quickly than phenols. The reaction of $p$-Me-thiophenol with PhCH(OCO\textsubscript{2}tBu)CH=CH\textsubscript{2}, 4, is a) made more regioselective in favour of the branched product by addition of 3 eq of diisopropylethylamine b) accelerated on addition of 3 eq of p-toluene sulfonic acid. Diisopropylethylamine has been shown to react with 3 while $p$-toluene sulfonic acid does not. However, $p$-toluene sulfonic acid will react with [RuCp*(CH\textsubscript{3}CN)\textsubscript{3}](PF\textsubscript{6}) to generate the sandwich complex 10 which has been demonstrated to be catalytically active in an allylic phenylsulfenylation reaction and in the allylation of indole.
5.3 Experimental

5.3.1 Phenolation and Phenylsulfonylation Reactions

In a typical reaction the allyl carbonate (0.07 mmol), phenol or thiophenol (0.21 mmol) and catalyst (0.0021 mmol) were dissolved in a little CD$_3$CN (total volume 0.5 mL) and transferred by syringe into an NMR tube. If required, an acid or base (0.21 mmol) was then added to the tube. The progress of the reaction was followed by $^1$H NMR. NMR spectra were normally recorded with Bruker DPX-250 and 300 MHz spectrometers. A typical spectrum is shown in Figure 5. The conversion was measured by comparing the integrals of the $t$Butyl protons belonging to free $t$BuOH at 1.27 ppm and to the carbonate group in the starting material at 1.40 ppm. In reactions where acid or base, which could destroy the carbonate group on the starting allyl substrate, was added, conversion had to be measured by comparing the integrals of the $p$-Me signals of the free and reacted $p$-Me-phenol or $p$-thiophenol. Branched to linear ratios could be determined by comparing the integrals of two isolated signals from the allyl fragments of the branched and linear products.

![Figure 5: The $^1$H NMR (300 MHz, CDCl$_3$) spectrum of the reaction of $p$-MeC$_6$H$_5$SH with PhCH(OCO$_2$tBu)CH=CH$_2$ using [RuCp*(η$^3$-CH$_2$CHCH$_2$)(CH$_3$CN)$_2$](PF$_6$) as the catalyst precursor.](image-url)
5.3.2 Synthesis of the Complexes

All reactions and manipulations were performed under an N\textsubscript{2} atmosphere using standard Schlenk techniques. The solvents and reagents were dried and distilled using standard procedures and stored under nitrogen. NMR spectra were normally recorded with Bruker DPX-250, 300 and 500 MHz spectrometers. Chemical shifts are given in ppm; coupling constants ($J$) in Hertz. Mass spectroscopic studies were performed at ETHZ.

[RuCp*($\eta^3$-CH\textsubscript{3}CHCH\textsubscript{2})(CH\textsubscript{3}CN)\textsubscript{2}](PF\textsubscript{6})\textsubscript{2}, 3\textsuperscript{21} was synthesised according to the literature procedure.

[RuCp*($p$-Me-C\textsubscript{6}H\textsubscript{4}S)\textsubscript{2}(CH\textsubscript{3}CN)](HN+{CHMe\textsubscript{2}}\textsubscript{2}{CH\textsubscript{2}CH\textsubscript{3}}), 8. [RuCp*(CH\textsubscript{3}CN)\textsubscript{3}]PF\textsubscript{6} (40.0 mg, 0.079 mmol) was dissolved in 2 mL acetonitrile then $p$-Me-thiophenol (9.8 mg, 0.079 mmol) was added. Diisopropylethylamine (0.07 mL, 0.396 mmol) was added and the pale yellow solution turned deep purple. The reaction mixture was stirred for 30 mins at room temperature after which time the solvent was reduced under vacuum. Diethyl ether was added to precipitate a brown solid (13.1 mg) which was found by $^1$H NMR to be mainly $p$-Me-thiophenol. This brown solid was filtered off and on further addition of diethyl ether to the filtrate, a red crystalline solid (27.2 mg) precipitated. This was collected, washed three times with diethyl ether and dried under vacuum. NMR studies revealed that ca. 80% of the red crystalline solid was species 8. The remainder appeared to be an unsubstituted Ru(II)Cp* complex. Yield of 8: 21.8 mg. $^1$H NMR (500 MHz, CD\textsubscript{3}CN) $\delta$ (ppm): 1.35 (m, 15H, 5 methyl groups of ammonium ion), 1.46 (s, 15H, Cp*), 2.37 (s, 6H, methyl group of $p$-Me-thiophenol), 3.19 (d of q, $J$ = 7.5 Hz, 4.5 Hz, ethyl CH\textsubscript{2}), 3.71 (m, 2H, isopropyl CH\textsubscript{2}Me\textsubscript{2}), 6.22 (1H, $J_{NH} = 52.5$ Hz, R\textsubscript{3}N$^+$H), 7.21 (d, 2H, $J = 7.5$ Hz, $p$-Me-thiophenol), 7.34 (d, 2H, $J = 7.5$ Hz, $p$-Me-thiophenol). $^{13}$C NMR (125 MHz, CD\textsubscript{3}CN) $\delta$ (ppm): 10.3 (Cp* CCH\textsubscript{3}), 16.8 (CH\textsubscript{2}CH\textsubscript{3}), 18.1 (CH(CH\textsubscript{2})\textsubscript{2}), 20.7 ($p$-CH\textsubscript{3}-thiophenol), 43.5 (CH\textsubscript{2}CH\textsubscript{3}), 55.5 (CH(CH\textsubscript{2})\textsubscript{2}), 97.1 (Cp* CCH\textsubscript{3}), 129.7 ($meta$ thiophenol carbons), 132.1 ($ortho$ thiophenol carbons), 136.5 ($ipso$ thiophenol carbon), 140.3 ($para$ thiophenol carbon). Mass Spectrometry: m/z: 843 (2Cp* 2Ru $3p$-Me-thiophenol), 719 (2Cp* 2Ru $2p$-Me-thiophenol), 629 (2Cp* 2Ru 1$p$-Me-thiophenol 1$S$).

[RuCp*($\eta^6$-C\textsubscript{6}H\textsubscript{5}SO\textsubscript{3}H)](PF\textsubscript{6}), 9. [RuCp*(CH\textsubscript{3}CN)\textsubscript{3}]PF\textsubscript{6} (59.6 mg, 0.118 mmol) was dissolved in 3 mL acetone then benzene sulfonic acid (18.6 mg, 0.118 mmol) was added. The
cloudy yellow reaction mixture was stirred for 2 h at room temperature after which time the solvent was removed under vacuum. The resulting yellow solid was washed three times with diethyl ether and dried under HV. It was found to be a 1:10 mixture of benzene sulfonic acid and 9. Yield: 60.1 mg. $^1$H NMR (400 MHz, acetone-$d_6$) δ (ppm): 1.94 (s, 15H, C$_5$Me$_5$, 9), 5.96 (m, 3H, 9), 6.22 (d, 2H, $J = 5.6$ Hz, 9), 7.53 (m, 3H, benzene sulfonic acid), 8.82 (d, 2H, $J = 7.6$ Hz, benzene sulfonic acid).

[RuCp*(η⁶-p-Me-C₆H₅SO₃H)](PF₆), 10. [RuCp*(CH₃CN)$_3$]PF₆ (60.0 mg, 0.119 mmol) was dissolved in 3 mL acetone then $p$-toluene sulfonic acid monohydrate (22.6 mg, 0.119 mmol) was added. The cloudy yellow reaction mixture was stirred for 2 h at room temperature after which time the solvent was removed under vacuum. The resulting yellow solid was washed three times with diethyl ether and dried under HV. It was found to be a 1:12 mixture of $p$-toluene sulfonic acid and 10. Yield: 54.5 mg. $^1$H NMR (400 MHz, acetone-$d_6$) δ (ppm): 1.90 (s, 15H, C$_5$Me$_5$, 10), 2.19 (s, 3H, 10), 2.34 (s, 3H, $p$-toluene sulfonic acid), 5.82 (d, 2H, $J = 5.6$ Hz, 10), 7.12 (d, 2H, $J = 5.6$ Hz, 10), 7.32 (d, 2H, $J = 7.6$ Hz, $p$-toluene sulfonic acid), 7.69 (d, 2H, $J = 7.6$ Hz, $p$-toluene sulfonic acid).

[RuCp*(η⁶-p-Cl-C₆H₅SO₃H)](PF₆), 11. [RuCp*(CH₃CN)$_3$]PF₆ (60.4 mg, 0.120 mmol) was dissolved in 3 mL acetone then $p$-chloro sulfonic acid (23.1 mg, 0.120 mmol) was added. The cloudy yellow reaction mixture was stirred for 2 h at room temperature after which time the solvent was removed under vacuum. The resulting yellow solid was washed three times with diethyl ether and dried under HV. It was found to be a 1:2 mixture of $p$-chloro sulfonic acid and 11. Yield: 64.6 mg. $^1$H NMR (400 MHz, acetone-$d_6$) δ (ppm): 2.02 (s, 15H, C$_5$Me$_5$, 11), 6.35 (m, 4H, 11), 7.73 (d, 2H, $J = 8.4$ Hz, $p$-chloro sulfonic acid), 7.32 (d, 2H, $J = 8.4$ Hz, $p$-chloro sulfonic acid).
5.4 References

Conclusions and Outlook

Following the rates of ruthenium catalysed alkylation reactions by $^1$H NMR led to the conclusion that when the coordination sphere of the metal is blocked by strongly coordinating ligands, for example Cl or chelating nitrogen ligands, such reactions are slow. To investigate these slow reaction kinetics, the rate of addition of an allyl carbonate to Ru(Cp*) complexes with bipyridine ligands was studied. Rather than forming the expected $\eta^3$-allyl complex, these reactions produce tucked-in complexes where a new C-C bond has been formed between a Cp* methyl group and the allyl moiety. This ruthenium mediated intramolecular alkylation of a Cp* methyl group is unprecedented.

Other Ru(Cp*) species with unexpected coordination chemistry were produced from the reaction of $[\text{Ru(Cp*)(CH}_3\text{CN}_3]\text{(PF}_6\text{)}$ with P(o-tolyl)$_3$. Rather than coordinate to the ruthenium metal centre through the lone pair of electrons on the phosphorus atom, the phospine ligand binds to the metal through the arene electrons of one of the o-tolyl rings resulting in the formation of a sandwich complex. Although it is known that for larger group 14 elements, arene substituents can effectively compete with the lone pair for binding to the metal centre, it is unusual to see this with phospine ligands. The fact that a small percentage (ca 4%) of sandwich complex is also formed when the ligand is the less sterically hindered P(p-tolyl)$_3$ suggests that the difference in stability constants between the sandwich complex and the phospine complex is not as large as we would have expected.

It is known that Ru(Cp) phospine complexes can catalyse the isomerisation of allyl alcohols into carbonyl compounds. The Ru(Cp*) sandwich complex with P(o-tolyl)$_3$ was tested for its catalytic activity in isomerisation reactions but was found to be a poor catalyst for this reaction. Although the literature for ruthenium catalysed isomerisations of allyl alcohols is dominated by Ru(II) species, the Ru(IV) complex $[\text{RuCp*}(\eta^3\text{-CH}_2\text{CHCH}_2\text{(CH}_3\text{CN})_2]\text{(PF}_6\text{)}$ was found an effective catalytic precursor in this transformation. Furthermore, $[\text{RuCp*}(\eta^3\text{-CH}_2\text{CHCH}_2\text{(CH}_3\text{CN})_2]\text{(PF}_6\text{)}$ was shown to be an active catalyst for allylic phenolation reactions. These allylic phenolation reactions are slow, typically taking days to go to completion. It was discovered that on moving from phenols to thiophenols as the nucleophile, the rate of reaction increases and the allylic phenylsulfenylation reactions go rapidly to completion. This prompted us to look at other reactions that are either slow or do not go at all with phenols as the nucleophiles and to try these reactions again with thiophenols.

It was found that simple allyl alcohol will react completely with thiophenol in 70 minutes in the presence of catalytic amounts of the commercially available $[\text{Ru(Cp*)(CH}_3\text{CN}_3]\text{(PF}_6\text{)}$.
This is a significant result since it was previously believed that the allyl substrate must first be equipped with a good leaving group, for example a carbonate or Cl, for facile reactions. Indeed, under the same conditions, no reaction takes place between phenol and simple allyl alcohol, although phenol will react with allyl carbonates and allyl chlorides in the presence of \([\text{Ru}(\text{Cp}^*)(\text{CH}_3\text{CN})_3](\text{PF}_6)\).

\([\text{RuCp}^*(\eta^1-\text{CH}_2\text{CHCH}_2)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2\) was subsequently shown to be an even better catalyst for allylic phenylsulfenylation reactions with allyl alcohols. Initial results demonstrate that this complex will rapidly catalyse the reaction of allyl alcohol not only with thiophenol and its derivatives but also with a number of other thiol nucleophiles. Further work is being carried out to develop other catalytic systems for these reactions and to extend the range of suitable substrates and nucleophiles.
Appendix

NMR Data for the Tucked-in Complexes

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<td>a 3.05; b 2.72</td>
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<td>54.7</td>
<td>cis 3.43; trans 2.05</td>
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<td>154.5</td>
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<tr>
<td>11</td>
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<td>137.8</td>
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<tr>
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<tr>
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<td>137.0</td>
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<tr>
<td>19</td>
<td>153.5</td>
<td>9.20</td>
</tr>
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15b

\[
\begin{array}{c}
\text{Position} & \text{\(^{13}\text{C} \text{ (ppm)}\)} & \text{\(^{1}\text{H} \text{ (ppm)}\)} \\
2 & 7.9 & 1.90 \\
3 & 8.9 & 1.35 \\
4 & 8.4 & 1.37 \\
5 & 9.4 & 2.11 \\
1 & 108.7 & \\
2 & 80.4 & \\
3 & 104.3 & \\
4 & 98.1 & \\
5 & 82.6 & \\
6 & 21.4 & 2.08; 2.12 \\
7 & 39.5 & a 3.05; b 2.77 \\
8 & 84.9 & 3.80 \\
9 & 54.80 & \text{cis 3.39; trans 2.00} \\
10 & 153.3 & 8.82 \\
11 & 127.5 & 7.46 \\
12 & 150.4 & \\
13 & 123.7 & 8.08 \\
14 & 153.9 & \\
15 & 154.0 & \\
16 & 124.0 & 8.05 \\
17 & 149.6 & \\
18 & 127.2 & 7.40 \\
19 & 152.1 & 8.93 \\
12 & 21.3 & 2.65 \\
17 & 21.2 & 2.61 \\
\end{array}
\]
Curriculum Vitae

Name: Helen Caldwell

Date of Birth: 22.06.1983

Nationality: British

