

CONTROLLING SELECTIVITY IN THE RHODIUM-CATALYSED INTERMOLECULAR HYDROACYLATION REACTION

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The work presented in this thesis was carried out between October 2008 and July 2012 under the supervision of Professor Andrew S. Weller. All of the work is my own unless otherwise stated and has not been submitted previously for any other degree at this, or any other, university.

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¹ C. Körner, E.-A. Raiber, S. E. M. Keegan, D. C. Nicolau, T. D. Sheppard and A. B. Tabor, *Tetrahedron Letters*, 2010, **51**, 6381-6383.

ABBREVIATIONS

Å	Angstrom (1×10^{-10} meters)
Ac	acetyl
AMS	accessible molecular surface
Ar	aryl
Ar ^F	[3,5-C ₆ H ₃ (CF ₃) ₂]
atm	atmospheres
β_n	natural bite angle
Bu	butyl
^t Bu	tertiary-butyl
calc.	calculated
cat.	catalyst
COD	cyclooctadiene
Cp	cyclopentadienyl
Cp*	(pentamethyl)-cyclopentadienyl
Cy	cyclohexyl
Cyp	cyclopentyl
δ	chemical shift
ΔG	change in Gibb's free energy
ΔH	change in enthalpy
ΔS	change in entropy
DMSO	dimethylsulphoxide
DPEphos	bis(2-diphenylphosphinophenyl)ether
dpp2	(1,2-diphenylphosphino)ethane
dpp3	(1,3-diphenylphosphino)propane
dpp4	(1,4-diphenylphosphino)butane
dpp5	(1,5-diphenylphosphino)pentane
dpp2-Mes	(1,2-dimesitylphosphino)ethane
dpp2- <i>o</i> -Me	(1,2-di(<i>ortho</i> -Me-C ₆ H ₄)phosphine)ethane
dpp2- <i>o</i> -Et	(1,2-di(<i>ortho</i> -Et-C ₆ H ₄)phosphine)ethane
dpp2- <i>o</i> - ⁱ Pr	(1,2-di(<i>ortho</i> - ⁱ Pr-C ₆ H ₄)phosphine)ethane

dpp2- <i>p</i> - ⁱ Pr	(1,2-di(<i>para</i> - ⁱ Pr-C ₆ H ₄)phosphine)ethane
dpp2- <i>o</i> - ^t Bu	(1,2-di(<i>ortho</i> - ^t Bu-C ₆ H ₄)phosphine)ethane
dpp2- <i>o</i> -Cy	(1,2-di(<i>ortho</i> - ^t Bu-C ₆ H ₄)phosphine)ethane
ESI-MS	electrospray ionisation mass spectroscopy
Et	ethyl
<i>fac</i>	facial
fwhm	full width at half maximum
HOMO	highest occupied molecular orbital
Hz	Hertz
ⁱ Pr	iso-propyl
<i>J</i>	coupling constant
<i>K</i> _{eq}	equilibrium constant
LUMO	lowest unoccupied molecular orbital
Me	methyl
<i>mer</i>	meridinal
Mes	mesityl
<i>m/z</i>	mass to charge ratio
NBA	norbornane
NBD	norbornadiene
NMR	nuclear magnetic resonance
Ph	phenyl
POP'	bis(2-diphenylphosphinoethyl)ether
ppm	parts per million
RDS	rate determining step
RT	room temperature
SALCs	symmetry adapted linear combinations
st. dev.	standard deviation(s)
THF	tetrahydrofuran
TOF	turnover frequency
Xphos	5,5'-oxybis(1-diphenylphosphino-2,4-dimethylbenzene)
XANTphos	4,5-bis(diphenylphosphino)-9,9-dimethylxanthene

ABSTRACT

This thesis explores the area of the intermolecular hydroacylation reaction, catalysed by rhodium diphosphine complexes. A range of latent low-coordinate rhodium diphosphine complexes have been synthesised, and their catalytic activity for the hydroacylation reaction has been investigated. In particular, emphasis has been placed on understanding how subtle changes in diphosphine steric properties affect, and can be used to control, selectivity of this catalysis.

Chapter 2 presents investigations into rhodium complexes incorporating the potentially hemilabile P-O-P ligands: POP', XANTphos and Xphos. The resulting complexes have been fully characterised and their activity for the catalytic intermolecular hydroacylation of aldehyde **I** ($\text{HCOC}_2\text{H}_4\text{SMe}$) and alkene **II** ($\text{H}_2\text{C}=\text{CHCO}_2\text{Me}$) established and compared to the DPEphos system. Further reactivity of Xphos for aromatic aldehyde **V** ($\text{HCOC}_6\text{H}_4\text{SMe}$) and alkene **II**, and aldehyde **V** and alkyne **XI** [$\text{HC}\equiv\text{CC}_6\text{H}_3(\text{CF}_3)_2$] has also been explored, and compared with the catalytic activity of $\{\text{Rh}(\text{PPh}_3)_2\}^+$.

Focus moved from potentially hemilabile ligands to chelating diphosphine ligands of the type $\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2$ (where $n = 2-5$), and then on to *ortho*-substituted bulky analogues of the type $\text{P}(o\text{-C}_6\text{H}_5\text{R})_2(\text{CH}_2)_2\text{P}(o\text{-C}_6\text{H}_5\text{R})_2$ (where $\text{R} = \text{Me}$ and $i\text{Pr}$) complexed to rhodium. Chapter 3 outlines the complexes synthesised, and their activity for the catalytic intermolecular hydroacylation of aldehyde **I** and alkene **II**, aromatic aldehyde **V** and alkene **II** or aldehyde **V** and alkyne **XI**. Possible explanations for the observed switch in selectivity from alkene to aldehyde hydroacylation, and linear alkyne to branched alkyne hydroacylation, have been explored and are detailed.

The final chapter concerns the structure of an interesting catalytic intermediate: the branched alkenyl species for the $\{\text{Rh}(\text{DPEphos})\}^+$ catalysed hydroacylation of aldehyde **V** and alkyne **XI**. Investigations into the kinetic and catalytic behaviour of this system were carried out, and a reaction scheme has been proposed which correlates well with kinetic modelling undertaken by Prof. Guy Lloyd-Jones of the University of Bristol.

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1.1 Overview

This thesis reports investigations into the synthesis, characterisation and activity of latent low coordinate diphosphine rhodium complexes as catalysts for the hydroacylation reaction. This introduction will cover the background to: fundamental steps in catalysis, pertinent to the hydroacylation reaction; general properties of rhodium, and phosphine ligands; and a short review of the hydroacylation reaction.

1.2 Selected properties of organotransition metal complexes

The use of organometallic and coordination complexes as homogeneous catalysts is widespread, including organic synthesis and industrial processes. The transition metals are particularly noted for their proficiency at forming complexes that are catalytically active. Early research by Cramer linked this phenomenon to the properties that are peculiar to transition metals: their ability to coordinate and activate C=C multiple bonds, and C-H bonds of organic molecules; and to form metal-hydrogen bonds.¹ This arises as a result of the capacity to donate and accept electrons, and can be understood by considering metal-ligand bonding (as modelled by crystal-field and ligand-field theory). Stable organotransition metal complexes usually contain 18 valence electrons or fewer; the number of valence

electrons, in combination with the number and type of ligands, dictates the coordination geometry about the metal centre. Walsh's rule for predicting the shapes of molecules states that a molecule will adopt a structure that provides the lowest energy HOMO, and is therefore the most stable configuration.^{2, 3}

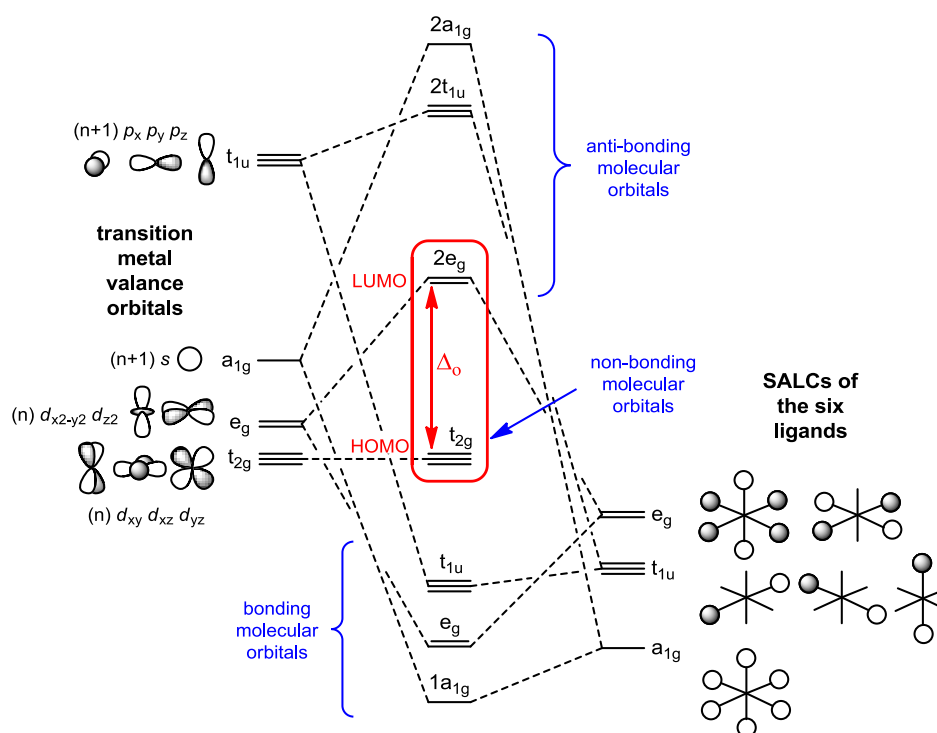


Figure 1.1: Molecular orbital diagram for a typical octahedral transition metal compound with ligands that are pure σ -donors. The frontier orbitals (HOMO and LUMO) are usually those indicated. Figure adapted from ref 4.

Figure 1.1 shows a molecular orbital diagram for the combination of a transition metal and the symmetry adapted linear combinations (SALCs) of the ligand orbitals for a simple octahedral complex with pure σ -donors.⁴ In a d^6 ion, 6 electrons from the metal and 12 electrons from the ligands will fill the bonding and non-bonding molecular orbitals of a complex, including the d_π set, but more than 18 electrons will require the occupation of anti-bonding molecular orbitals.

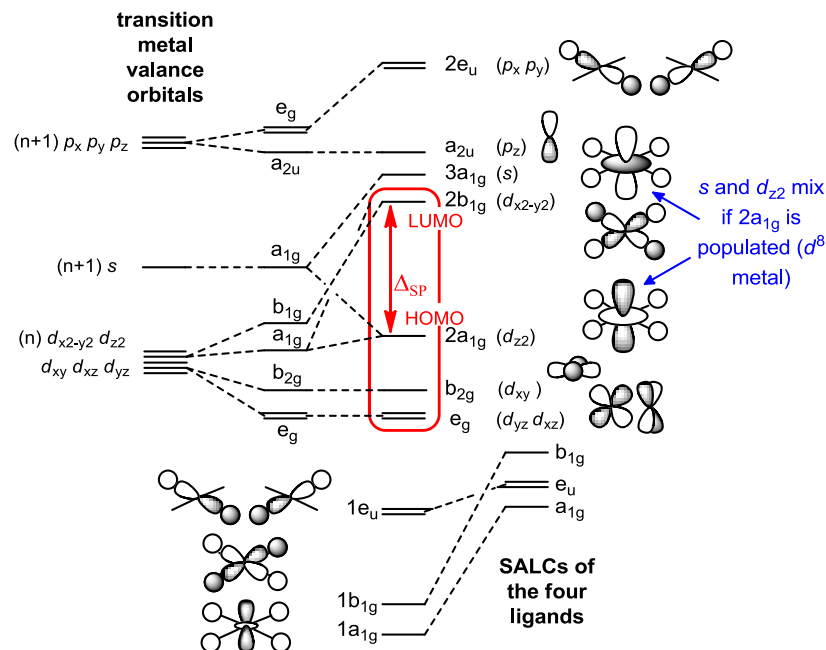


Figure 1.2: Molecular orbital diagram for a typical square-planar transition metal compound with ligands that are pure σ -donors. The frontier orbitals (HOMO and LUMO) are usually those indicated.

Figure 1.2 shows a molecular orbital diagram for the combination of a transition metal and the SALCs of the ligand orbitals for a square planar complex with pure σ -donors (derived from the free atom). When a $4d$ or $5d$ organotransition metal complex is 4-coordinate and contains 16 valence electrons, such as a d^8 ion, it can adopt a stable square-planar configuration, with mixing of the s and d_{z^2} orbitals lowering the energy of the HOMO ($2a_{1g}$). It is this ability of transition metals to access a range of relatively stable complexes of varying coordination number, oxidation number and number of valence electrons, which allows them to donate and accept electrons.

1.3 Selected aspects of the organometallic chemistry of rhodium

Rhodium (Rh $[\text{Kr}]4d^85s^1$) is one of the platinum group metals, the six transition metals most noted for their catalytic ability. These metals have the optimal ability

to interact with substrates, forming bonds which are strong enough to permit reactivity to occur, without forming inactively strong bonds; this qualitative concept is known as the Sabatier principle.^{5, 6}

Rhodium can exist in oxidation states –III $[\text{Rh}(\text{CO})_3]^{3-}$ to +VI (RhF_6),⁷ but the low spin octahedral d^6 rhodium(III) oxidation state is the most important, due to the greater Δ_o of the heavier elements, and therefore the stabilising influence of the high CFSE associated with the t_{2g}^6 configuration.⁷ With π -acceptor ligands the d^8 rhodium(I) oxidation state is also stable and well documented, usually forming 16 electron square-planar complexes.⁴ The proficiency of rhodium as a catalyst is due to this ability to change coordination number and oxidation state; particularly the capacity to access oxidation states which differ by 2 (+I and +III) and are of comparable stability, and to form bonds which are not too strong. Rhodium is a ‘soft’ metal acid (a metal that is less electropositive, with relatively full d orbitals) and so forms the most stable complexes with ‘soft’ ligands, which have empty π orbitals available to accept electron density from the metal, such as phosphorus and sulphur donors.⁷

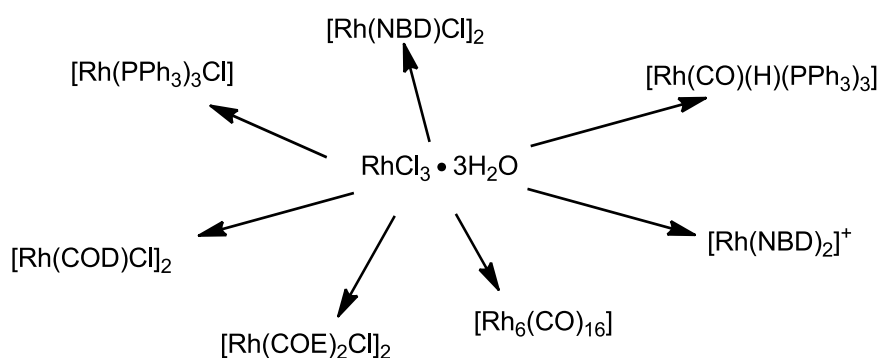


Figure 1.3: A selection of rhodium starting materials, accessed from $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ is the most common simple compound of rhodium, prepared from the metal sponge heated with KCl in a stream of Cl_2 . This compound is usually the starting point for the preparation of a wide range of rhodium precursor complexes, such as $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$,⁸ $[\text{Rh}(\text{CO})\text{H}(\text{PPh}_3)_3]$,⁹ $[\text{Rh}(\text{NBD})_2]^+$,¹⁰ $[\text{Rh}_6(\text{CO})_{16}]$,¹¹ $[\text{Rh}(\text{COE})_2\text{Cl}]_2$,¹² $[\text{Rh}(\text{COD})\text{Cl}]_2$,¹³ and $[\text{Rh}(\text{NBD})\text{Cl}]_2$,¹⁴ (Figure 1.3).

1.4 Phosphine ligands

1.4.1 Bonding in metal-phosphine complexes

Phosphine ligands are one of the most common classes of ligand in organometallic and coordination chemistry. As soft electron donors, phosphines find a good counterpart in soft low-valent metals. PR_3 monodentate ligands are one of the few series of ligands which can be systematically altered to give a wide range of steric and electronic properties.

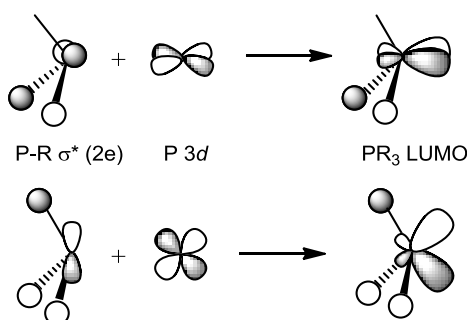


Figure 1.4: Mixing of P-R σ^* antibonding orbitals with P 3d orbitals to form PR_3 LUMO.¹⁵⁻¹⁷ Figure adapted from ref 18.

The PR_3 LUMO orbitals which interact with the metal, are formed from mixing of the P-R σ^* anti-bonding orbitals with the P 3d orbitals (Figure 1.4).^{4, 15-18} Bonding

in metal-phosphine complexes is through lone-pair electron donation from the phosphine P-R HOMO, forming a σ -bond, and π back-donation from a filled metal d_π orbital into the P-R LUMO (Figure 1.5).

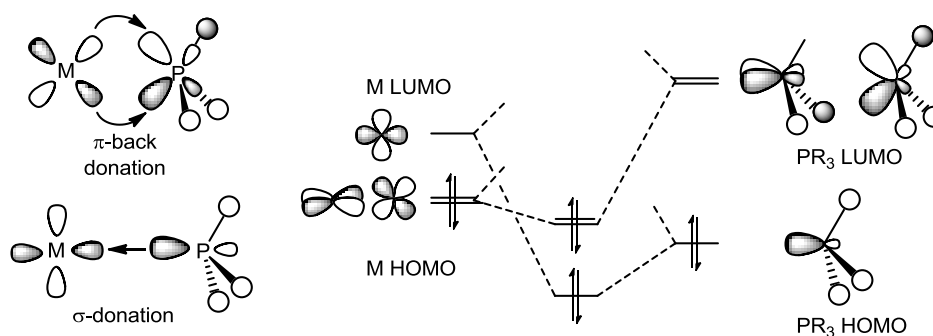


Figure 1.5: Metal-phosphine bonding occurs through electron donation from the PR_3 HOMO to the empty d_σ orbital on the metal, and back-donation from the filled metal d_π orbital to the PR_3 LUMO.

1.4.2 Steric and electronic properties of monodentate phosphine ligands

The electronegativity of the R substituents affects the energy of the P-R σ^* antibonding orbital. More electronegative R substituents stabilise both the σ and σ^* P-R molecular orbitals, providing a better match with the metal orbitals. This also affects the magnitude of back-donation from the metal (which decreases the electron density on the metal) by making the σ^* orbital more accessible (Figure 1.6). This electronic effect of the R substituent has been quantified by Tolman, who compared the ν_{CO} stretching frequencies for a range of $\text{Ni}(\text{CO})_3\text{PR}_3$ complexes (Figure 1.6).¹⁹ Stronger electron donors (with less electronegative R substituents) increase the electron density on Ni, which in turn increases the electron density back donated to the CO ligands, lowering the ν_{CO} stretching frequency. This means

that R substituents can be chosen to control the electronic nature of the metal centre.

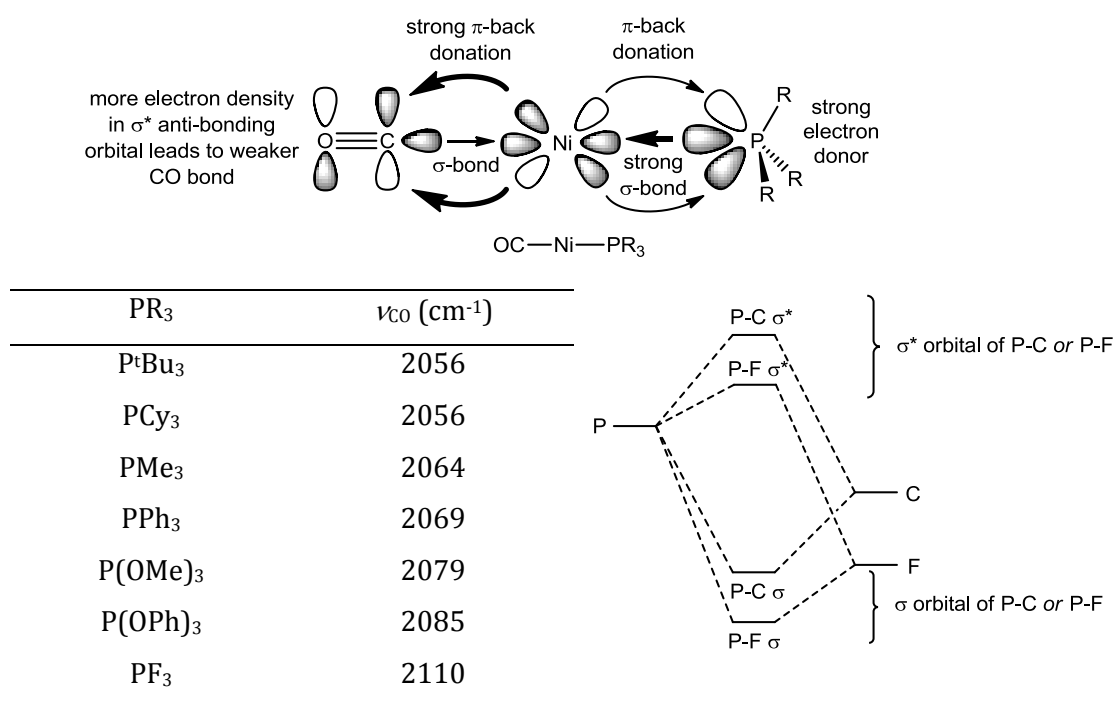
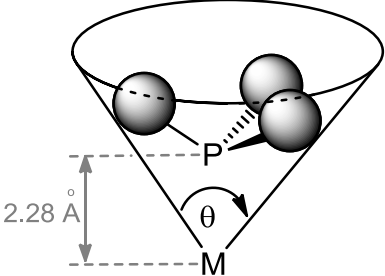


Figure 1.6: ν_{CO} stretching frequencies for $\text{Ni}(\text{CO})_3\text{PR}_3$.¹⁹ More electronegative R substituents (such as F) lower the energy of σ and σ^* orbitals of PR_3 , increasing the magnitude of back-donation from the metal.²⁰

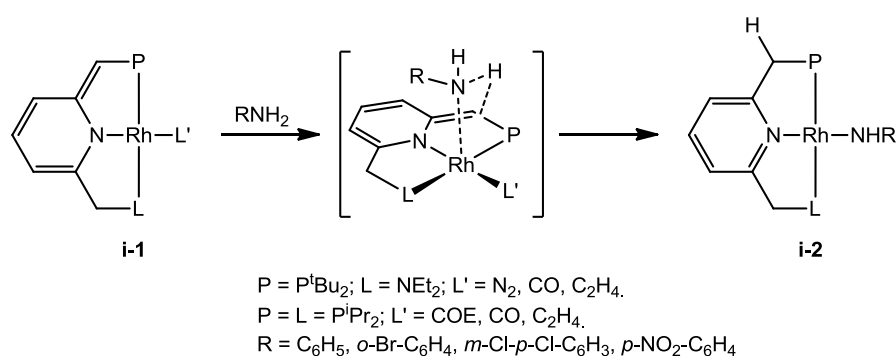
Tolman also quantified the steric effect of substituents in PR_3 ligands by measuring the angle of a cone which encompasses the steric bulk of the phosphine substituents of a space-filling model (Table 1.1). The M-P bond length was set at 2.28 Å, and free rotation around the M-P bond was assumed.¹⁹ This simple concept explains many areas of organometallic chemistry, such as why complexes of PCy_3 can only accommodate two ligands ($\theta = 180^\circ$); this ligand property can be used to access stable low valent complexes such as the 14 electron complex $[\text{Pt}(\text{PCy}_3)_2]$, which reacts readily with substrates such as H_2 , $\text{C}_6\text{H}_5\text{F}$, HOPh , HNHC_6F_5 and $\text{C}_4\text{H}_5\text{N}$, to form *trans*- $[\text{Pt}(\text{H})(\text{PCy}_3)_2(\text{R})]$.²¹

Table 1.1: Tolman cone angle parameter, and values for common PR₃ ligands.¹⁹

Tolman cone angle θ	PR ₃	cone angle (θ°)
	PF ₃	104
	P(OMe) ₃	107
	PMe ₃	118
	P(OPh) ₃	128
	PPh ₃	145
	PCy ₃	170
	P ^t Bu ₃	182

1.4.3 Chelating diphosphine ligands

Phosphines are usually spectator ligands, although examples exist of phosphine ligands displaying cooperative behaviour, such as the N-H activation of RNH₂ substrates to form [Rh(PNL)(NHR)] (**i-2**, Scheme 1.1) by [Rh(PNL*)L'] (**i-1**) [where PNL* = deprotonated PNL].²² However, even when diphosphine ligands do not participate directly in catalytic activity, they have been shown to have an impact on catalytic activity by affecting the metal coordination sphere and electronic nature of the metal complex.

**Scheme 1.1:** Phosphine ligands displaying cooperative behaviour.²²

Many attempts have been made to quantify the properties of diphosphine ligands, to rationalise the electronic and steric influence of the ligand over a reaction according to certain parameters, in a similar manner to the electronic parameter, χ , and cone angle, θ , devised by Tolman for monodentate phosphine ligands.¹⁹ A range of parameters have been devised, and include: *chelate ring size*, *pocket angle*, *accessible molecular surface* and the *ligand bite angle*.

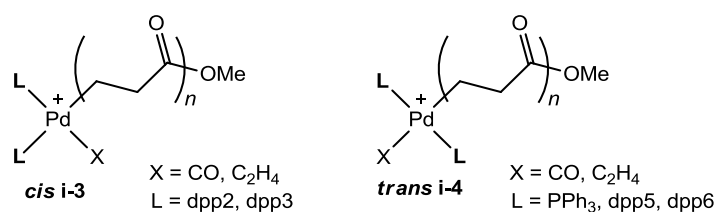


Figure 1.7: Chelate ring size determines which configuration is adopted by a ligand.

The *chelate ring size* is a simple count of the number of atoms forming the chelate-metallacycle, where the ability of the diphosphine to complex in geometries which are relevant to the catalytic cycle (e.g. square-planar and trigonal bipyramidal, *cis* and *trans*) determines which diphosphine ligand gives the best results. Ligands which can adopt a *cis* configuration form better co-polymerisation catalysts of CO and ethene, such as $[\text{Pd}(\text{L})_2\text{X}(\text{C}_2\text{H}_4\text{CO})_n\text{OMe}]^+$ (**i-3**, Figure 1.7), than ligands which adopt a *trans* configuration (**i-4**), because CO and ethene require a *cis* orientation to insert into the polymer.²³

Pocket angle was a concept introduced by Barron *et al.*, which calculates the size of the active site at a metal centre from crystallographic data, allowing for free rotation of phosphine substituents (**i-5**, Figure 1.8).²⁴

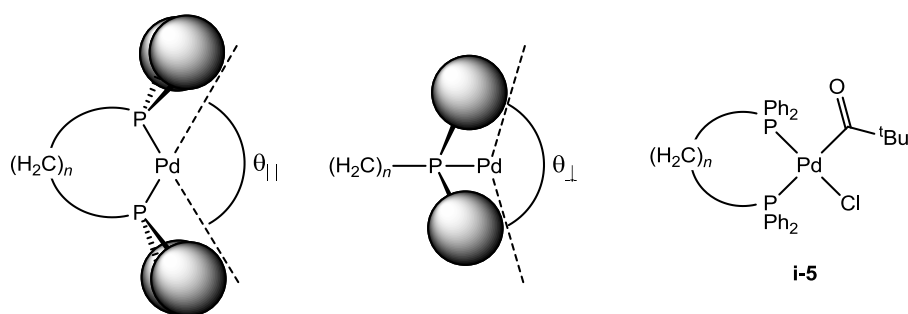


Figure 1.8: The pocket angle is measured both perpendicular ($\theta_{\perp}$) and parallel ($\theta_{\parallel}$) to the MP_2 plane.²⁴

The pocket angle is measured both parallel ($\theta_{\parallel}$) and perpendicular ($\theta_{\perp}$) to the MP_2 plane, and relates the size and shape of the active catalytic site as determined by the ligand, to the catalyst's activity, where the optimum pocket angle for a given reaction is determined by a balance of factors including the ability of a substrate to coordinate to the metal and the propensity for the catalyst to decompose.

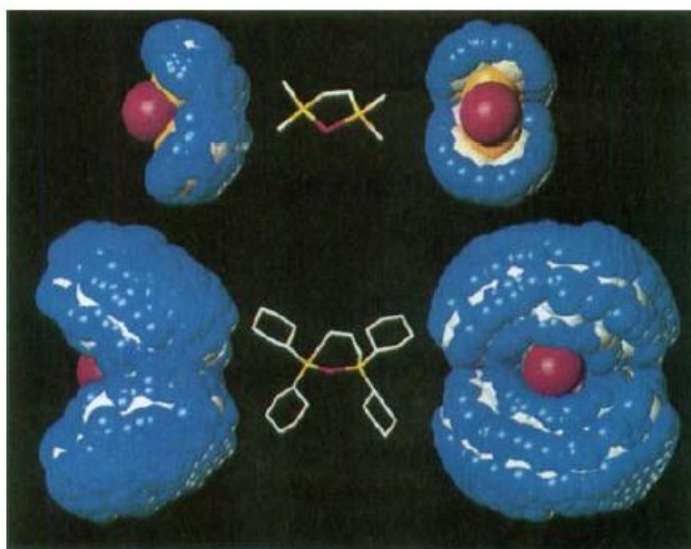


Figure 1.9: Front and side view of the van der Waals surface of the superimposed results of a full conformational search for the fragments $[P_2Rh]$ with $P_2 = dmpe$ (top) and $dpp4$ (bottom), demonstrating the accessible molecular surface. Figure reproduced from ref 25.

The *accessible molecular surface* (AMS) model was developed by Leitner *et al.* to enhance a simple steric model of a chelating phosphine, by incorporating the

super-imposed conformational dependence of the steric properties – through computation – to give a pseudo-dynamic structure of the catalyst fragment $\{\text{RhP}_2\}^+$ (Figure 1.9).²⁵ The AMS model is a useful tool for understanding the ligand effects on activity and selectivity in processes which are largely governed by steric rather than electronic factors.

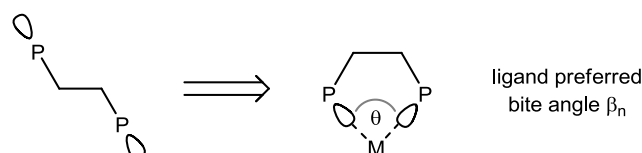


Figure 1.10: Ligand preferred P-M-P “natural bite angle” (β_n) is determined by molecular mechanics with a dummy metal atom to direct the lone pair donation.

The *ligand bite angle* is an attractively simple parameter to quantify ligand steric properties, involving just the P-M-P angle (Figure 1.10).²⁶ The natural bite angle (β_n) is the “ligand-preferred” P-M-P angle, as determined by molecular mechanics, and can be combined with the flexibility range: the range of bite angles which a diphosphine may easily adopt if conformations with energies which are slightly above the minimum structure (i.e. conformation energy ≤ 3 kcal mol⁻¹) are considered. This allows ligands to be assessed according to their ability to adopt a range of coordination modes which may occur during a catalytic cycle.²⁷ Figure 1.11 shows the conformational energies of the ligands $\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2$ (where $n = 2-5$), for a range of bite angles.²⁸ The ligands dpp2 and dpp3 form favourable 5- and 6-membered metallacycles, demonstrated in the low conformational energy at the optimal bite angles. However, these ligands have a much more restricted flexibility range in comparison to dpp4 and dpp5. In fact, the conformational energy for complexes of dpp5 increases as the bite angle widens from the

minimum at 98.9°, appearing to begin to decrease again after 130°, which suggests dpp5 may form two relatively stable conformations of significantly different bite angles, i.e. *cis* and *trans*.

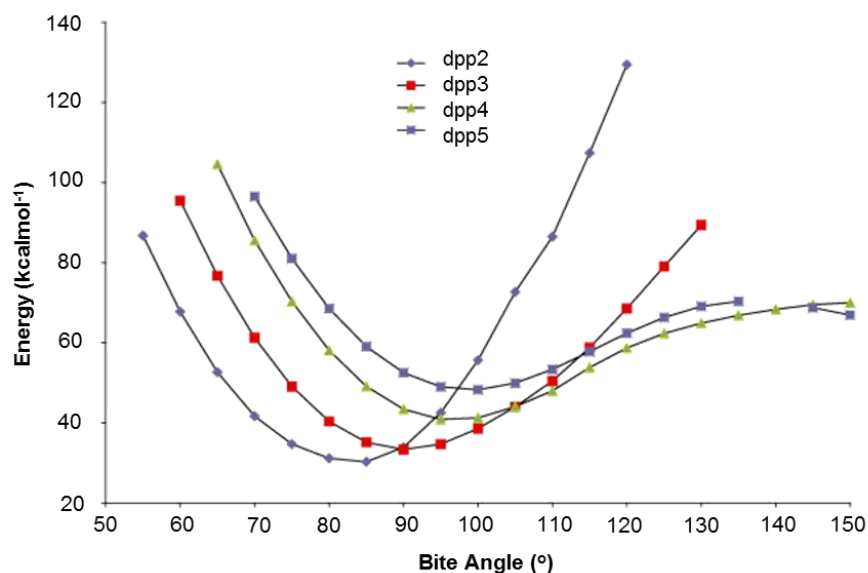
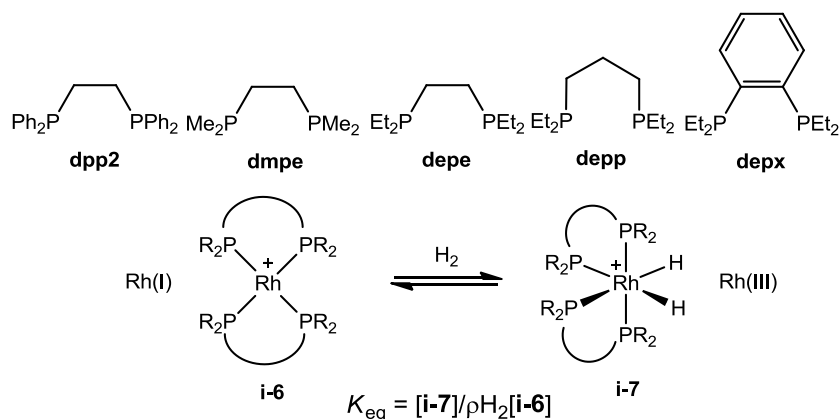


Figure 1.11: Natural bite angles (β_n) and flexibility range for the diphosphine ligands $\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2$ (where $n = 2-5$). Figure adapted from ref 28.

As discussed by Kamer and van Leeuwen,²⁹ ligands with geometrical constraints can influence the reactivity and selectivity of metal catalysts by stabilising or destabilising the initial, transition or final states. Large bite angle ligands with rigid backbones can enforce a certain coordination mode, and so influence reaction steps in the catalytic cycle where that geometry may increase the rate of reactivity, or conversely hinder it. For instance, large bite angle ligands resemble the P-M-P angle in the transition state for migration reactions, and so can accelerate the rate of migration in certain d^n configurations, particularly $d^8 \rightarrow d^{10}$.³⁰

1.4.3.1 Effect of diphosphine ligands on metal activity

An example of how ligand bite angle, alongside electronic effects of the phosphine substituents, can affect the reactivity of similar metal diphosphine complexes is provided by Dubois *et al.*, who reported a variation in the thermodynamic driving force for the oxidative addition of H_2 to complexes of the form $[Rh(\text{diphosphine})_2][CF_3SO_3]$ (**i-6**), in CD_3CN and THF solutions (Scheme 1.2).³¹ The diphosphines studied were: dpp2 (where no oxidative addition of H_2 was observed, even under 2-3 atm. of H_2), dmpe (which had an equilibrium constant for H_2 addition of $1.7 \pm 0.2 \text{ atm}^{-1}$), depe (which had an equilibrium constant for H_2 addition of $0.25 \pm 0.05 \text{ atm}^{-1}$), and both depp and depx (which showed complete oxidative addition in each case).



Scheme 1.2: H_2 oxidative addition by complexes of the form $[Rh(\text{diphosphine})_2][CF_3SO_3]$. $[CF_3SO_3]^-$ anions not shown.

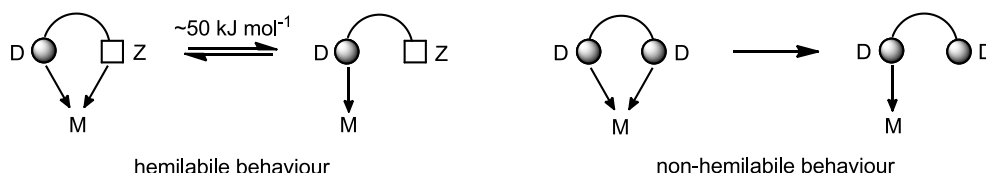
The variation in binding ability of the diphosphine complexes is attributed to a mixture of factors: how electron rich the ligand is ($dmpe > depe >> dpp2$), and the natural bite angle of the ligand ($depx > depp > depe$). A larger binding constant is observed for the diphosphine complexes with more electron rich substituents, suggesting that increasing the electron density at the metal centre favours the

oxidative addition of H₂. In addition to these electronic effects, the size of the ligand bite angle also affects the binding ability of the complex, with an increase in the natural bite angle of 78° in depp, to 90° in depx, resulting in at least a 12 kcal mol⁻¹ increase in the free energy for the addition of H₂. It is believed that the actual increase in free energy just arising from bite angle is probably somewhat larger, as ethyl substituents are better electron donors than benzyl substituents, and so the bite angle effect will be partially offset by this electronic substituent effect. The bite angle effect is attributed to the energy of the *d*⁸ square planar rhodium(I) LUMO decreasing, as bite size increases (cf. Figure 1.2). This is caused by an increasingly large tetrahedral distortion as the bite angle increases, resulting in a decrease in antibonding orbital overlap between the phosphine σ orbital and metal *d*_{xy} orbital of the complex.³² This results in a geometry which is better optimised to interact with H₂.

Research by van Leeuwen has shown that larger bite angle ligands give rise to lower activation energy barriers for the hydrocyanation reaction, catalysed by Pd(diphosphine) complexes.³³ Computational studies determined that this effect was due to electronic not steric factors. The most stable reactant square-planar complexes were formed with bite angles of close to 90°; while the most stable transition states were achieved with ligands whose bite angles were closer to 103°. Therefore the largest bite angle ligands gave the least stable reactants, and most stable transition state, thus the lowest barrier to activation.

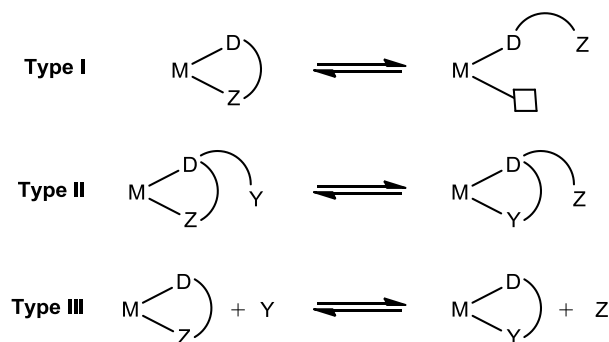
1.4.4 Hemilabile ligands

Hemilability has been classified as a property of some hybrid ligands which are able to coordinate to a metal through two or more chemically different donor functionalities, and which display reversible ambidentate chelation (Scheme 1.3). One of these functionalities must be more labile than the other, and can therefore be displaced by more strongly coordinating ligands. The energy difference between the dynamic coordination modes is often in the order of 50 kJ mol^{-1} , and so both configurations are relatively accessible.³⁴



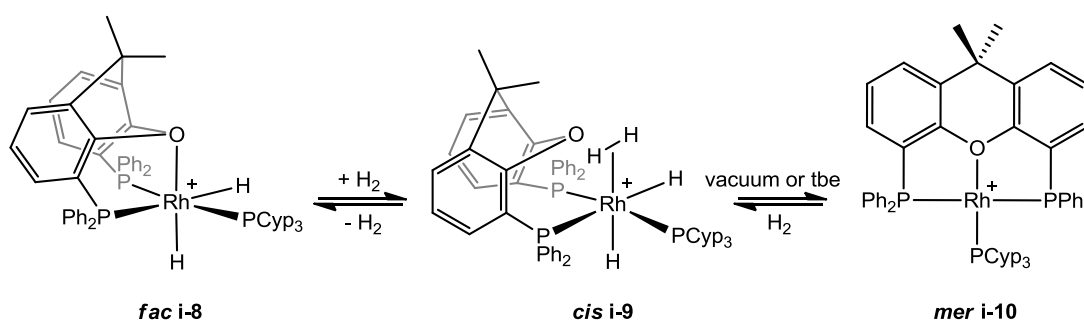
Scheme 1.3: Classification of ligand behaviour as hemilabile.

This can be used to stabilise reactive organometallic intermediates by reversibly blocking the vacant site necessary for many catalyst-deactivating reactions, such as β -elimination of alkyl-phosphine ligands, and decarbonylation of acyl ligands. The term was first coined by Jeffrey and Rauchfuss, to describe the behaviour of a phosphine-ether ligand,³⁵ which displayed ambidentate-chelation ability.



Scheme 1.4: Classification of hemilabile ligands by type.

Braunstein later classified hemilability into three categories (Scheme 1.4).³⁴ Type 1 involves the spontaneous opening of the D-Z chelate, and usually occurs with metal centres which can easily access variable coordination numbers. Type 2 corresponds to intramolecular competition with another donor function, which may be chemically identical or different. Type 3 refers to the opening of the D-Z chelate in the presence of an external reagent.



Scheme 1.5: Hemilability displayed by XANTphos ligand.

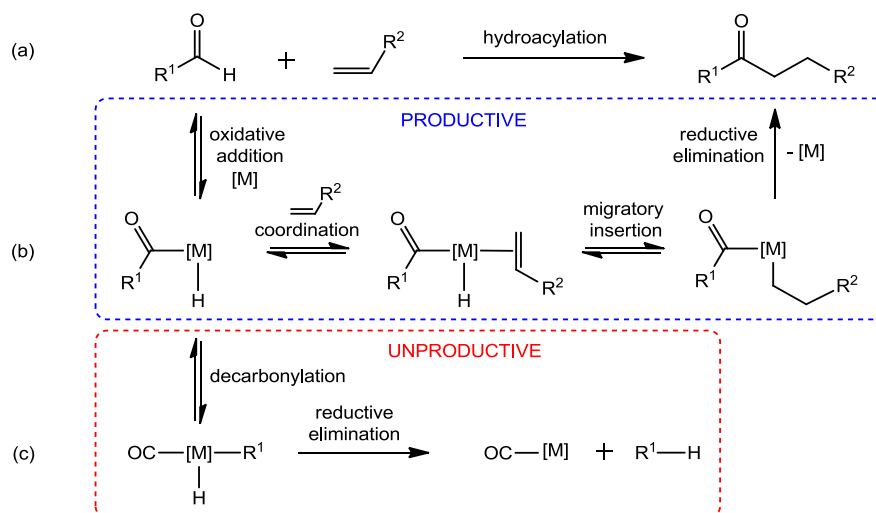
Hemilabile ligands have been used within the Weller group for their ability to vary coordination geometry (**fac i-8** and **mer i-10**, Scheme 1.5) as well as number of donor groups (**cis i-9**);³⁶ particularly in the hydroacylation reaction (*vide infra*).

1.5 Fundamental steps in catalysis, pertinent to hydroacylation

1.5.1 The hydroacylation catalytic cycle

The activation of a C-H bond in an organic molecule creates the possibility of further transformation and functionalization to give products that are often inaccessible using standard functional group interconversions.³⁷ Therefore, given

their abundance, the ability to selectively activate C-H bonds is highly desirable.³⁸
³⁹ The transition-metal-catalysed hydroacylation of alkenes and alkynes combines both C-H bond activation and C-C bond formation (Scheme 1.6a).⁴⁰



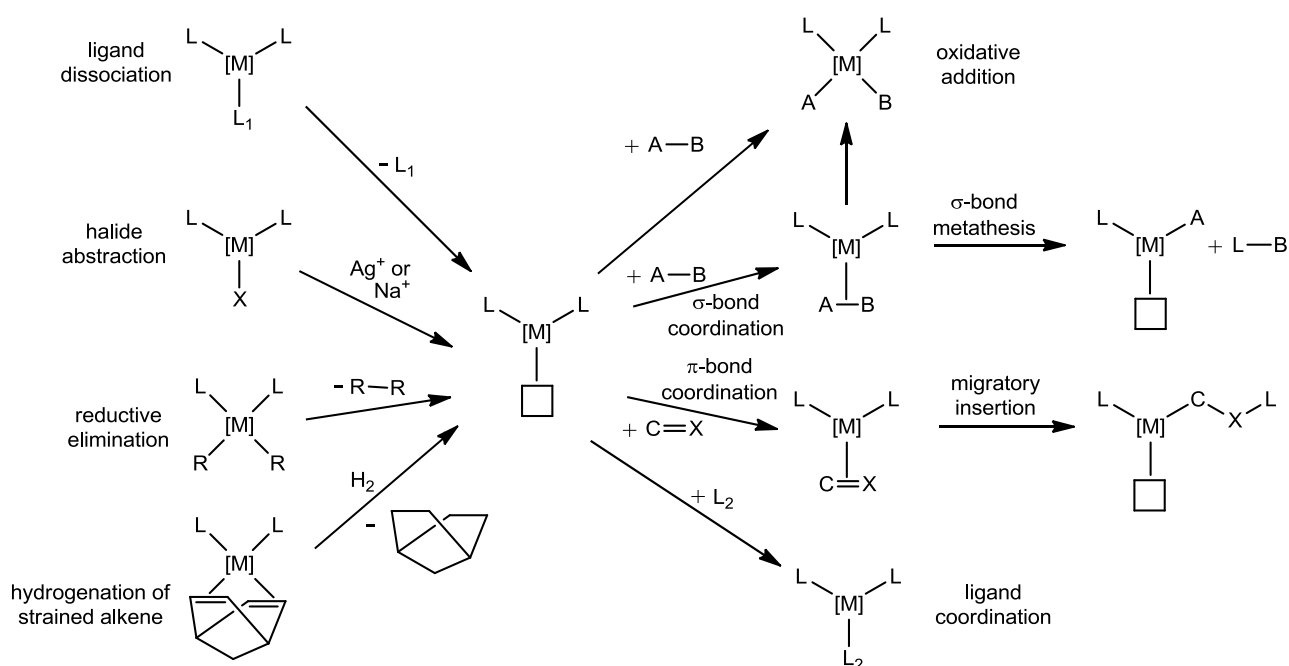
Scheme 1.6: Metal mediated intermolecular hydroacylation reaction, and unproductive decarbonylation side reaction.

The C-H bond of an aldehyde is activated to generate an acyl-metal-hydride species which then adds across a C=C multiple bond to give a product containing a ketone on reductive elimination (Scheme 1.6b). This potentially wide-ranging and atom-efficient transformation, which has no direct organic counterpart, is not yet an established synthetic route because of catalyst deactivation through the competing reductive decarbonylation reaction (Scheme 1.6c).

1.5.2 Low coordinate complexes

Before oxidative addition of an aldehyde can occur – the first step in the hydroacylation catalytic cycle – the catalyst must have the capacity to

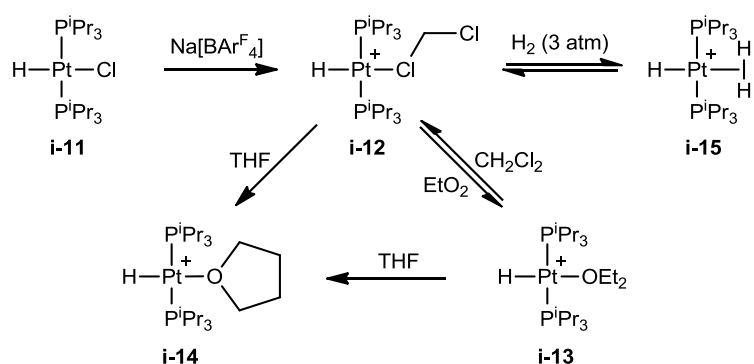
accommodate aldehyde coordination through the formation of a low coordinate species with a vacant site (Scheme 1.7). Low coordinate transition metal complexes are necessary for many fundamental catalytic steps to occur, such as oxidative addition and substrate or ligand coordination. Furthermore, low coordinate complexes are often generated through other catalytic steps, such as reductive elimination, halide abstraction and ligand dissociation. By their nature, they are coordinatively and electronically unsaturated, and therefore often highly reactive. However, isolation of latent low coordinate complexes may be achieved through the stabilising effect of weak interactions with solvent, counterion or inter- and intramolecular σ -interactions.⁴¹ These – easily displaced – interactions occupy vacant sites in the metal coordination sphere and donate electron density to the metal centre, stabilising the complex to decomposition.



Scheme 1.7: Low coordinate complexes are generated by many catalytic steps, and often required for further reactivity.

1.5.2.1 Solvent interactions

A weakly bound solvent molecule is capable of stabilising a low coordinate complex, but is easily displaced by an incoming ligand.²⁰ Examples of solvents which fulfil this role are CH_2Cl_2 , $(\text{CH}_3)_2\text{CO}$, $\text{C}_6\text{H}_5\text{F}$, 1,2- $\text{C}_6\text{H}_4\text{F}_2$ and Et_2O , demonstrated in the system below (Scheme 1.8).⁴²

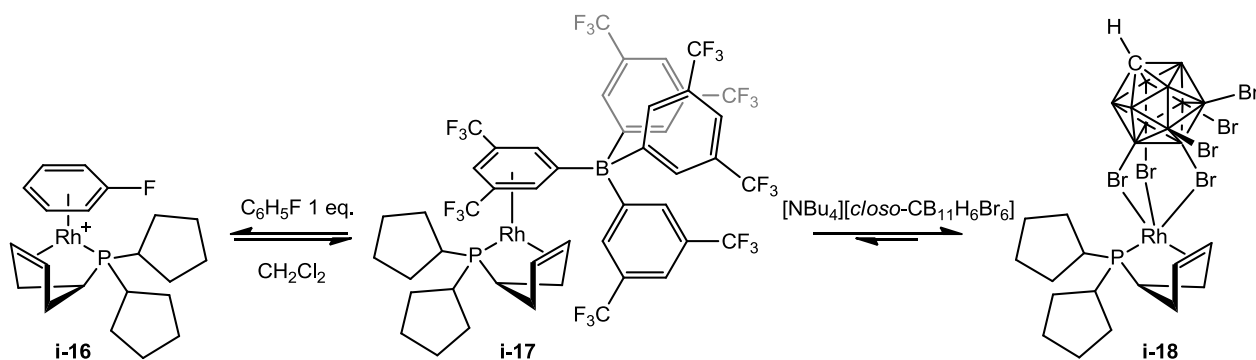


Scheme 1.8: Et_2O , CH_2Cl_2 and THF act as weakly coordinating solvents which may be displaced by H_2 . $[\text{BAr}^{\text{F}}_4]^-$ anions not shown.

Use of $\text{Na}[\text{BAr}^{\text{F}}_4]$ as a chloride abstracting agent with $[\text{Pt}(\text{P}^i\text{Pr}_3)_2(\text{H})\text{Cl}]$ (**i-11**) generates a vacant site on the metal centre which is occupied by the solvent (CH_2Cl_2) to give $[\text{Pt}(\text{P}^i\text{Pr}_3)_2(\text{H})(\text{CH}_2\text{Cl}_2)][\text{BAr}^{\text{F}}_4]$ (**i-12**), the first example of a fully characterised coordinated-dichloromethane complex (Scheme 1.8).⁴² Another example of a weakly coordinated solvent complex is $[\text{Pt}(\text{P}^i\text{Pr}_3)_2(\text{H})(\text{OEt}_2)][\text{BAr}^{\text{F}}_4]$ (**i-13**). Addition of H_2 (3 atm) to **i-12** results in the formation of $[\text{Pt}(\text{P}^i\text{Pr}_3)_2(\text{H})(\eta^2\text{-H}_2)][\text{BAr}^{\text{F}}_4]$ (**i-15**), demonstrating the lability of the CH_2Cl_2 ligand. More strongly coordinating solvents can block vacant sites and prevent further reactions, which can be used to isolate reactive intermediates, as demonstrated on addition of the more strongly coordinating solvent THF to either **i-12** or **i-13**, forming $[\text{Pt}(\text{P}^i\text{Pr}_3)_2(\text{H})(\text{THF})][\text{BAr}^{\text{F}}_4]$ (**i-14**).

1.5.2.2 Anion interactions

Many anions are optimistically classed as non-coordinating, through the negative charge being delocalised over the whole of a large molecule. Examples of some of the least coordinating anions include: $[\text{BAr}^{\text{F}}_4]^-$ [where $\text{Ar}^{\text{F}}_4 = \text{C}_6\text{H}_3(\text{CF}_3)_2$] which makes use of a central Lewis acidic atom bound to weakly coordinating ligands;⁴³ and the carborane anions $[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$ and $[\text{CB}_{11}\text{H}_{12}]^-$, which are icosahedral with σ -aromaticity and a large HOMO-LUMO gap, leading to increased stability.⁴⁴ Nevertheless, examples exist where these anions have coordinated to low coordinate metal centres (Scheme 1.9), or even undergone bond cleavage.⁴⁵ For example, the weakly coordinating borate anion $[\text{BAr}^{\text{F}}_4]^-$ is observed to coordinate to the metal centre in the neutral complex $[\text{Rh}\{\text{PCyp}_2(\eta^2\text{-C}_5\text{H}_7)\}]\{\eta^6\text{-C}_6\text{H}_3(\text{CF}_3)_2\text{B}\{\text{C}_6\text{H}_3(\text{CF}_3)_2\}_3\}$ (**i-17**) (Scheme 1.9).⁴⁶



Scheme 1.9: Examples of latent low coordinate complexes stabilised by weakly coordinating $\text{C}_6\text{H}_5\text{F}$, $[\text{BAr}^{\text{F}}_4]^-$ and $[\text{closo-CB}_{11}\text{H}_6\text{Br}_6]^-$. $[\text{BAr}^{\text{F}}_4]^-$ anion not shown for cationic complex.

Addition of $[\text{NBu}_4][\text{closo-CB}_{11}\text{H}_6\text{Br}_6]$ to **i-17** forms the weakly coordinated carborane complex $[\text{Rh}\{\text{PCyp}_2(\eta^2\text{-C}_5\text{H}_7)\}](\eta^3\text{-CB}_{11}\text{H}_6\text{Br}_6)]$ (**i-18**), which is in equilibrium with **i-17**. The $[\text{BAr}^{\text{F}}_4]^-$ anion binds more strongly than the $[\text{closo-CB}_{11}\text{H}_6\text{Br}_6]^-$ anion, but the equilibrium favours the formation of **i-18** due to a large

negative ΔS contribution resulting from dissociation and solvation of the [*closo*-CB₁₁H₆Br₆]⁻ anion. These weak anion interactions are easily displaced by addition of solvent (C₆H₅F) to give **i-16**.

1.5.2.3 σ -interactions

1.5.2.3.1 σ -complexes

A σ -complex is formed when an X-H bond coordinates to a metal centre through an intermolecular 3-centre-2-electron bond. The bond is formed from donation of the electron density in X-H bonding σ -orbital to the metal, and back donation from a filled π -orbital on the metal into the X-H empty σ^* -orbital (Figure 1.12).

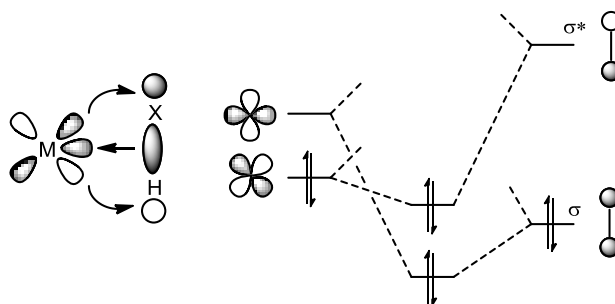
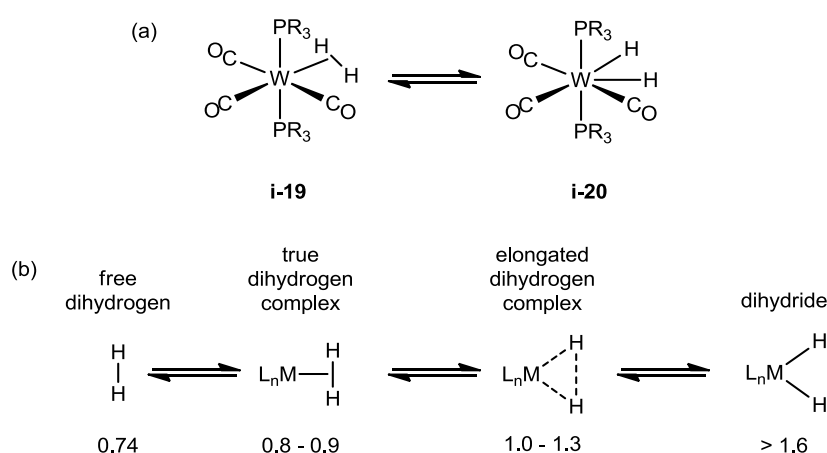


Figure 1.12: Bonding of a σ -donor to a metal. Electron donation is from the filled X-H σ bond to the empty d_σ orbital on the metal, and back-donation is from the filled metal d_π orbital to the empty X-H σ^* orbital. Figure adapted from ref 4.

Complexation of the X-H σ -bond leads to a lengthening of the X-H bond as the back donation from the metal into the X-H σ^* -antibonding orbital weakens the X-H bond, and can lead to the X-H bond breaking to form the product of formal oxidative addition, as demonstrated for H₂ binding by Kubas (Scheme 1.10b).⁴⁷⁻⁴⁹

X-H bond lengthening can be observed in the first example of a dihydrogen complex $[W(PR_3)(CO)_3(\eta^2-H_2)]$ (**i-19**), prepared by Kubas in 1984, in which the H-H bond length is 0.82 Å (by neutron diffraction), compared to the H-H bond length in free hydrogen of 0.74 Å (Scheme 1.10b).⁴⁸ This complex was also later demonstrated to undergo reversible oxidative addition of the H-H bond, forming the dihydride complex $[W(PR_3)(CO)_3(H)_2]$ (**i-20**), which is in equilibrium with **i-19** (Scheme 1.10a).⁴⁷



Scheme 1.10: (a) $[W(PR_3)(CO)_3(\eta^2-H_2)]$ (**i-19**) (where $R = Cy_3$, iPr_3) exists in equilibrium with $[W(PR_3)(CO)_3(H)_2]$ (**i-20**). (b) Elongation and cleavage of an H-H bond occurs through back-donation into the H-H σ^* -antibonding orbital (H-H length in Å).

In principle any A-X bond may coordinate to a metal centre, but σ -complexes are known only for X-H: i.e. H-H,⁴⁸ B-H,⁵⁰ C-H,⁵¹ Si-H,⁵² Ge-H⁵³ and Sn-H;⁴⁹ and C-C.^{49, 54} The first example of a σ -complex was the silane complex $[Mn(\eta^5-C_5H_5)(CO)_2(\eta^2-HSiPh_3)]$ (**i-21**), isolated by Jetz and Graham in 1971 (Figure 1.13).⁵² The isolation of the series of σ -borane complexes $[Mn(\eta^5-C_5H_4Me)(CO)_2(\eta^2-HBR)]$ (**i-22**) (where $R = B\text{-pin}, B\text{-cat}, Me_2$ or Cy_2 ; HBpin = pinacolborane, HBcat = catecholborane) by Hartwig, demonstrated that electronically saturated boranes

can accept back-donation into empty p -orbitals, which are lower in energy than H-X σ^* orbitals.⁵⁰ Genuine instances of alkane C-H σ -complexes are uncommon due to the electronically saturated, not significantly polarised, low lying orbitals of alkane C-H bonds, and so well-characterised complexes are rare. Examples of fully characterised (by NMR spectroscopy) alkane C-H σ -complexes include [Rh(PONOP)(η^2 -CH₄)] (**i-23**) [where PONOP = 2,6-(^tBu₂PO)₂C₅H₃N⁻], by Brookhart in 2009, which is only stable below -87 °C;⁵¹ and CpRe(CO)₂(η^2 (CH)-C₅H₁₀) (**i-24**) and CpRe(CO)₂(η^2 (CH)-C₅H₁₄) by Ball in 1998 and 2005.^{55, 56}

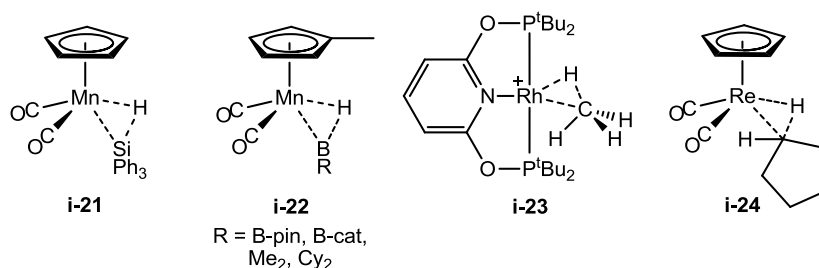
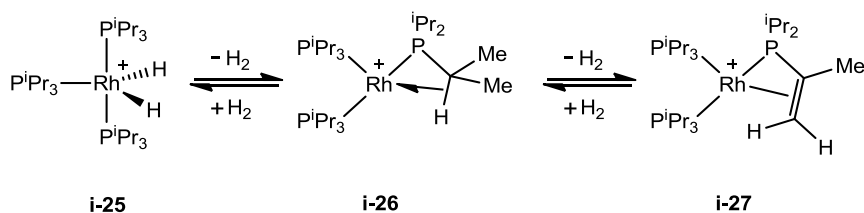


Figure 1.13: Examples of σ -complexes of Si-H,⁵² B-H⁵⁰ and C-H.^{51, 55} [BAr^F₄]⁻ anion not shown.⁴⁹

1.5.2.3.2 Agostic interactions

Donation from a σ -bond to a metal, which occurs intramolecularly between a C-H bond and the metal centre, is called an agostic interaction and has the same bonding as described in a σ -complex (i.e. 3-centre 2-electron) (Figure 1.12).⁵⁷ Agostic interactions between low coordinate metal centres and ligand C-H bonds are relatively common, providing stabilisation of the complex, and arising as a result of both steric and electronic factors.⁵⁷⁻⁵⁹



Scheme 1.11: Examples of an agostic interaction in the low coordinate complex $[\text{Rh}(\text{P}^i\text{Pr}_3)_2\{\text{P}(\eta^2\text{-C}_3\text{H}_7)\text{iPr}_2\}][\text{BAR}^{\text{F}}_4]^{60}$ (**i-26**). $[\text{BAR}^{\text{F}}_4]^-$ anions not shown.

For example, Weller *et al.* have isolated an example of a β -agostic interaction in the low coordinate complex $[\text{Rh}(\text{P}^i\text{Pr}_3)_2\{\text{P}(\eta^2\text{-C}_3\text{H}_7)\text{iPr}_2\}][\text{BAR}^{\text{F}}_4]^{60}$ (**i-26**), which can be formed by reductive elimination of H_2 from $[\text{Rh}(\text{P}^i\text{Pr}_3)_3(\text{H})_2][\text{BAR}^{\text{F}}_4]$ (**i-25**), creating a vacant site on the metal centre (Scheme 1.11). The C-H β -agostic interaction in **i-26** also undergoes spontaneous dehydrogenation to give $[\text{Rh}(\text{P}^i\text{Pr}_3)_2\{\text{P}(\eta^2\text{-C}_3\text{H}_5)\text{iPr}_2\}][\text{BAR}^{\text{F}}_4]$ (**i-27**), demonstrating that the agostic interaction may be considered as arrested oxidative addition, and in this instance followed by β -hydrogen elimination.

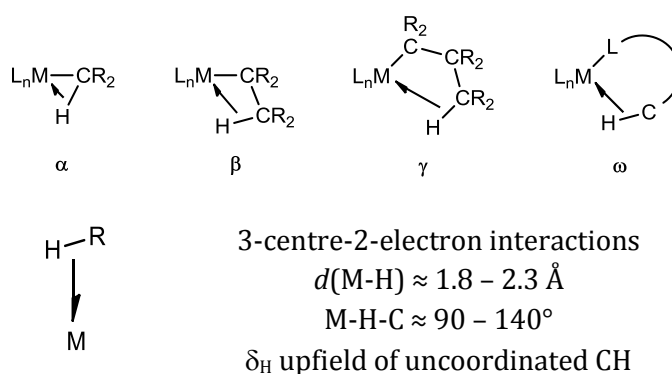


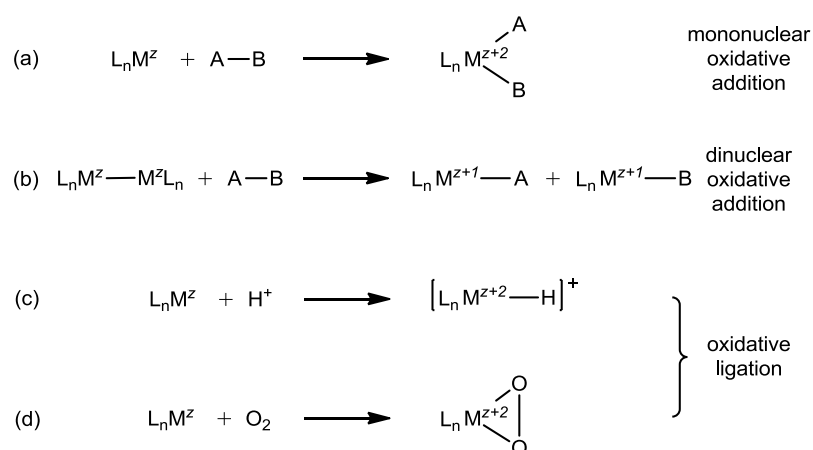
Figure 1.14: Structural and spectroscopic markers, and classification of agostic interactions. Figure adapted from ref 57.

There are several spectroscopic methods for identifying agostic interactions. In the solid state, the position of the hydrogen cannot usually be reliably identified;

however, both a short M-C distance and an M-C-X bond angle that is distorted to place the hydrogen in a position for an agostic interaction, provide compelling evidence. In solution, a reduced $\nu_{\text{C-H}}$ stretching frequency may be observed in the IR spectrum, and in ^{13}C and ^1H NMR spectroscopy an upfield shift of the carbon and hydrogen atoms involved in the interaction may also be observed (Figure 1.14).⁴

1.5.3 Oxidative Addition

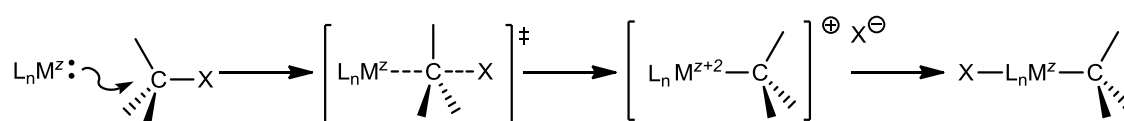
Having generated a low coordinate complex, the first step in the hydroacylation catalytic cycle is the oxidative addition of the aldehyde C-H bond, to form a metal-acyl-hydride complex (Scheme 1.6b).³⁸



Scheme 1.12: Classification of oxidative addition reactions.⁴

Mononuclear oxidative addition reactions are characterised by an increase in the metal oxidation state (by 2), an increase in the number of metal valence electrons (by 2) and an increase in the coordination number (by 2) (Scheme 1.12). As a

result, there are general trends in the reactivity of metal complexes toward oxidative addition. These include oxidative addition being favoured by more electron-rich, less-hindered metal centres, which have 16 electrons or fewer and a vacant site.⁴ Alternative methods of activation include oxidative addition by an S_N2 pathway (Scheme 1.13), by a radical mechanism, or by an ionic mechanism.⁴ However, for the purpose of this introduction, only mononuclear oxidative addition will be discussed in detail and C-H activation in particular.



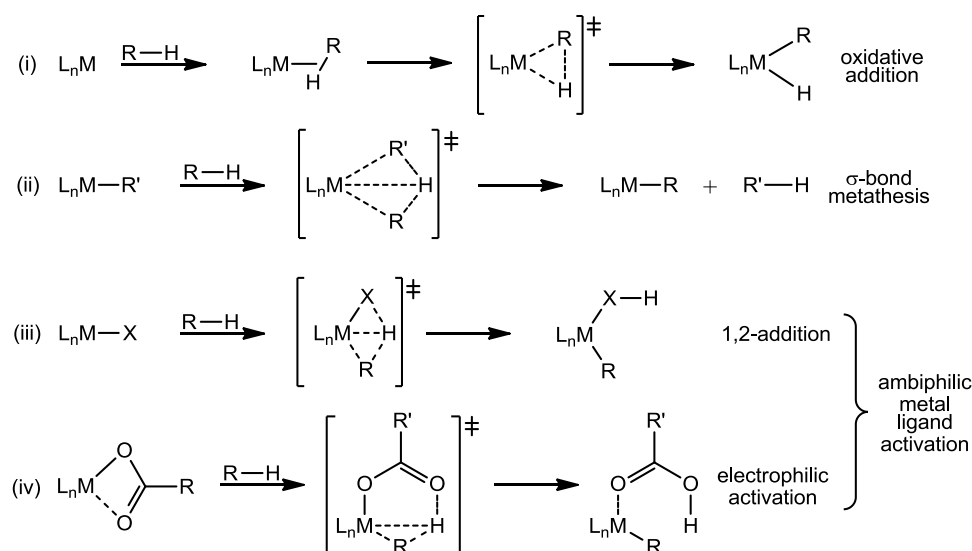
Scheme 1.13: Oxidative addition by an S_N2 pathway.

1.5.3.1 Thermodynamics of oxidative addition

For any possible reaction, the change in Gibbs free energy ($\Delta G = \Delta H - T\Delta S$) must be less than zero for the process to occur spontaneously.⁶¹ The change in entropy for a process which generates one product from two reactants – as takes place in oxidative addition – would be expected to be large and negative ($T\Delta S$ is predicted to be $\sim -10 \text{ kcal mol}^{-1}$ [-42 kJ mol^{-1}] at 293 K for a reaction of this type, which gives a ΔS value of $\sim -142 \text{ J K}^{-1} \text{ mol}^{-1}$),⁴ therefore the enthalpic contribution becomes very important in determining whether oxidative addition takes place. For any reaction to be enthalpically favourable, ΔH for the process must thus be negative. With respect to oxidative addition, this requires the strengths of the two new metal-ligand bonds to be greater than the strength of the cleaved bond.⁴

1.5.3.2 Mechanisms of C-H activation

The mechanisms by which organometallic complexes activate C-H bonds can be broadly categorised as (i) classical oxidative addition, usually at a low-valent electron-rich transition metal centres; (ii) sigma-bond metathesis, usually at electrophilic early transition metal centres; (iii) 1,2-addition in a system with a heteroatom-based group containing a lone pair of electrons to act as a proton acceptor; and (iv) electrophilic activation at an electron deficient late transition metal centre, involving a carboxylate or carbonate as a base (Scheme 1.14).⁶²



Scheme 1.14: Mechanisms of C-H activation.⁴

The activation of an aldehyde C-H bond by a transition metal complex in a low oxidation state usually generates a metal-acyl-hydride complex and is generally assumed to proceed *via* a classical oxidative addition pathway.⁶³ In concerted oxidative addition (Scheme 1.14i), an associative reaction ensues in which coordination of the C-H bond occurs first to give a σ -complex as the transition state or intermediate. The bonding and orbital interactions involved are the same

as that described in Figure 1.12 for an isolable σ -complex (or agostic complex), and indeed if the complex formed is stable, the reaction may also stop at this point.

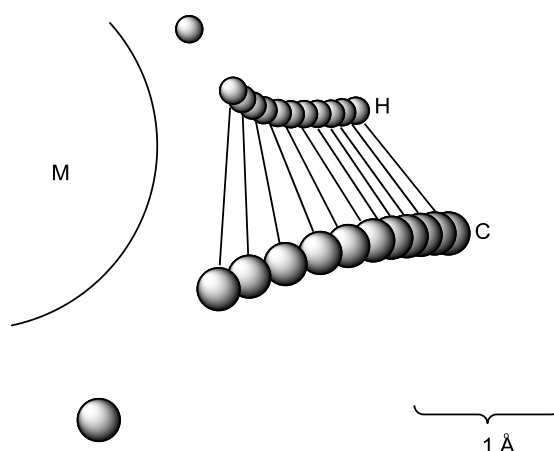
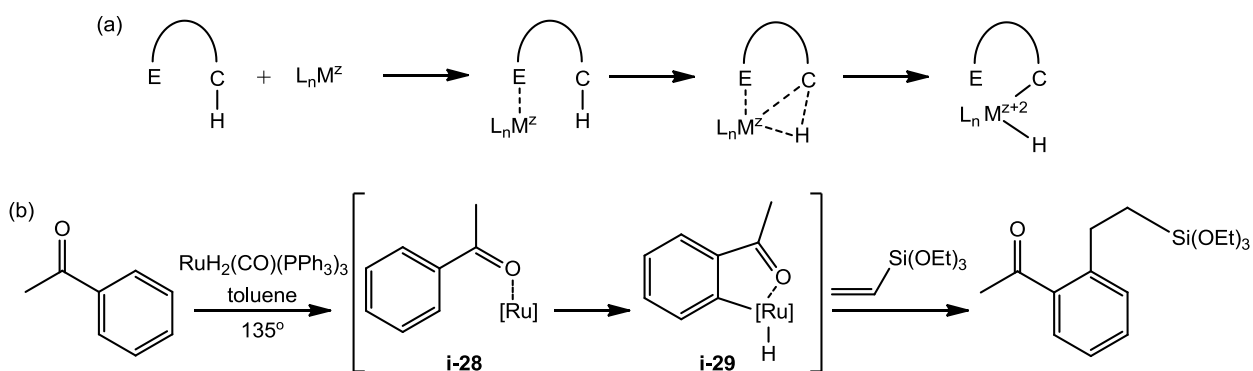


Figure 1.15: The trajectory for oxidative addition of C-H to give C-M-H, as determined by Crabtree from X-ray data for a series of agostic complexes. Figure adapted from ref 64.

Crabtree *et al.* constructed the trajectory described in Figure 1.15, for the approach and oxidative addition of a C-H bond to a metal, from X-ray data of a series of agostic complexes.⁶⁴ The H atom has a smaller atomic radius and carries no lone pairs or substituents, allowing the hydrogen end of the C-H bond a closer approach to the metal, with back-donation occurring preferentially into the lobe of the C-H σ^* anti-bonding orbital located on the H atom.²⁰ This leads to a structure which is canted, in comparison to the side-on approach of the symmetric H₂ ligand in forming a dihydrogen complex (Scheme 1.10). As oxidative addition occurs, the C-H bond rotates and elongates before cleaving to give a C-M-H complex with the ligands located *cis* to each other.

1.5.3.3 Intramolecular and intermolecular C-H oxidative addition

Intramolecular C-H activation occurs more easily than the intermolecular cleavage of a C-H bond, due to being both kinetically and thermodynamically more favourable ($\Delta S \sim 0$ for an intramolecular process), and gives rise to a more stable σ -organyl hydride complex: the product of cyclometallation.⁶⁵ A donor atom, such as O, N, P or As, may coordinate more readily to a metal centre, followed by cyclometallation through activation of a tethered C-H bond (Scheme 1.15a).⁶⁶

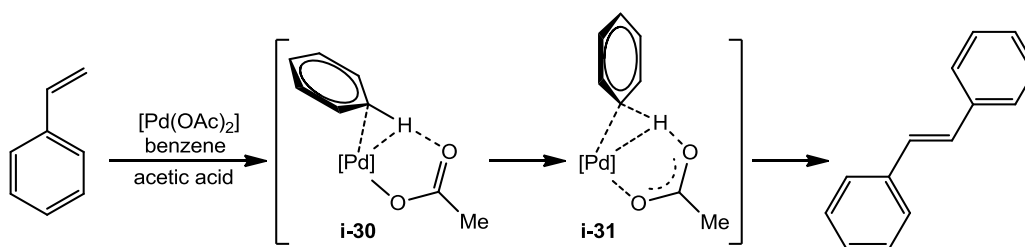


Scheme 1.15: (a) Schematic for cyclometallation (E is a donor atom e.g. O, N, P, As),⁶⁵ (b) example of cyclometallation.⁶⁷

This is observed in the *Murai* reaction, where initial coordination of the substrate is *via* the ketone (**i-28**), oxidative addition of a C-H bond generates a cyclometallated complex (**i-29**) and the resulting σ -aryl is functionalised by addition across a vinylsilane C=C bond (Scheme 1.15b).⁶⁷

Examples of complexes containing M-C σ -bonds, formed from intermolecular C-H activation, do exist and can be derived from alkanes, arenes, alkenes and monosubstituted acetylenes.⁶⁵ The activation of arene C-H bonds is favoured over

alkane C-H bonds both thermodynamically – despite arene C-H bonds being stronger than alkane C-H bonds – and kinetically. The thermodynamic driving force for arene C-H activation over alkane C-H activation is due to the difference in metal-aryl and metal-alkyl bond strength being greater than the difference in aryl C-H and alkyl C-H bond strengths. The kinetic contribution has been attributed to factors such as the ability of the arene to form an η^2 -coordinated complex (therefore mimicking an intramolecular reaction), and the greater steric accessibility of an arene C-H bond.⁴



Scheme 1.16: C-H activation assisted by a co-ligand.

Oxidative addition of a C-H bond, where the activation is assisted by a co-ligand, can also be known as intermolecular C-H activation, or ambiphilic metal ligand activation (Scheme 1.14, iii and iv).⁶² PdCl_2 was used to catalyse the coupling of benzene with an alkene in acetic acid, and experimental results determined the necessity for the presence of a carboxylic acid.⁶⁸ Theoretical studies on this system indicated $[\text{Pd}(\text{OAc})_2]$ as the more likely catalyst, with C-H activation occurring *via* displacement of one of the bidentate acetate's donor atoms (**i-30**, Scheme 1.16), with the formation of a strong O-H bond helping to drive the reaction (**i-31**).⁶⁹ This resembles the heterolytic activation of X-H bonds, assisted by a heteroatom-ligand capable of acting as an H-acceptor.

1.5.4 Olefin Coordination

Once the aldehyde C-H bond has oxidatively added to the metal centre, forming an acyl-metal-hydride complex, the next step in the hydroacylation catalytic cycle is coordination of the olefin (Scheme 1.6b). Most ligands form an M-L σ bond by donation of a lone pair of electrons, often the HOMO and therefore most basic electrons in the molecule. A different type of ligand, in which the M-L σ bond is formed by donation from a H-X σ bond to the metal, forming a σ -complex or agostic complex, has already been discussed.

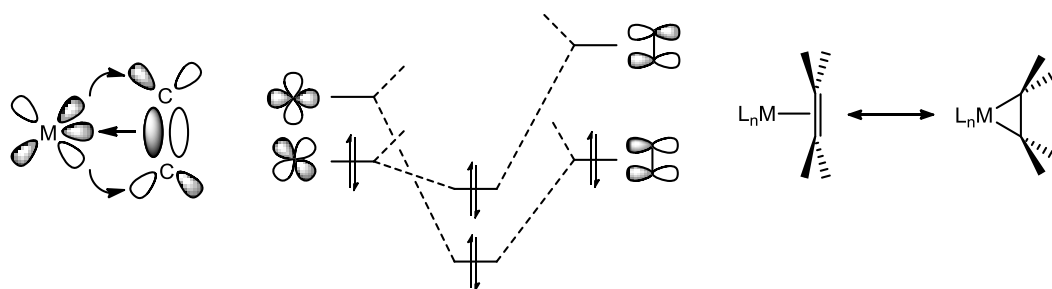
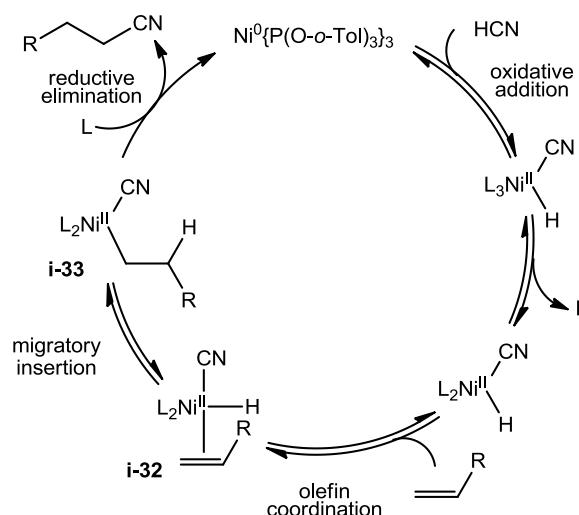


Figure 1.16: Bonding of a π -donor (e.g. ethene) to a metal. Electron donation is from the filled C=C π bond to the empty d_σ orbital on the metal, and back-donation is from the filled metal d_π orbital to the empty C=C π^* orbital. Figure adapted from ref 4.

Another type of ligand, found in organometallic chemistry, forms a π -complex through donation of the electron density in the (usually C=X) π -bond, to the metal centre.⁴ These complexes form in a similar manner to σ -complexes, with significant back-donation from the metal filled d_π orbital, to the π^* anti-bonding orbital of the C=X (Figure 1.16), observed as an elongation of the C=X bond length in solid state structures as the bond order decreases. An example of this decrease in bond order is observed in the solid state structure of $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-H}_2\text{C=CH}_2)]$ with a bond distance of 1.43 Å that falls between a C-C double (~ 1.34 Å) and C=C

single bond ($\sim 1.54 \text{ \AA}$).⁴ A rehybridisation from sp^2 to sp^3 can also occur and is observed as a distortion of the C=C substituents away from a planar geometry.

Several factors affect the magnitude of σ -donation and π -acceptance in a π -complex, including the electronic nature of the metal (electron-rich/poor) and any C=X substituents (electron-donating/withdrawing), with electron-rich metal centres binding more strongly to C=X with electron-withdrawing substituents and *vice versa*.⁴ Metal complexes in which the metal has a formal oxidation state higher than +1, or has a d^0 electron count, tend to form less stable π -complexes and so are less common (although Zeise's salt was one of the first reported organometallic complexes);⁷⁰ however, they are important intermediates in the many catalytic processes including the hydrocyanation of olefins (**i-32**, Scheme 1.17), and olefin polymerisation. Dienes capable of bidentate chelation, form particularly stable complexes which are often used as precursor complexes, such as $[\text{Rh}(\text{NBD})\text{Cl}]_2$.¹⁴



Scheme 1.17: Hydrocyanation of olefins, by $\text{Ni}\{\text{P}(\text{O}-o\text{-Tol})_3\}_3$, showing $\text{Ni}(\text{II})$ coordinated-olefin intermediate (**i-32**). Figure adapted from ref 4.

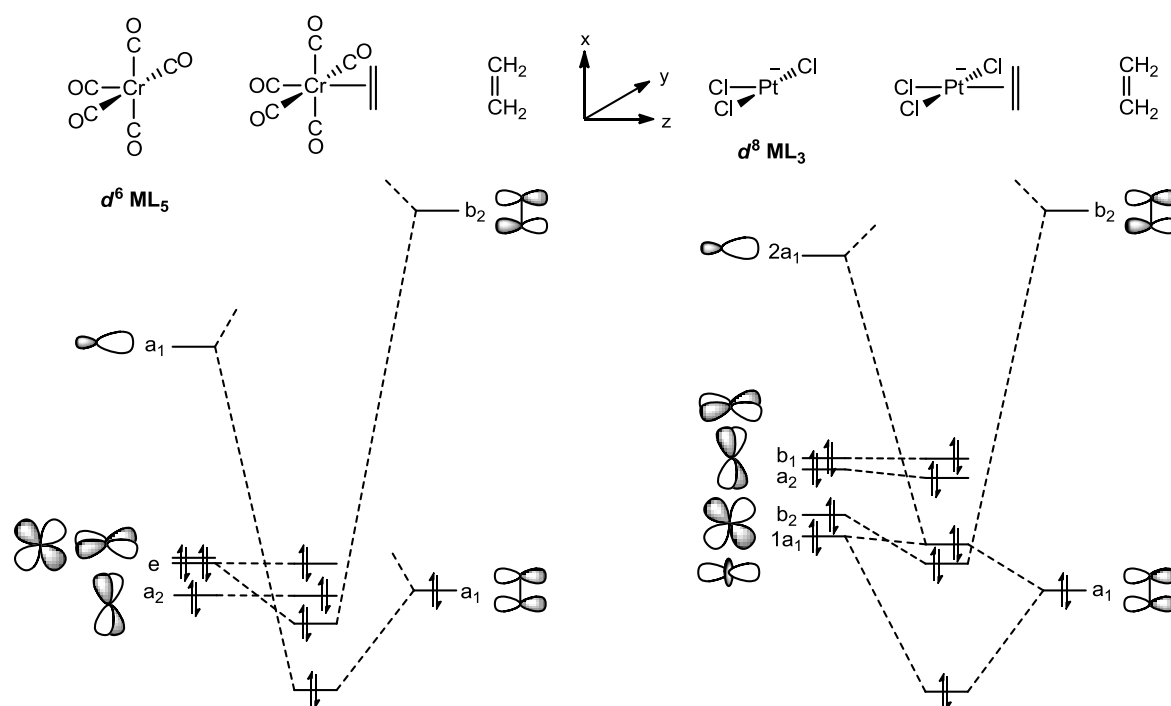


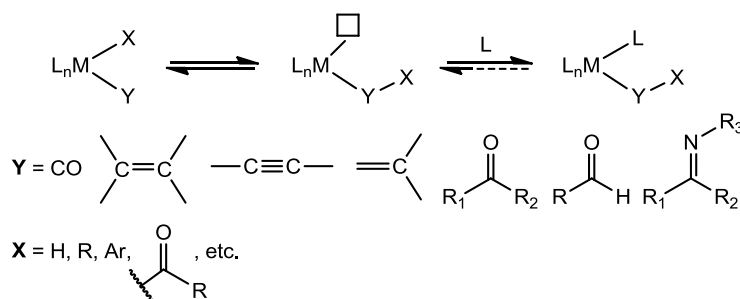
Figure 1.17: Bonding of ethane to a d^6 ML_5 fragment, and a d^8 ML_3 fragment. Figure adapted from ref 71.

Sterics and electronics have a large effect on the orientation the C=C ligand in π -complexes, as outlined in the Dewar-Chatt-Duncanson model.⁷² There is often an orientation of the olefin, relative to the other ligands at the metal, which is more stable; although the barrier to rotation about the M-C=C bond axis is often relatively low (~ 10 -25 kcal mol⁻¹ or ~ 42 -105 kJ mol⁻¹).⁴ The orientation of the metal HOMO which would donate electron density into the C=C π^* anti-bonding orbital has some impact on the final orientation of the olefin ligand. But, as can be seen in Figure 1.17, the b_2 symmetry of the C=C π^* anti-bonding orbital would achieve reasonable overlap with the b_1 orbital of the ML_3 fragment if the olefin were orientated 'in-plane' i.e. along the y-axis, yet steric repulsion by the chloride ligands favours the 'upright' orientation. Likewise, the b_2 symmetry of the C=C π^* anti-bonding orbital would achieve reasonable overlap with a linear combination

of the e set of orbitals in the ML_5 fragment if the olefin were rotated 45° ; however, this orientation is disfavoured by a large repulsion between the ethylene π and $ML_5 a_2$ orbitals.⁷¹

1.5.5 Migratory Insertion

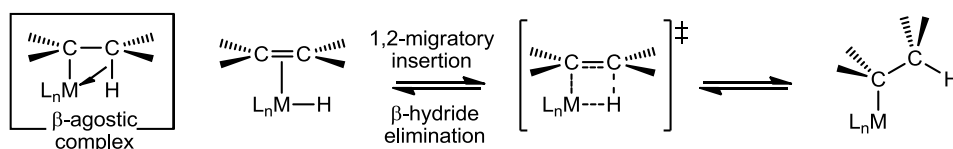
After olefin coordination has taken place, the penultimate step of the hydroacylation reaction is insertion of the olefin into the metal-hydride bond. The migration of an unsaturated ligand (Y) within the coordination sphere of the metal, into a metal-ligand bond (M-X) which is *cis* to Y, is common to all the transition metals and is called migratory insertion (Scheme 1.18).⁴ It is distinct from electrophilic or nucleophilic attack on the M-Y bond.



Scheme 1.18: Migratory insertion of an unsaturated ligand (Y) into a *cis* metal-ligand bond (M-X). Figure adapted from ref 4.

Many large-scale industrial processes involve migratory insertion, such as hydroformylation (1,1-migration of alkyl onto a metal-CO bond) and olefin hydrogenation (1,2-migration of hydride onto a metal-alkene bond).^{4, 20} Migratory insertion reactions lead to a change in coordination number (a vacant site is generated) and valence electron count; however, there is no change in the metal

oxidation state. Migration may occur by Y inserting into the M-X bond, or X may migrate onto the coordinated Y group, to give the same product, but located in different coordination sites on the metal. The 1,2-migratory insertion step for an olefin into a metal-hydride bond is intramolecular, and is fastest when the metal, olefin carbons and hydride are co-planar, forming a four-centred transition state (Scheme 1.19). This transition state is related to a β -agostic complex, to give *syn*-addition, retaining the stereochemistry at both carbons. Migration of a hydride onto the Ni-alkene bond takes place in the hydrocyanation of olefins, by $\text{Ni}\{\text{P}(\text{O}-o\text{-Tol})_3\}_3$ (**i-32** $\rightarrow$ **i-33**, Scheme 1.17).⁴



Scheme 1.19: Mechanism of migratory insertion, *via* a four-centred transition state, which is comparable to a β -agostic complex.^{4, 20}

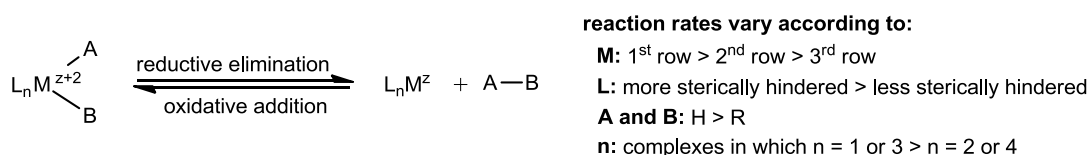
1.5.6 Reductive Elimination

The final step of the hydroacylation catalytic cycle is reductive elimination of the alkyl and acyl groups forming a new C-C bond in the ketone product (Scheme 1.6b). Reductive elimination is the reverse process of oxidative addition, and so the reaction takes place *via* the same intermediates and transition states for the same substrates. Both classes of reaction exist in equilibrium with each other; however, thermodynamics will always favour the reaction in one direction over the other. The mechanism by which the process occurs varies according to the

metal centre and ligands undergoing reductive elimination. In *mononuclear* reductive elimination the metal centre decreases in oxidation state and coordination number by 2, and the number of *d* electrons increases by 2; these are the opposite of the changes which occur in *mononuclear* oxidative addition.

1.5.6.1 Factors affecting rates of reductive elimination

The steric and electronic factors which disfavour oxidative addition, instead favour the reductive elimination process (Scheme 1.20). The reductive elimination process increases the electron density at the metal centre, so is usually favoured by electron-poor metals, depending on the energy of the molecular orbitals which the electrons will go into.⁴ A sterically hindered metal centre usually increases the rate of reductive elimination due to relief of steric congestion on release of the product, provided the necessary geometry of the transition state can be achieved.^{73, 74}



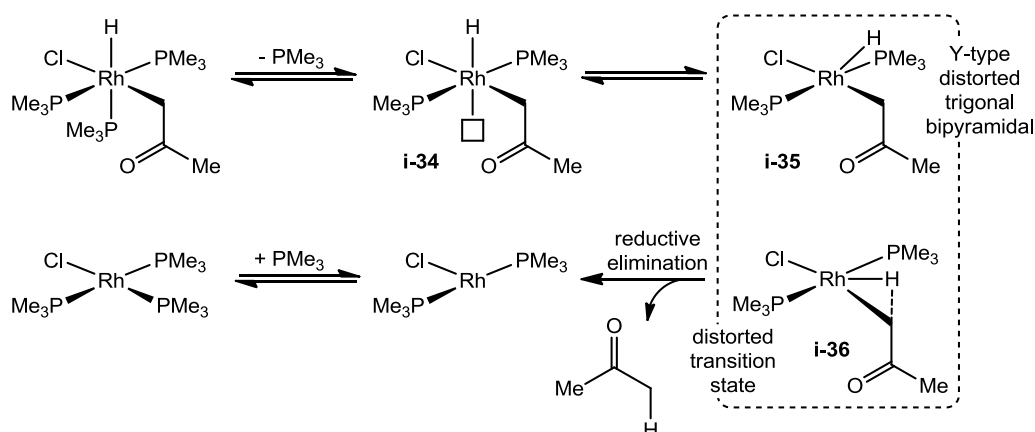
Scheme 1.20: Factors affecting the rates of reductive elimination.⁴

Steric hindrance may occur on ancillary ligands as well as the ligands undergoing the bond forming reaction. However, the properties of the participating ligands which stabilise the transition state for the oxidative addition reaction provide the same stability for the reverse process. In the same way that C-H activation occurs more readily than C-C activation, there is an increased rate of reductive

elimination in C-H bond forming reactions over C-C bond forming reactions, demonstrated in *cis*-[Pt(H)(CH₃)(PPh₃)₂], which undergoes reductive elimination at -25 °C, while *cis*-[Pt(CH₃)₂(PPh₃)₂] is stable to 237 °C.⁷⁵ One explanation for this is the better overlap between an H *s* orbital and C *sp*³ hybridised orbital than occurs between two directional *sp*³ hybridised orbitals.⁷⁶ Two more factors affecting the rate of reductive elimination are geometric considerations: the coordination number and location of the participating ligands, which will be discussed in the following section.

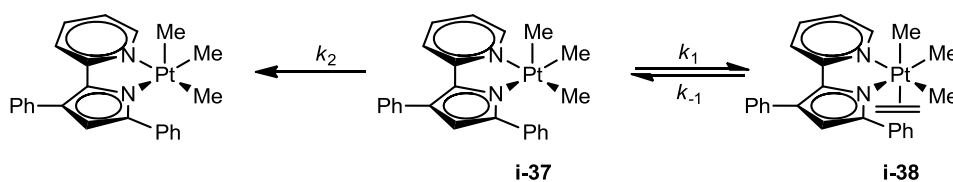
1.5.6.2 Mechanism of reductive elimination from 6-coordinate octahedral complexes

Kinetic and mechanistic studies undertaken by Puddephatt, Milstein, Crabtree, and Goldberg, have shown that reductive elimination in a 6-coordinate octahedral transition metal complex proceeds *via* a significantly distorted transition state (**i-36**, Scheme 1.21) which is accessed from an 5-coordinate Y-type distorted trigonal bipyramidal geometry (**i-35**), requiring initial dissociation of a ligand (**i-34**).⁷⁷⁻⁸¹



Scheme 1.21: Mechanism for reductive elimination from Milstein's 6-coordinate octahedral transition metal complex.^{20, 81, 82}

Furthermore, studies on the effect of different solvents on C-C reductive elimination from *fac*-[(L₂)Pt(Me)₃(py)]OTf, by Goldberg, demonstrated no solvent dependence on switching from acetone, to THf, to benzene, only a reaction rate which was inversely proportional to the concentration of pyridine.⁸⁰ This indicates the 5-coordinate complex, formed on dissociation of pyridine, remains unsaturated during reductive elimination. An exception to this rule is reductive elimination of H₂, which undergoes reductive elimination readily in *cis*-hydride 6-coordinate complexes such as [Ir(^tBuPNP)(CO)*cis*(H)₂]₂PF₆.⁸³ In fact H₂ elimination is promoted in *d*⁶ 5-coordinate bis-hydride complexes by ligand association.⁸⁴ Generally though, when ligand dissociation does not occur from a 6-coordinate complex, reductive elimination is very slow, even if the bond forming reaction is favourable and the ligands are located *cis* to each other. Likewise, if the ligands undergoing the bond forming reaction are located *trans* to each other the complex must first isomerise to give the *cis* configuration, leading to slower rates of reductive elimination.

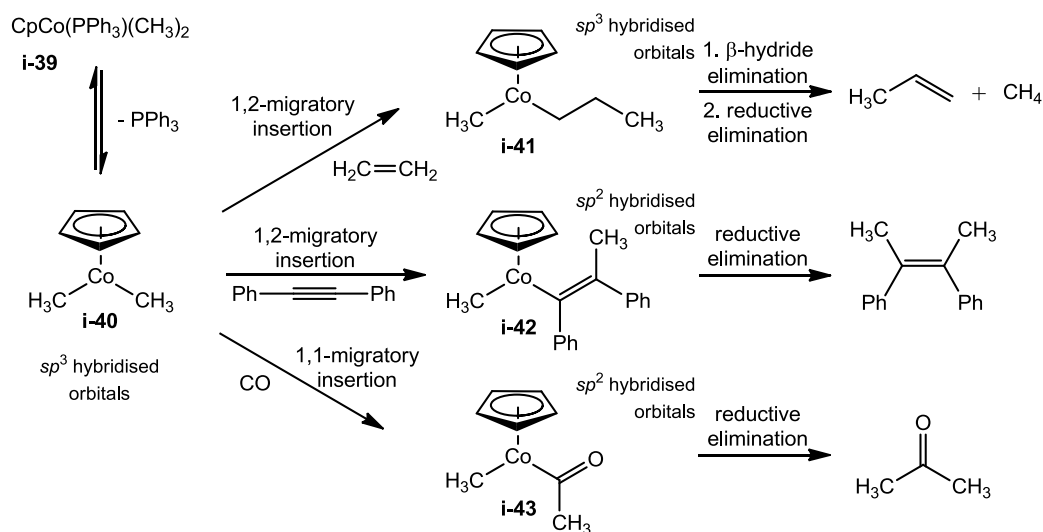


Scheme 1.22: Reductive elimination occurs from a 5-coordinate complex, and is inhibited by ethylene coordination.

Goldberg obtained a value for the rate of reductive elimination of ethane from the complex (LX)PtMe₃ (**i-37**) [where LX = 3,5-diphenyl-2-(2-pyridyl)pyrrolide] (Scheme 1.22).⁷⁹ Reductive elimination only occurred from the 5-coordinate complex requiring dissociation of ethene from **i-38**.

1.5.6.3 C-C bond forming reductive elimination

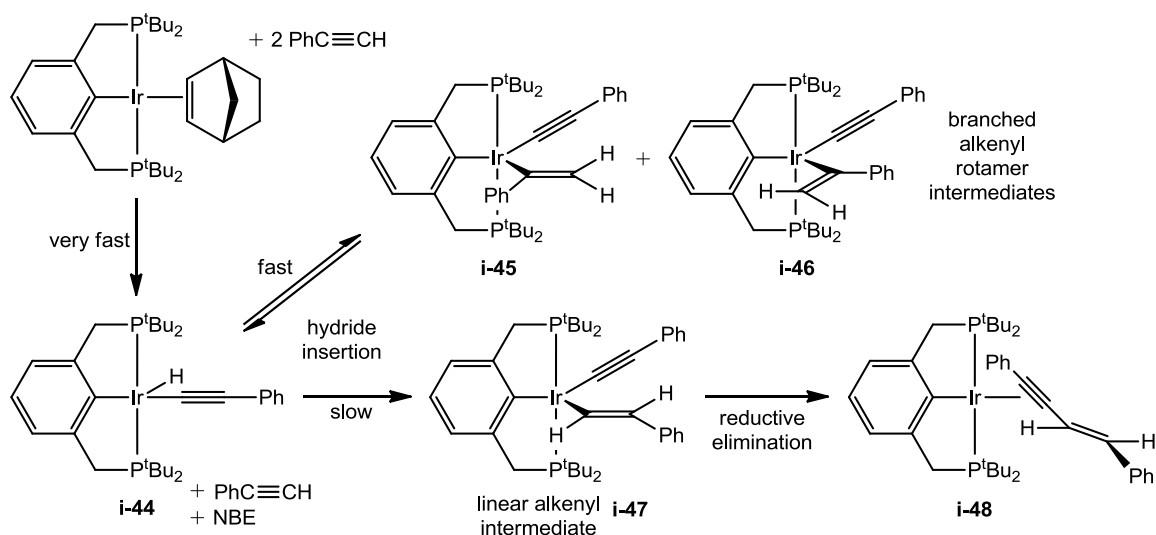
C-C bond forming reductive elimination usually occurs *via* a concerted mechanism, therefore requiring a *cis* coordination geometry.⁸⁵ The transition state is higher-energy than the equivalent transition states for C-H bond forming reductive elimination. Furthermore, reductive elimination involving sp^2 hybridised carbon atoms is usually *via* a lower energy transition state than is accessed in the elimination of sp^3 hybridised carbon atoms. This is thought to be due to the less directional nature of the orbitals involved, while also creating less steric hindrance during the distorted transition state. Likewise, the π -system of unsaturated ligands such as acyls, aryls and vinyls, is thought to be able to interact with the metal to lower the energy of the transition state for reductive elimination.



Scheme 1.23: The effect of participating groups on the rate of reductive elimination.⁸⁵

Bergman *et al.* demonstrated this in a series of reactions beginning with $[\text{CpCo}(\text{PPh}_3)(\text{CH}_3)_2]$ (**i-39**, Scheme 1.23).⁸⁵ Dissociation of a ligand from this forms the unsaturated complex $[\text{CpCo}(\text{CH}_3)_2]$ (**i-40**), which contains two sp^3 hybridised

ligands that do not undergo reductive elimination. Addition of ethene to **i-40** forms $[\text{CpCo}(\text{CH}_2\text{CH}_3)(\text{CH}_3)]$ (**i-41**) which still contains two sp^3 hybridised ligands that undergo β -hydride elimination to form propene, and then C-H bond forming reductive elimination of the resulting methyl and hydride groups to form methane. Addition of $\text{Ph-C}\equiv\text{C-Ph}$ to **i-40** however, forms a complex containing an sp^2 hybridised group (**i-42**), as does addition of CO to **i-40**, forming the acyl complex **i-43**. Both of these complexes are able to undergo reductive elimination.



Scheme 1.24: The dimerization of $\text{PhC}\equiv\text{CH}$, by $\{\text{Ir}(\text{PCP})\}$, occurs *via* reversible hydride insertion to give both the branched and linear alkenyls, however, reductive elimination only occurs from the linear intermediate.

In the dimerization of phenylacetylene by $\{\text{Ir}(\text{PCP})\}$ [$\text{PCP}^- = \kappa^3\text{-C}_6\text{H}_3\text{-2,6-}(\text{CH}_2\text{P}^t\text{Bu}_2)_2^-$], the reaction was found to proceed *via* the mechanism outlined in Scheme 1.24.⁷⁴ Initial C-H activation of 1 equivalent of $\text{PhC}\equiv\text{CH}$ forms the pseudo-square-pyramidal complex **i-44**, into which another equivalent of $\text{PhC}\equiv\text{CH}$ may insert to give either the (1,2-addition) branched (**i-45** and **i-46**) or (2,1-addition)

linear (**i-47**) alkenyl intermediates. There are two noteworthy aspects to this mechanism; firstly, that the more sterically-crowded branched intermediate (which forms as two rotamers **i-45** and **i-46**), unexpectedly form more readily than the linear intermediate, and show fast, reversible, hydride-insertion, but do not undergo reductive elimination. Secondly, the less sterically-crowded linear (**i-47**) alkenyl intermediate, once slowly formed, is the only pathway to give rise to productive reductive elimination (Figure 1.18). This gives rise to the unusual result of product regioselectivity that is determined by the C-C reductive elimination step, rather than by migratory insertion into the Ir-H bond.

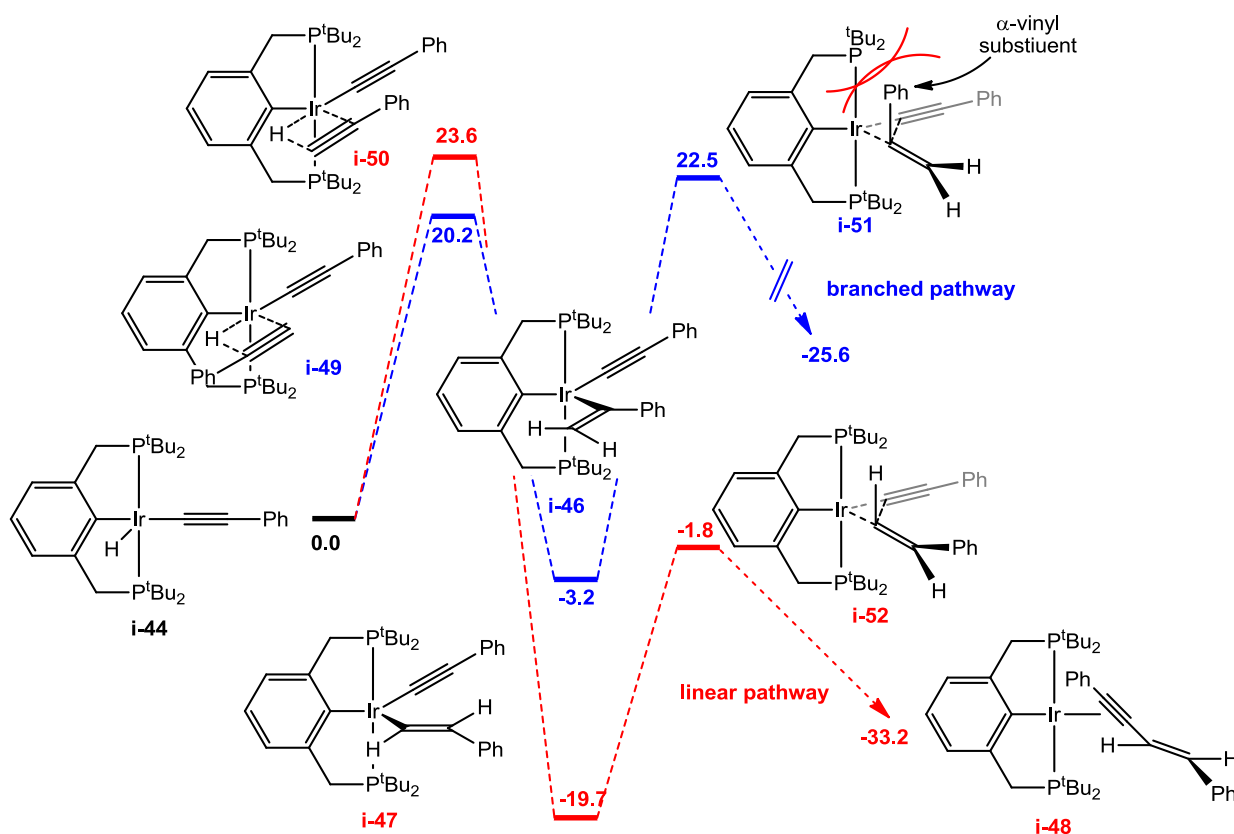


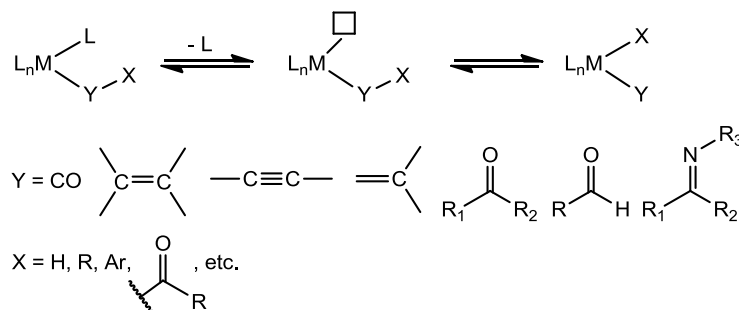
Figure 1.18: Reductive elimination only occurs from the linear transition state due to the rotation of the vinyl group being inhibited by the α -vinyl substituent in the branched isomer.

Computational studies confirmed the experimental observations (Figure 1.18).⁷³,⁷⁴ The branched (1,2-addition) isomer is the kinetically favoured pathway due to forming a (marginally) lower energy transition state (**i-49**). Steric crowding in the branched isomer would be expected to disfavour its formation. However, in the transition state the phosphine alkyl groups are pointed away from the vacant site, so that 1,2-addition (**i-49**) is less sterically demanding than 2,1-addition (**i-50**). Once insertion is complete, however, the linear intermediate (**i-47**) is the lower energy thermodynamic product, due to steric crowding around the metal centre in the branched intermediate. The free energy for the 1,2-addition to give the branched intermediates (**i-45** and **i-46**) is calculated as $\Delta G = -3.2 \text{ kcal mol}^{-1}$, which, in combination with a transition state barrier of $20.2 \text{ kcal mol}^{-1}$, is in agreement with a reversible process. Finally, reductive elimination from the more sterically-hindered, higher energy branched intermediate (**i-51**) does not take place, with reductive elimination from the more stable linear intermediate (**i-52**) being favoured instead. That is, even though reductive elimination relieves crowding, there is greater barrier to elimination from the branched intermediates, than from the linear intermediate. This is attributed to the necessary rotation of the vinyl group in the transition state being inhibited by the presence of an α -vinyl substituents (**i-51**) (Figure 1.18).

1.5.7 β -Elimination

Many organometallic complexes undergo the microscopic reverse reaction of migratory insertion, which is de-insertion of the fragment Y to form an unsaturated Y ligand and a new M-X bond (Scheme 1.25). When Y is CO this

process is known as decarbonylation, which is the competing side reaction to hydroacylation, leading to catalyst deactivation and reduced substrates (Scheme 1.6c).



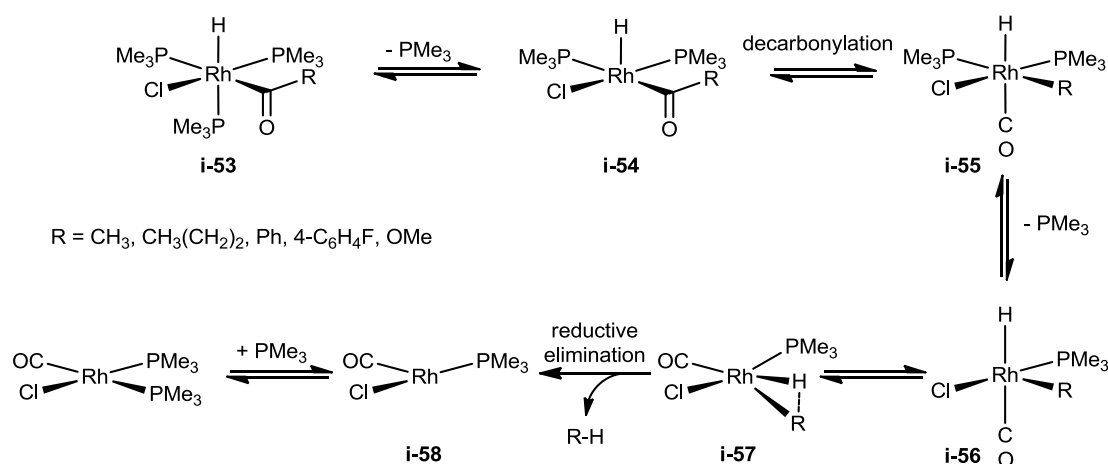
Scheme 1.25: De-insertion of Y fragment to form an unsaturated ligand (Y) and a new metal-ligand bond (M-X). Figure adapted from ref 4.

Other common classes of this reaction include when X = H (α - or β -hydride elimination) and X = alkyl or aryl (β -alkyl/aryl elimination), otherwise known as β -eliminations due to the β location of the X substituent. As the reverse process to migratory insertion, the opposite conditions are required for the elimination to occur, specifically, a vacant coordination site located *cis* to the group undergoing elimination. In addition, the migratory de-insertion mechanism is the reverse of migratory insertion, with the same intermediates and transition states, and so occurs more readily in complexes capable of adopting a *syn* co-planar arrangement of the metal and participating ligand substituents.

1.5.7.1 Decarbonylation from metal-acyl-hydride complexes

Decarbonylation is a common reaction pathway from the acyl-metal-hydride complexes generated from oxidative addition of an aldehyde.⁶³ It is not in itself a problem in hydroacylation, in fact hydroacylation was initially observed as a side

product of the decarbonylation of aldehydes by Wilkinson's catalyst $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$.⁸⁶ Metal-carbonyl complexes are extremely stable, and decarbonylation of the acyl-metal-hydride species (**i-53**), to form a carbonyl-alkyl-hydride complex (**i-55**) is the thermodynamically preferred route when available;⁴⁰ however, it is the subsequent irreversible reductive elimination of the alkyl-metal-hydride that deactivates the catalyst (**i-57** $\rightarrow$ **i-58**, Schemes 1.6c and 1.26). A vacant site is required *cis* to the acyl-group for migratory de-insertion of the carbonyl to take place (**i-54**); therefore dissociation of a ligand from a 6-coordinate complex must occur first before it may undergo decarbonylation (Scheme 1.26). As has already been shown, reductive elimination from a 6-coordinate octahedral transition metal complex also requires initial dissociation of a ligand (**i-56**) (Scheme 1.21).⁷⁷⁻⁸¹ Thus both potentially deleterious processes require coordinative unsaturation.



Scheme 1.26: Mechanism for reductive decarbonylation from a 6-coordinate acyl-metal-hydride.^{81, 87, 88}

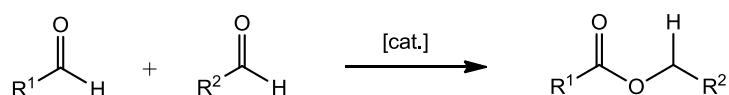
1.6 An overview of developments within the hydroacylation reaction

Research into the catalytic hydroacylation reaction has been extensive, and a range of approaches have been taken to tackle the issues which prevent its wide spread use as a synthetic tool. In particular, these issues include: preventing reductive decarbonylation of the metal-acyl-hydride, encouraging intermolecular hydroacylation, and controlling product selectivity.

1.6.1 Selectivity within the hydroacylation reaction

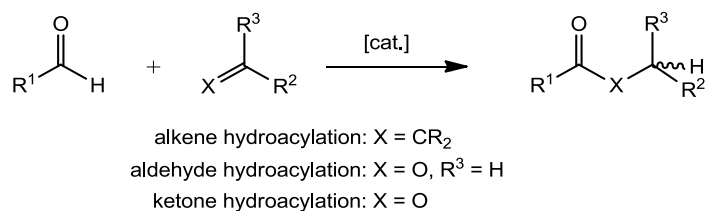
1.6.1.1 Alkene, aldehyde and ketone hydroacylation

In addition to the reductive decarbonylation reaction, another competing reaction which can occur under the conditions used for catalysis of the hydroacylation reaction, is the Tishchenko reaction: the coupling of two aldehydes (Scheme 1.27).⁸⁹



Scheme 1.27: The Tishchenko reaction.

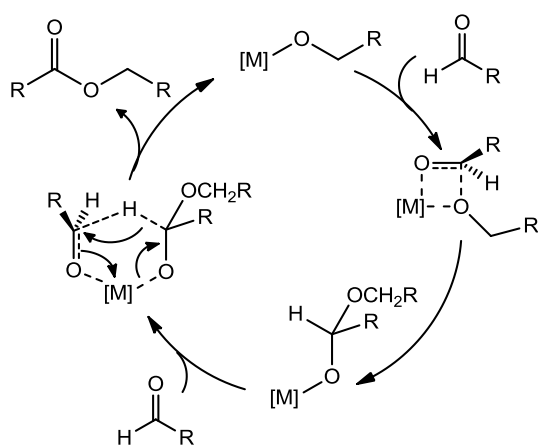
Coupling can occur between two different aldehydes ($\text{R}^1 \neq \text{R}^2$), although under hydroacylation conditions it can only occur between the one type of aldehyde present ($\text{R}^1 = \text{R}^2$).⁸⁹⁻⁹¹ As the addition of an aldehyde across an equivalent aldehyde C=O double bond, this can also be considered as the hydroacylation of an aldehyde (Scheme 1.28). The related ketone hydroacylation reaction is the addition of an aldehyde across a ketone C=O double bond.^{6, 92-98}



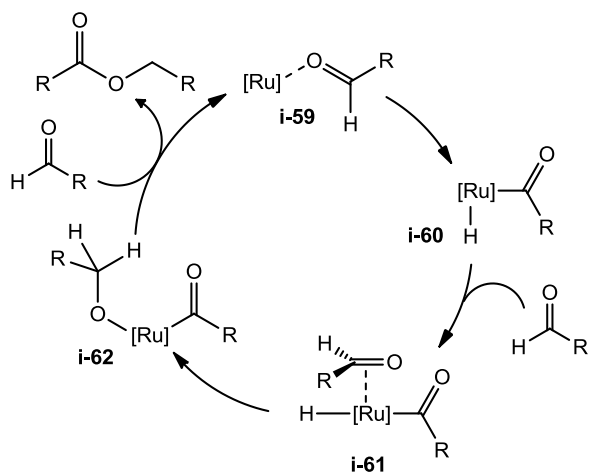
Scheme 1.28: Intermolecular hydroacylation of an aldehyde and an alkene ($\text{X} = \text{CR}_2$) or another aldehyde ($\text{X} = \text{O}, \text{R}^3 = \text{H}$), or a ketone ($\text{X} = \text{O}$).

There are two widely accepted mechanisms for the Tishchenko reaction, the Ogata-Kawasaki model, which involve (usually aluminium) alkoxides (Scheme 1.29a); and the Ito-Yamamoto model, which has been proposed to occur in reactions catalysed by transition-metal complexes (Scheme 1.29b).⁸⁹ The Ito-Yamamoto mechanism most closely resembles the mechanism proposed for hydroacylation: C-H activation of an aldehyde (**i-59** $\rightarrow$ **i-60**) is followed by migratory insertion of the hydride into a second coordinated aldehyde (**i-61** $\rightarrow$ **i-62**). Reductive elimination forms the ester product and regenerates the catalyst.

(a) Ogata-Kawasaki model ($\text{M} = \text{Al}^{3+}$)

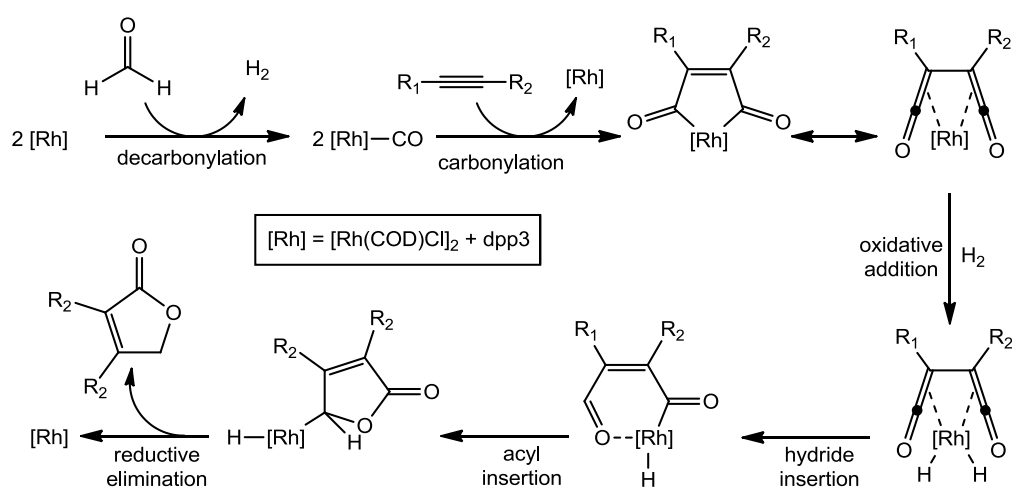


(b) Ito-Yamamoto model [$\text{Ru} = \text{Ru}(\text{PPh}_3)_3$]



Scheme 1.29: (a) Ogata-Kawasaki model ($\text{M} = \text{Al}^{3+}$), and (b) Ito-Yamamoto model [$\text{Ru} = \text{Ru}(\text{PPh}_3)_3$]; mechanisms for the Tishchenko reaction.

More recent developments within the Tishchenko reaction have included catalysis of aromatic aldehydes (which are much more challenging) by metal-amide complexes of heavier alkaline earth metals and lanthanides, $[M\{N(\text{SiMe}_3)_2\}_2]$ ($M = \text{Ca, Sr or Ba};^{99} \text{Ln, Y or Sm}^{100, 101}$), as well as by the organoactinide complexes $[\text{Cp}^*\text{ThMe}_2, \text{Th}(\text{NEtMe})_4 \text{ or } \text{Me}_2\text{SiCp}''\text{Th}(\text{C}_4\text{H}_9)_2]$.^{90, 91} The reactions are proposed to occur *via* an alkoxide mechanism in all cases (Ogata-Kawasaki model, Scheme 1.29a). A further development is the hydrocarbonylation of alkynes to form cyclic α,β -butenolides by Morimoto.¹⁰² This elegant, atom-efficient system combines decarbonylation of formaldehyde, hydroformylation of an alkyne, and intramolecular aldehyde hydroacylation to generate the cyclic enolide product. Scheme 1.30 outlines the proposed mechanism, although no justification for the suggested intermediates has been given.

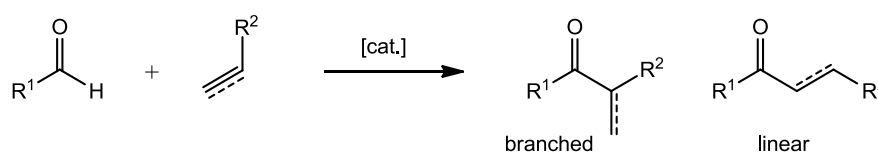


Scheme 1.30: Cyclocarbonylation of alkynes with formaldehyde to give α,β -butenolides.

The hydroacylation of ketones has been investigated by – amongst others – Dong *et al.*, and will be discussed later in this introduction.

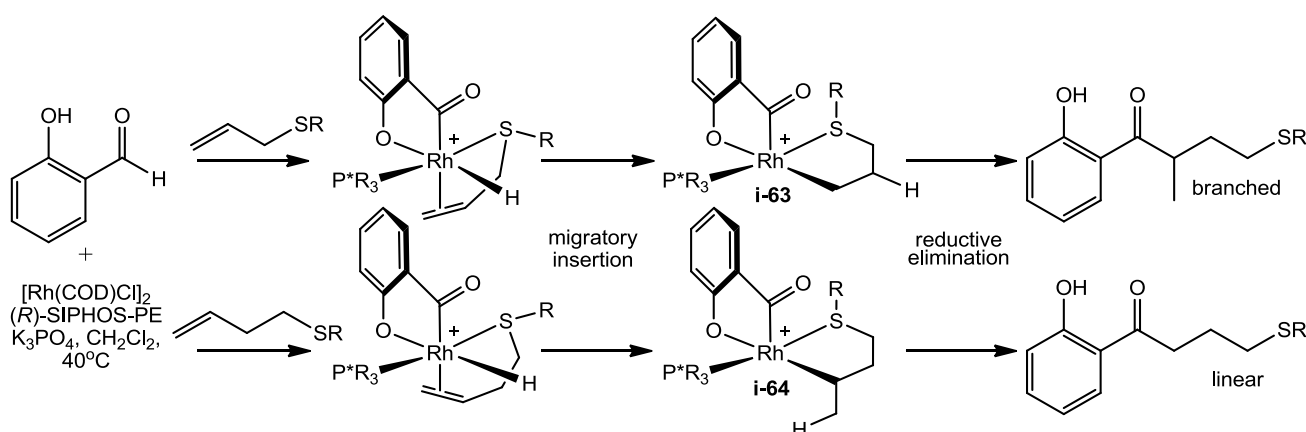
1.6.1.2 Linear and branched alkene/alkyne hydroacylation

A further area of selectivity within the hydroacylation reaction is the regioselective addition of the aldehyde across an alkene or alkyne multiple bond to form linear or branched products (Scheme 1.31). The linear reaction pathway is the most common for alkene and alkyne hydroacylation.



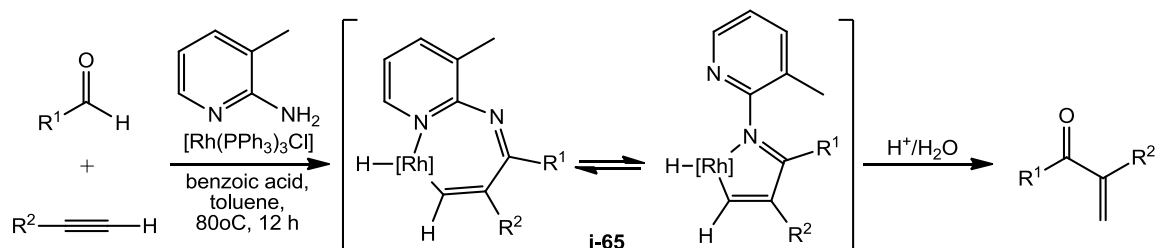
Scheme 1.31: Intermolecular hydroacylation of an aldehyde and an alkene or alkyne can give rise to linear or branched products.

Branched regioselectivity is much rarer, but has been achieved by a number of groups, including Krische¹⁰³ and Ryu,¹⁰⁴ for the hydroacylation of dienes; and Suemune,^{105, 106} for the hydroacylation of chelating alkenes. Dong *et al.* also made use of chelating alkenes, and preferential hydride insertion to give 5-membered metallacyclic intermediates (**i-63** and **i-64**), to control the regioselectivity in intermolecular hydroacylation of salicylaldehyde (Scheme 1.32).⁹³



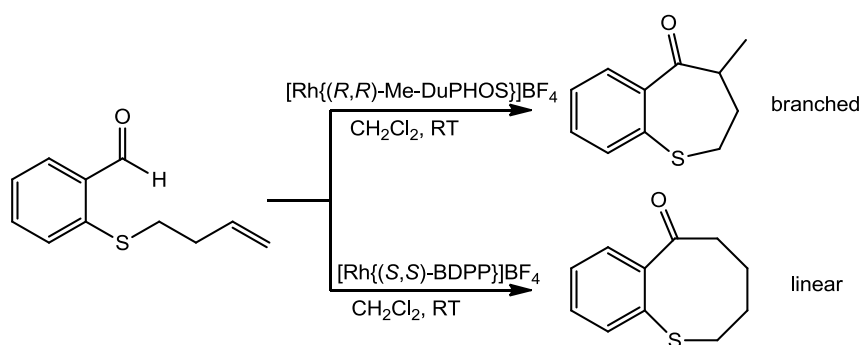
Scheme 1.32: Linear and branched product selectivity in the intermolecular hydroacylation of a chelating alkene is determined by formation of a 5-membered metallacyclic intermediate. Cl⁻ anion not shown.

Jun made use of a chelation assisted catalytic system comprising $\text{Rh}(\text{PPh}_3)_3\text{Cl}$, 2-amino-3-picoline and benzoic acid to achieve branched selectivity for the combination of terminal alkynes and aromatic aldehydes.^{40, 107} This selectivity is suggested to be due to a mechanism which occurs *via* the carbometallation of the alkyne (**i-65**, Scheme 1.33), instead of the hydrometallation observed for the catalysis of alkenes by the same system (**i-96**, Scheme 1.44, *vide infra*).



Scheme 1.33: Intermolecular branched-selective hydroacylation of terminal alkynes by a rhodium/picoline co-catalytic system.

Until recently only Dong had demonstrated the ability to selectively form either linear or branched products of the intramolecular hydroacylation for a single substrate set, by use of two different catalysts (Scheme 1.34).⁹² Details of new branched and linear selective catalyst systems are discussed in the course of this thesis.



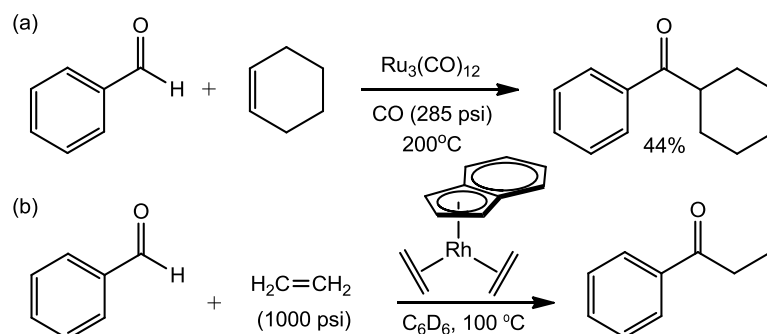
Scheme 1.34: Intramolecular branched and linear-selective hydroacylation of a single substrate by rhodium-based catalysts.

1.6.2 Preventing reductive decarbonylation

A major area of research in the area of hydroacylation has been finding a way of preventing the reductive decarbonylation of the metal-acyl-hydride intermediate. Three approaches have been used to prevent decarbonylation: (i) the rate of decarbonylation relative to hydroacylation can be reduced; (ii) the rate of hydroacylation relative to decarbonylation can be increased; (iii) the substrates and metal/ligand set can be changed in such a way that reductive elimination of the alkyl-hydride is no longer possible.¹⁰⁸⁻¹¹¹

1.6.2.1 Coordinative saturation of the metal-acyl-hydride intermediate

Intermolecular hydroacylation of non-chelating substrates, which occurs *via* C-H activation, is rare, and requires certain conditions to occur. To stabilise the metal-acyl-hydride intermediate to decarbonylation it is necessary for the intermediate to be coordinatively saturated. This can be achieved by use of strongly coordinating olefins capable of competing for the vacant site, or harsh conditions of high pressures of ethylene or CO and high temperatures.¹¹²⁻¹¹⁷ Experimental evidence also suggests that aromatic aldehydes (particularly those with electron-donating *para*-substituents) suppress reductive decarbonylation in comparison to aliphatic aldehydes, which is suggested to be due to the strength of the acyl sp^2 - sp^2 C-C bond in aryl aldehydes.¹¹⁸

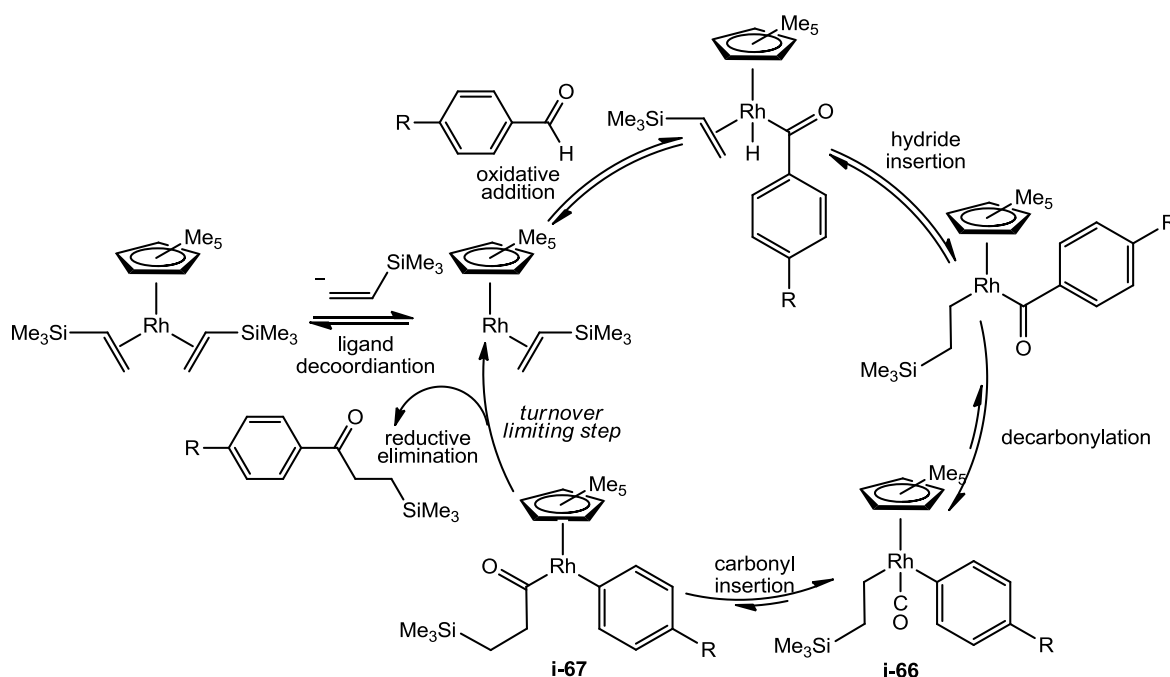


Scheme 1.35: Hydroacylation of Ph-COH using high pressures of (a) CO, or (b) ethylene, and high temperatures.

Milstein used high pressures of ethylene in the presence of a rhodium(I) indenyl catalyst to generate propiophenone, but could not apply the same method with longer chain alkenes (Scheme 1.35b).¹¹⁴ Wantanabe stabilised the acyl-metal-hydride intermediate with a ruthenium(0) carbonyl complex, using high pressures of CO, but found it necessary to use harsh conditions to obtain any product (Scheme 1.35a).^{112, 113}

Lenges and Brookhart were able to develop a coordinatively saturated system that works under mild conditions, by using vinylsilane as both substrate and ligand.^{111, 116, 117} The acyl-metal-hydride species undergoes observed reversible decarbonylation, but as this is a 6-coordinate complex (**i-66**, Scheme 1.36) it cannot reductively eliminate. However, carbonyl insertion into the olefin generates a 5-coordinate complex (**i-67**) which can reductively eliminate to give the hydroacylation product. Replacing the Cp^* ligand with an electron-deficient $\text{Cp}^\ddagger$ ligand ($\text{Cp}^\ddagger = \text{C}_5\text{Me}_4\text{CF}_3$) results in an increase in the rate of reductive elimination (the turnover limiting step in this system), as well as better linear

product selectivity and broader reaction scope. The limitation of this elegant system is that it only tolerates vinylsilane as the substrate.

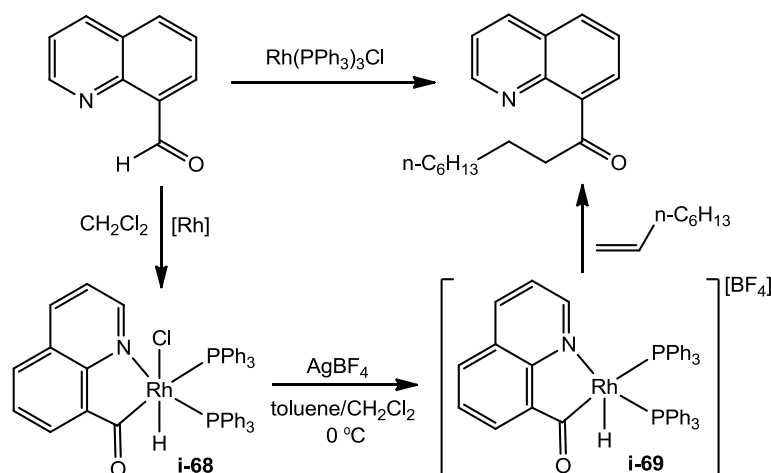


Scheme 1.36: Intermolecular hydroacylation using vinylsilane.

1.6.2.2 Five- and six-membered metallacyclic intermediates: chelation assistance

A different way to stabilise the acyl-metal-hydride complex, and therefore reduce the rate of decarbonylation, is to create a metallacycle.⁴⁰ The chelate effect is most pronounced in the formation of five- and six-membered rings.⁷ Intramolecular hydroacylation benefits from the favourable formation of metallacyclic intermediates. Likewise, aldehydes with the ability to chelate undergo the more favourable intramolecular (rather than intermolecular) oxidative addition, forming metallacyclic complexes which may then undergo intermolecular hydroacylation without recourse to harsh conditions.^{37, 110, 119-125}

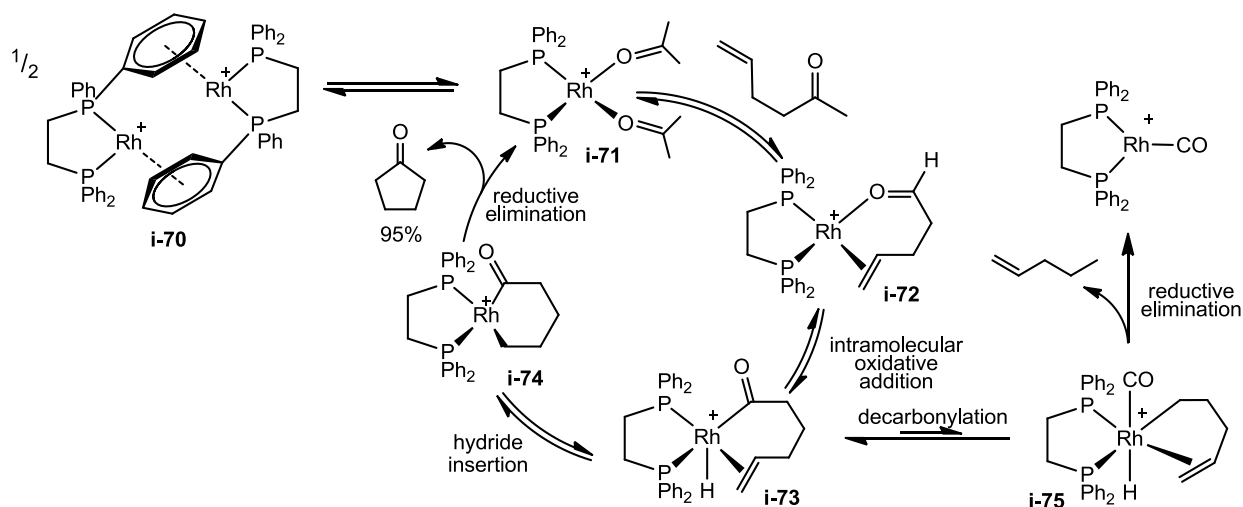
Suggs initially used 8-quinolinecarbaldehyde to isolate the first example of an acyl-metal-hydride intermediate (**i-68**, Scheme 1.37). The aldehyde forms a stable 5-membered metallacycle, from which the active catalytic species (**i-69**) can be generated by addition of AgBF_4 .¹²² Unfortunately the protocol has limited utility, as the quinolinyl group is difficult to transform into different functional groups.



Scheme 1.37: Hydroacylation using 8-quinolinecarbaldehyde

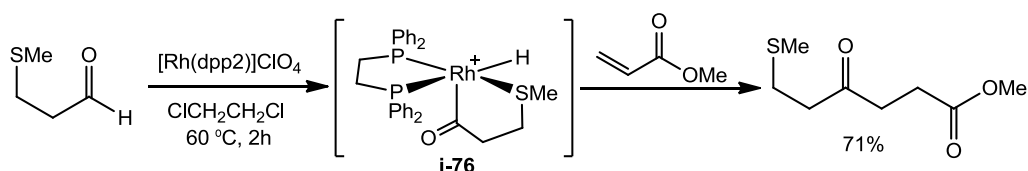
Bosnich was historically the first to study in detail the hydroacylation mechanism in a practical catalyst. His strategy aimed to increase the rate of hydroacylation, rather than slowing the rate of decarbonylation.³⁷ He speculated that acceleration of the steps involved in hydroacylation could be achieved by coordinative unsaturation.^{126, 127} To that end, a dimeric rhodium(I) complex: $[\text{Rh}(\text{dpp2})]_2[\text{ClO}_4]_2$, was chosen (**i-70**, Scheme 1.38). The active catalyst is the solvent stabilised 12-electron rhodium(I) monomeric species $\{\text{Rh}(\text{dpp2})\}^+$ (**i-71**), to which 4-pentenal initially coordinates to, through the olefin and carbonyl groups in an $\eta^2\text{-}\eta^1$ fashion (**i-72**), before undergoing intramolecular C-H oxidative addition, migratory insertion and reductive elimination. The acyl-metal-hydride

species (**i-73**) in this system is stabilised by the coordination of the olefin group in the aldehyde substrate forming a metallacyclic complex.⁴⁰



Scheme 1.38: Intramolecular hydroacylation using low coordinate rhodium catalysts. $[\text{ClO}_4]^-$ anions not shown.

This reaction is limited to pentanone products, as a result of the 6-membered chelate ring of the migratory inserted intermediate (**i-74**) being more favourable than larger ring sizes. Although coordination unsaturation also leads to rapid decarbonylation (**i-75**), the effect is less marked, proposed to be due to the electropositive nature of the cation. This stabilises the acyl-metal-hydride species over the alkyl-metal-carbonyl species, by disfavours the formation of the π -acidic carbonyl ligand on the electron deficient rhodium(III) centre, which therefore favours hydroacylation.^{118, 128} Moreover, reductive elimination, which is usually the turnover limiting step, is accelerated in cationic species.¹¹⁸ Bosnich's system is a highly efficient catalyst for the intramolecular hydroacylation of 4-pentenal and its derivatives.¹¹⁹ However, after 100 turnovers, roughly half of the catalyst forms the inactive reductive decarbonylation complex

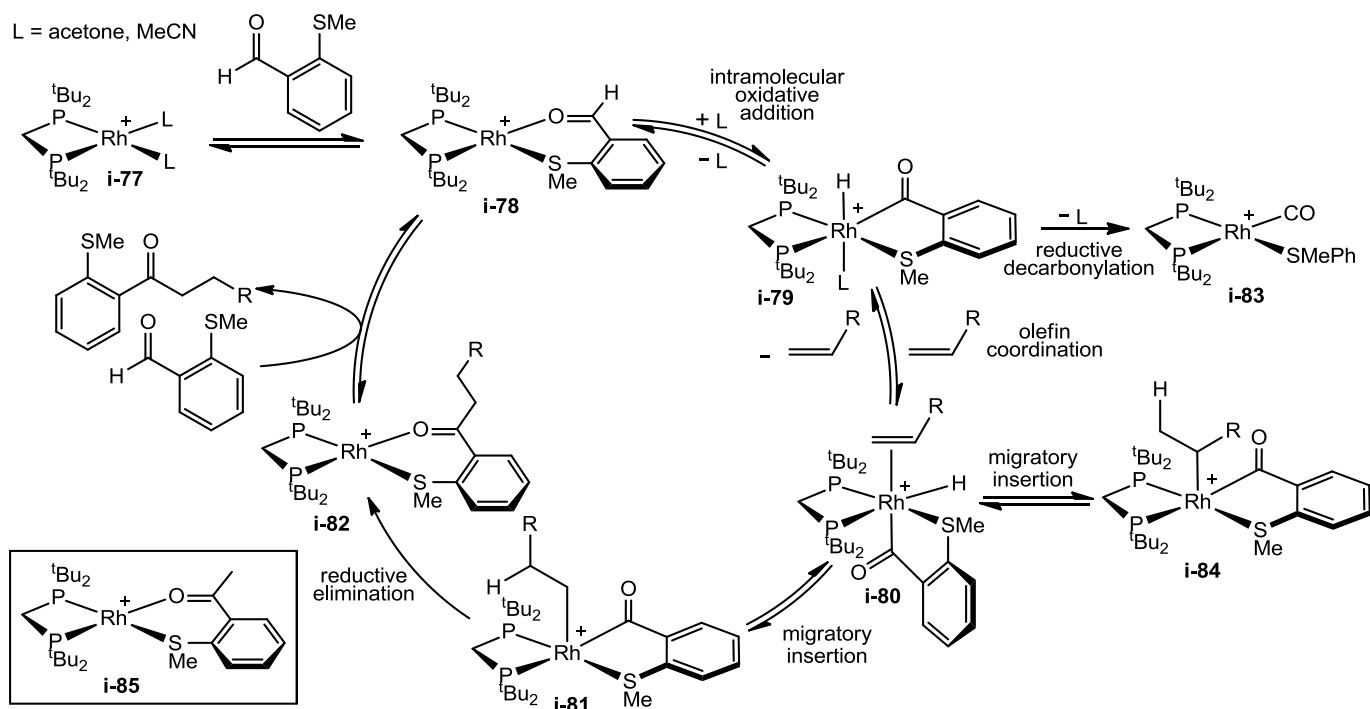


Scheme 1.39: Chelation controlled intermolecular hydroacylation. ClO₄⁻ anion not shown.

Willis developed a novel intermolecular hydroacylation system combining Bosnich's catalyst with the stabilising effect of a chelating aldehyde to disfavour decarbonylation.^{125, 129-131} Various aldehydes were screened with oxygen or sulphur as the coordinating heteroatom, and it was determined that the *S*-aldehyde, capable of forming a 5-membered metallacyclic complex (**i-76**), gave the best turnover of product (Scheme 1.39). The system is tolerant of a range of functionalised alkenes, and operates under mild conditions. However, mechanistic studies, in collaboration with Weller, showed that the 5-coordinate acyl-metal-hydride species (**i-76**) rapidly reductively decarbonylates with unfunctionalised alkenes.¹³²

Using a β -chelating aldehyde increases the coordinative saturation of the metal-acyl-hydride, which works against the accelerated rates achieved by Bosnich, but does allow intermolecular reactions. Small bite angle ligands have been shown by Dubois *et al.* (Scheme 1.2) to favour the formation of rhodium(I) over rhodium(III) complexes, which should encourage reductive elimination. Therefore an alternative way of increasing the reaction rate is through the use of small bite angle ligands.³¹ Weller *et al.* have recently shown the efficient intermolecular linear-selective hydroacylation of β -S aldehydes with alkenes and alkynes by small

bite angle, electron-rich ligands of the type $R_2PCH_2PR'_2$ ($R, R' = Cy, ^tBu$) (catalyst loadings of 0.1 mol% and $TOF = 300\ h^{-1}$, compared to 10 mol% and $TOF = 5\ h^{-1}$ for the 1st generation dpp2 system)¹²⁵ (Scheme 1.40).¹³³ These catalysts were also subject to relatively rapid decarbonylation; however, use of coordinating solvents such as acetonitrile or acetone limits this side-reaction (**i-77**).



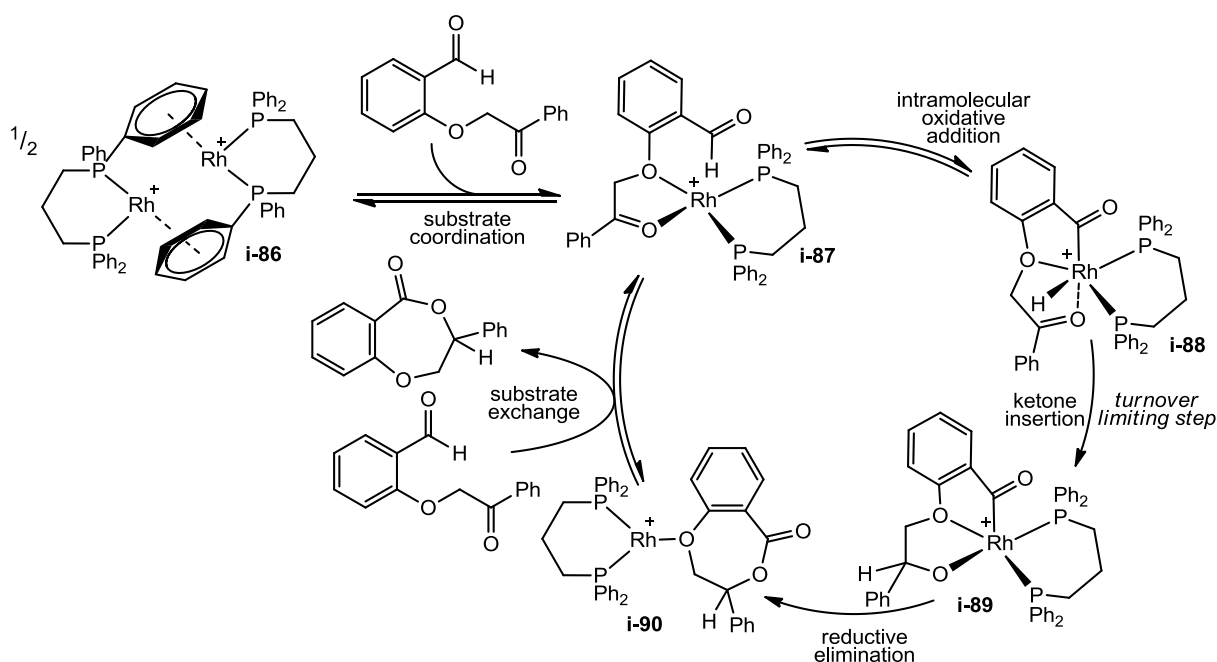
Scheme 1.40: Intermolecular hydroacylation of β -S aldehydes using catalysts containing small bite angle ligands. $[BAr^F_4]^-$ anion not shown.

Use of deuterium labelled aldehyde showed the formation of the branched intermediate complex (**i-84**), although only the linear isomer is observed as the final product, indicating reversible hydride insertion (**i-84** $\rightleftharpoons$ **i-80** $\rightleftharpoons$ **i-81**). Under stoichiometric conditions, an equilibrium was also observed between the coordinated aldehyde (**i-78**) and acyl-hydride (**i-79**) complexes. The ketone analogue of **i-78**, $[Rh(^tBu_2PCH_2P^tBu_2)(k^2_{(OS)}-SMeC_6H_4COMe)][BAr^F_4]$ (**i-85**, Scheme

1.40), was also prepared, demonstrating similar spectroscopic data to both **i-78** and **i-82**. Under catalytic conditions, only the product bound complex (**i-82**) is observed as the resting state. Kinetic studies showed a significant difference between the pseudo-first order rates of ketone formation [$2.0(2) \times 10^{-3} \text{ s}^{-1}$] and reductive decarbonylation (forming **i-81**) [$1.08(4) \times 10^{-4} \text{ s}^{-1}$], confirming the original hypothesis that small bite angle ligands can be used to increase the rate of reductive elimination over decarbonylation.

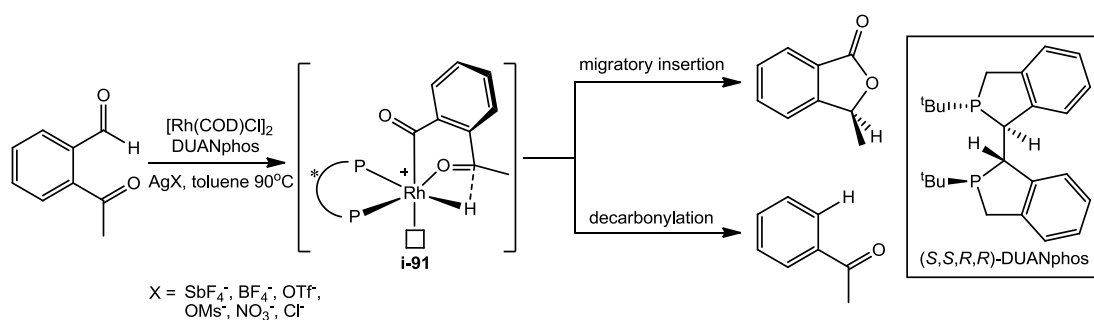
1.6.2.3 Ketone hydroacylation

Dong has developed a system for intramolecular ketone hydroacylation using a chelating aldehyde.⁹⁸ This works in a similar way to Bosnich's system, with the substrate coordinating to the metal through the oxygen substituents (**i-87**, Scheme 1.41), then undergoing intramolecular oxidative addition to form a 6-coordinate intermediate (**i-88**) in which the substrate stabilises the complex to decarbonylation by blocking the vacant site. The hydride inserts into the carbonyl to give an alkoxide intermediate (**i-89**) which then undergoes reductive elimination of the ester product (**i-90**). The catalyst is the dpp3 analogue of Bosnich's $[\text{Rh}(\text{dpp2})]_2[\text{ClO}_4]_2$ catalyst: $[\text{Rh}(\text{dpp3})]_2[\text{BF}_4]_2$ (**i-86**) and benefits in the same way from coordinative unsaturation. Mechanistic studies showed ketone insertion to be the turnover limiting step in this system.⁹⁸



Scheme 1.41: Intramolecular ketone hydroacylation using low coordinate rhodium catalysts, and a chelating substrate. $[\text{BF}_4]^-$ anions not shown.

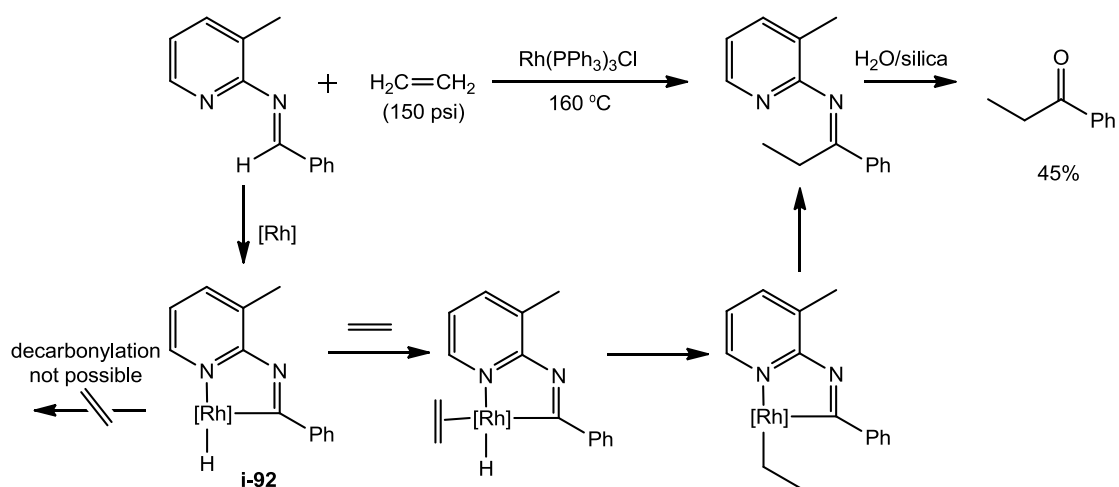
Dong also suggested that, in the absence of the chelating substrate-ether (as observed in **i-88**), strongly coordinating counterions can stabilise the acyl-hydride intermediate (**i-91**) to reductive decarbonylation, by providing blocking the vacant site (Scheme 1.42).⁹⁶ A series of counterions with varying coordinating strengths were screened: $\text{SbF}_6^- < \text{BF}_4^- < \text{OTf}^- < \text{OMs}^- < \text{NO}_3^- < \text{Cl}^-$, and showed the catalysts with more strongly coordinating counterions gave better selectivity for hydroacylation over decarbonylation (Scheme 1.42).



Scheme 1.42: The selectivity for intramolecular ketone hydroacylation over decarbonylation is improved by coordinating counterions.^a

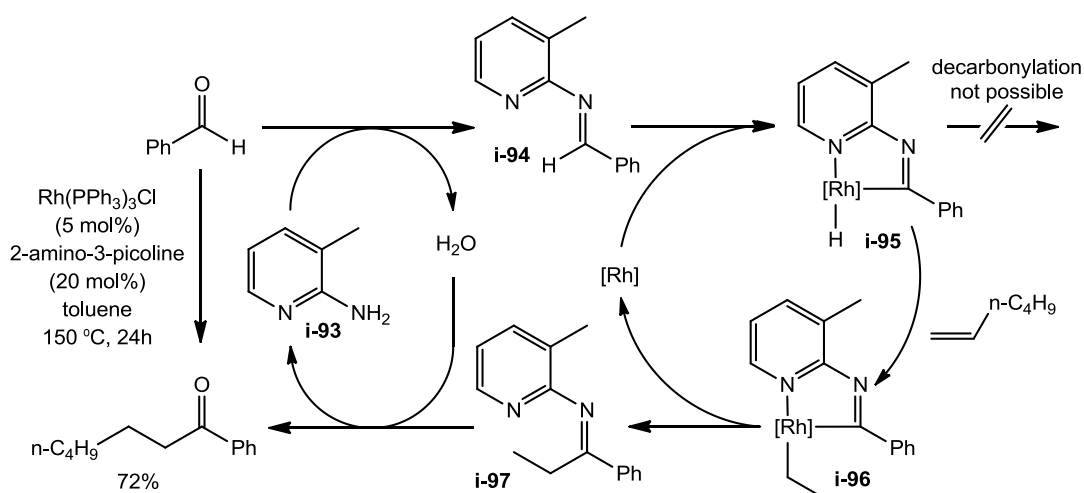
1.6.2.4 Masking the metal-acyl-hydride intermediate

Having employed a chelating ligand to isolate a metal-acyl-hydride complex, Suggs took a different approach to stabilising the intermediate to decarbonylation, instead masking the aldehyde in the form of an aldimine, so that decarbonylation was no longer possible (**i-92**, Scheme 1.43).¹¹⁰ Hydrolysis of the resulting ketimine produces the ketone.



Scheme 1.43: Hydroimination with aldimine

Jun developed Sugg's method so that it could be applied to a range of aldehydes and alkenes, by using 2-amino-3-picoline as a co-catalyst (**i-93**, Scheme 1.44).^{108,}
¹⁰⁹ The aldimine (**i-94**) is formed from the aldehyde by condensation with 2-amino-3-picoline; then it undergoes hydroimination *via* intramolecular oxidative addition (**i-95**). The resulting ketimine (**i-97**) is hydrolysed to give the ketone product, without the potential for decarbonylation, as no metal-acyl-hydride intermediate forms.

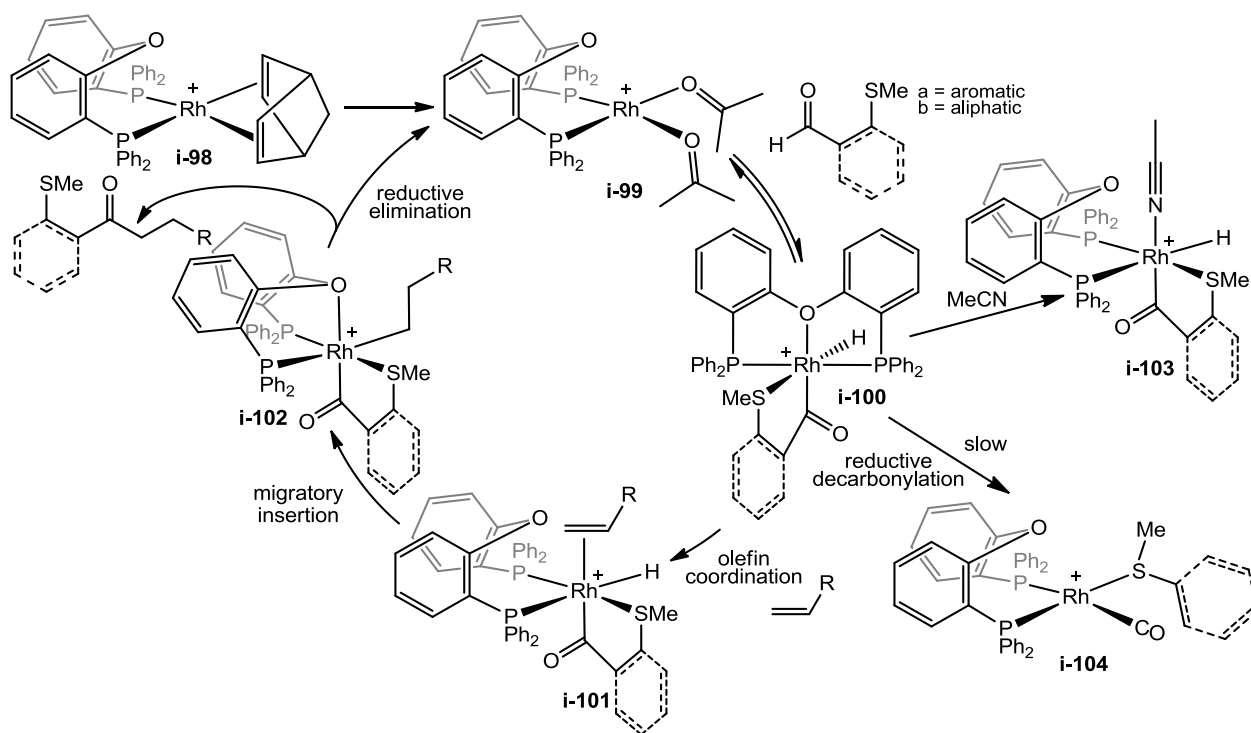


Scheme 1.44: Hydroimination using 2-amino-3-picoline (**i-93**) as a co-catalyst

1.6.2.5 Hemilabile ligand stabilisation

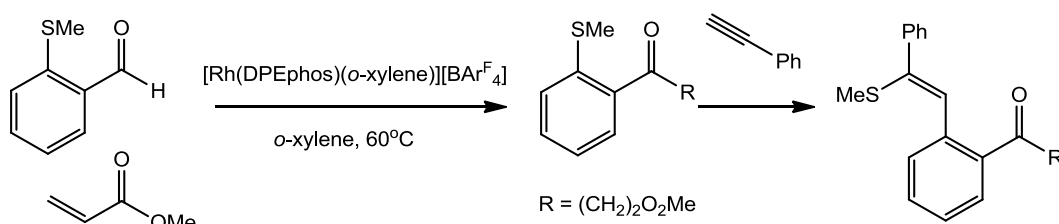
The 1st generation intermolecular hydroacylation system developed by Willis, using the chelating β -S aldehyde and $\{\text{Rh}(\text{dpp}_2)\}^+$, was limited by decarbonylation from the 5-coordinate acyl-hydride intermediate when unfunctionalised alkenes were used (Scheme 1.39). Weller and Willis reasoned that by introducing a hemilabile ligand capable of selectively stabilising the intermediate (**i-100**), that allowed the alkene access to the vacant site (**i-101**), an unfunctionalised alkene could undergo hydroacylation. A variety of catalysts were screened, and it was determined that for this system, the catalyst that gave the fastest rate was $[\text{Rh}(\text{DPEphos})(\text{NBD})][\text{CB}_{11}\text{H}_6\text{Br}_6]$ (**i-98**), which gave 100% conversion of aldehyde **I** and alkene **II** to linear alkene hydroacylation product in 30 min.¹³⁴⁻¹³⁶ Each step of the catalytic cycle for this 2nd generation system has been characterised in detail by Weller (Scheme 1.45).¹³² Solid-state structures of **i-98**, **i-99**, **i-100**, **i-103** and **i-104** were obtained, and their solution existence substantiated by NMR spectroscopy and ESI-MS. Furthermore, the existence of

three short-lived (< 30 min.) geometric isomers of **i-102**, in which the acyl, alkyl and thioether ligands adopt a *facial* configuration, with different groups *trans* to the phosphine ether group in each isomer, were observed by low temperature NMR spectroscopy.¹³⁷



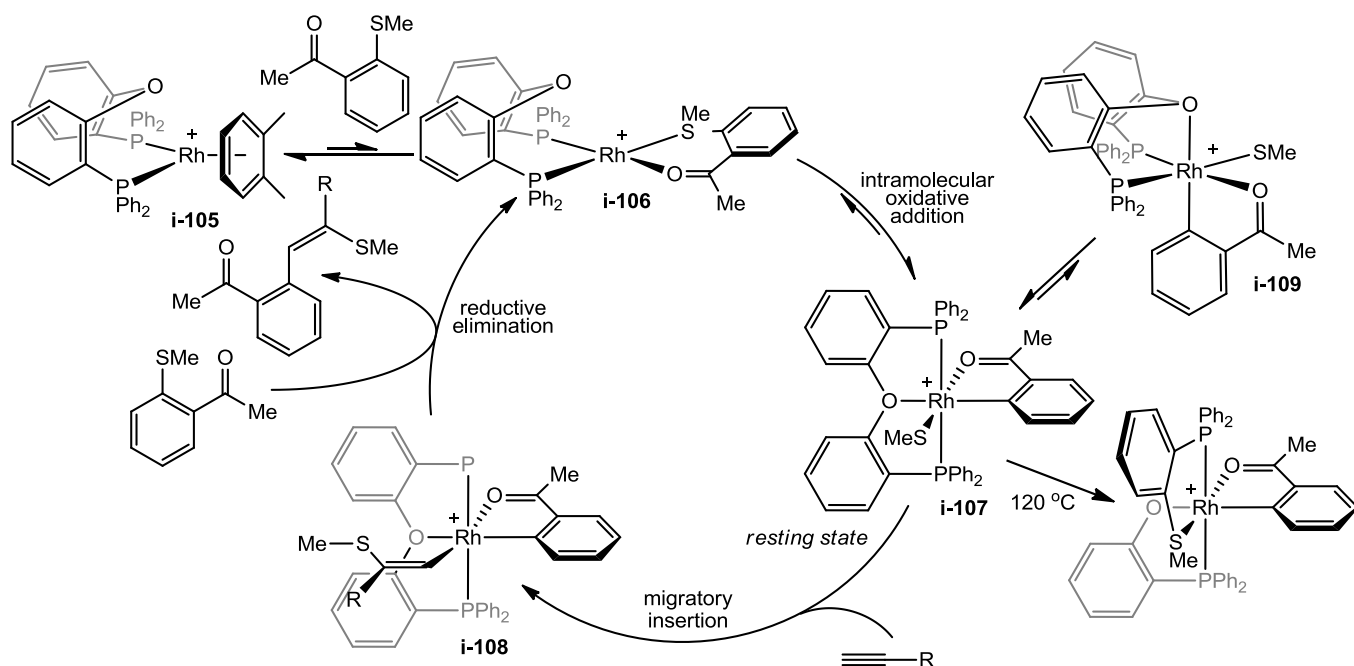
Scheme 1.45: Intermolecular hydroacylation using a hemilabile ligand. $[\text{CB}_{11}\text{H}_6\text{Br}_6]^-$ anion not shown.

While this system is tolerant over a wide range of functionalised and unfunctionalised alkenes, it still requires a sulphur group pendant to the carbonyl. However, this limitation is reduced by the recent development of a tandem catalytic process which involves the C-S activation of the β -S ketone products, and further functionalization using the DPEphos catalyst system (**i-105**) Schemes 1.46 and 1.47).¹³⁸



Scheme 1.46: Tandem hydroacylation and carbothiolation reactions.

The C-S activated complex with the *meridonially* coordinated DPEphos ligand (**i-107**) is the resting state during catalysis, but also exists as a *facially* coordinated isomer (**i-109**) outside the catalytic cycle (Scheme 1.47). Addition of the thioether across the alkyne $\text{C}\equiv\text{C}$ bond (to give **i-108**) followed by reductive elimination forms an alkenyl sulphide product which can be treated to remove the thioether in a variety of ways (Scheme 1.47).¹³⁸



Scheme 1.47: Alkyne carbothiolation of β -S ketone hydroacylation products. $[\text{BARF}_4]^-$ anion not shown.

1.7 Summary

The area of hydroacylation has developed enormously since the first report by Sakai in 1972.⁸⁶ A range of systems exist for the inter- and intramolecular hydroacylation of chelating and non-chelating substrates, and different approaches have been taken towards reducing decarbonylation of the acyl-metal-hydride intermediate. The mechanisms by which these reactions occur are reasonably well understood, and have also been calculated by computational studies. However, the ability to combine any aldehyde with any alkene or alkyne is still a goal, as well as the ability to control product selectivity.

The range of inputs which may affect a given reaction catalysed by a homogeneous organometallic complex includes the metal, ligands, substrates, solvents, co-catalysts, and reaction conditions.¹⁶ Furthermore, each step of the catalytic cycle may be affected in different – and potentially conflicting – ways by changes in these variables. Therefore the development of new catalysts is best achieved by understanding and optimising current systems. To that end, this thesis aims to build on previous results obtained within the Weller and Willis groups, by studying in detail the role of the ligand (bite angle, hemilability and sterics) in the intermolecular hydroacylation of β -S aldehydes and alkenes or alkynes, beginning with the 2nd generation DPEphos system.

1.8 References

1. R. Cramer, *Accounts of Chemical Research*, 1968, **1**, 186-191.
2. T. A. Abright, J. K. Burdett and M. H. Whangbo, *Orbital Interactions in Chemistry*, Wiley, New York, 1985.
3. T. J. Hoffman and E. M. Carreira, *Angewandte Chemie International Edition*, **50**, 10670-10674.
4. J. Hartwig, *Organotransition Metal Chemistry*, University Science Books, 2010.
5. J. Cheng and P. Hu, *Journal of the American Chemical Society*, 2008, **130**, 10868-10869.
6. L. W. Chung, O. Wiest and Y. D. Wu, *The Journal of Organic Chemistry*, 2008, **73**, 2649-2655.
7. N. N. Greenwood and E. Earnshaw, *Chemistry of the Elements*, 2nd edn., Elsevier, 1997.
8. F. H. Jardine and G. Wilkinson, *Journal of the Chemical Society C: Organic*, 1967, **0**, 270-271.
9. C. P. Casey, G. T. Whiteker, M. G. Melville, L. M. Petrovich, J. A. Gavney and D. R. Powell, *Journal of the American Chemical Society*, 1992, **114**, 5535-5543.
10. R. Usón, L. A. Oro, J. A. Cuchi and M. A. Garralda, *Journal of Organometallic Chemistry*, 1976, **116**, C35-C37.
11. S. H. H. Chaston and F. G. A. Stone, *Chemical Communications (London)*, 1967, **18**, 964-964.
12. L. Porri and A. Lionetti, *Journal of Organometallic Chemistry*, 1966, **6**, 422-424.
13. G. Giordano and R. H. Crabtree, *Inorganic Syntheses* 1990, **28**, 88.
14. M. Kranenburg, Y. E. M. van der Burgt, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz and J. Fraanje, *Organometallics*, 1995, **14**, 3081-3089.
15. D. G. Gilheany, *Chemical Reviews*, 1994, **94**, 1339-1374.
16. N. Fey, A. G. Orpen and J. N. Harvey, *Coordination Chemistry Reviews*, 2009, **253**, 704-722.
17. A. G. Orpen and N. G. Connelly, *Organometallics*, 1990, **9**, 1206-1210.
18. A. G. Orpen and N. G. Connelly, *Journal of the Chemical Society, Chemical Communications*, 1985, **19**, 1310-1311.
19. C. A. Tolman, *Chemical Reviews*, 1977, **77**, 313-348.
20. R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, 4th edn., John Wiley & Sons, Inc., New Jersey, 2005.
21. J. Fornies, M. Green, J. L. Spencer and F. G. A. Stone, *Journal of the Chemical Society, Dalton Transactions*, 1977, **10**, 1006-1009.
22. M. Feller, Y. Diskin-Posner, L. J. W. Shimon, E. Ben-Ari and D. Milstein, *Organometallics*, 2012, **31**, 4083-4101.
23. E. Drent, J. A. M. van Broekhoven and M. J. Doyle, *Journal of Organometallic Chemistry*, 1991, **417**, 235-251.
24. Y. Koide, S. G. Bott and A. R. Barron, *Organometallics*, 1996, **15**, 2213-2226.
25. K. Angermund, W. Baumann, E. Dinjus, R. Fornika, H. Görls, M. Kessler, C. Krüger, W. Leitner and F. Lutz, *Chemistry – A European Journal*, 1997, **3**, 755-764.
26. P. W. N. M. van Leeuwen, P. C. J. Kamer, J. N. H. Reek and P. Dierkes, *Chemical Reviews*, 2000, **100**, 2741-2770.
27. M.-N. Birkholz, Z. Freixa and P. W. N. M. van Leeuwen, *Chem. Soc. Rev.*, 2009, **38**, 1099 - 1118.
28. P. D. Achord, P. Kiprof and B. Barker, *Journal of Molecular Structure: THEOCHEM*, 2008, **849**, 103-111.
29. P. C. J. Kamer, P. W. N. M. van Leeuwen and J. N. H. Reek, *Accounts of Chemical Research*, 2001, **34**, 895-904.
30. G. P. C. M. Dekker, C. J. Elsevier, K. Vrieze, P. W. N. M. van Leeuwen and C. F. Roobeek, *Journal of Organometallic Chemistry*, 1992, **430**, 357-372.
31. D. L. DuBois, D. M. Blake, A. Miedaner, C. J. Curtis, M. R. DuBois, J. A. Franz and J. C. Linehan, *Organometallics*, 2006, **25**, 4414-4419.
32. A. Miedaner, R. C. Haltiwanger and D. L. DuBois, *Inorganic Chemistry*, 1991, **30**, 417-427.
33. E. Zuidema, P. W. N. M. van Leeuwen and C. Bo, *Organometallics*, 2005, **24**, 3703-3710.
34. P. Braunstein and F. Naud, *Angewandte Chemie International Edition*, 2001, **40**, 680-699.
35. J. C. Jeffrey and T. B. Rauchfuss, *Inorganic Chemistry*, 1979, **18**, 2658-2666.
36. R. Dallanegra, A. B. Chaplin and A. S. Weller, *Organometallics*, 2012, **31**, 2720-2728.
37. D. P. Fairlie and B. Bosnich, *Organometallics*, 1988, **7**, 936-945.
38. Bergman, *Nature*, 2007, **446**, 391.

39. Labinger and Bercaw, *Nature*, 2002, **417**, 507.
40. C.-H. Jun, E.-A. Jo and J.-W. Park, *European Journal of Organic Chemistry*, 2007, **2007**, 1869-1881.
41. I. Krossing and I. Raabe, *Angewandte Chemie International Edition*, 2004, **43**, 2066-2090.
42. M. D. Butts, B. L. Scott and G. J. Kubas, *Journal of the American Chemical Society*, 1996, **118**, 11831-11843.
43. W. E. Buschmann, J. S. Miller, K. Bowman-James and C. N. Miller, in *Inorganic Syntheses*, ed. C. Dimitri, 2002, vol. 33, p. 83.
44. C. A. Reed, *Accounts of Chemical Research*, 2009, **43**, 121-128.
45. W. V. Konze, B. L. Scott and G. J. Kubas, *Chemical Communications*, 1999, 1807-1808.
46. T. M. Douglas, E. Molinos, S. K. Brayshaw and A. S. Weller, *Organometallics*, 2006, **26**, 463-465.
47. G. R. K. Khalsa, G. J. Kubas, C. J. Unkefer, L. S. Van der Sluys and K. A. Kubat-Martin, *Journal of the American Chemical Society*, 1990, **112**, 3855-3860.
48. G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini and H. J. Wasserman, *Journal of the American Chemical Society*, 1984, **106**, 451-452.
49. G. J. Kubas, *Metal Dihydrogen and σ -Bond Complexes*, Kluwer Academic/Plenum Publishers, New York, 2001.
50. S. Schlecht and J. F. Hartwig, *Journal of the American Chemical Society*, 2000, **122**, 9435-9443.
51. W. H. Bernskoetter, C. K. Schauer, K. I. Goldberg and M. Brookhart, *Science*, 2009, **326**, 553-556.
52. W. A. G. Graham and W. Jetz, *Inorganic Chemistry*, 1971, **10**, 4-9.
53. D. L. Lichtenberger and A. Rai-Chaudhuri, *Journal of the Chemical Society, Dalton Transactions*, 1990, **7**, 2161-2166.
54. A. B. Chaplin, J. C. Green and A. S. Weller, *Journal of the American Chemical Society*, 2011, **133**, 13162-13168.
55. S. Geftakis and G. E. Ball, *Journal of the American Chemical Society*, 1998, **120**, 9953-9954.
56. D. J. Lawes, S. Geftakis and G. E. Ball, *Journal of the American Chemical Society*, 2005, **127**, 4134-4135.
57. M. Brookhart, M. Green and G. Parkin *Proceedings of the National Academy of Sciences of the United States of America*, 2007, **104**, 6908-6914.
58. A. C. Cooper, E. Clot, J. C. Huffman, W. E. Streib, F. Maseras, O. Eisenstein and K. G. Caulton, *Journal of the American Chemical Society*, 1998, **121**, 97-106.
59. A. C. Cooper, W. E. Streib, O. Eisenstein and K. G. Caulton, *Journal of the American Chemical Society*, 1997, **119**, 9069-9070.
60. A. B. Chaplin, A. I. Poblador-Bahamonde, H. A. Sparkes, J. A. K. Howard, S. A. Macgregor and A. S. Weller, *Chemical Communications*, 2009, **2**, 244-246.
61. P. Atkins and J. de Paula, *Atkins' Physical Chemistry*, 8th edn., Oxford University Press, Oxford, 2006.
62. Y. Boutadla, D. L. Davies, S. A. Macgregor and A. I. Poblador-Bahamonde, *Dalton Transactions*, 2009, **30**, 5820-5831.
63. M. A. Garralda, *Dalton Transactions*, 2009, **19**, 3635-3645.
64. R. H. Crabtree, E. M. Holt, M. Lavin and S. M. Morehouse, *Inorganic Chemistry*, 1985, **24**, 1986-1992.
65. A. E. Shilov and G. B. Shul'pin, *Chemical Reviews*, 1997, **97**, 2879-2932.
66. M. Albrecht, *Chemical Reviews*, 2009, **110**, 576-623.
67. S. Murai, N. Chatani and F. Kakiuchi, *Pure Appl. Chem*, 1997, **69**, 589-594.
68. I. Moritanl and Y. Fujiwara, *Tetrahedron Letters*, 1967, **8**, 1119-1122.
69. B. Biswas, M. Sugimoto and S. Sakaki, *Organometallics*, 2000, **19**, 3895-3908.
70. W. C. Zeise, *Annalen der Physik*, 1831, **97**, 497-541.
71. T. A. Albright, R. Hoffmann, J. C. Thibeault and D. L. Thorn, *Journal of the American Chemical Society*, 1979, **101**, 3801-3812.
72. J. Chatt and L. A. Duncanson, *Journal of the Chemical Society (Resumed)*, 1953, **0**, 2939-2947.
73. R. Ghosh, T. J. Emge, K. Krogh-Jespersen and A. S. Goldman, *Journal of the American Chemical Society*, 2008, **130**, 11317-11327.
74. R. Ghosh, X. Zhang, P. Achord, T. J. Emge, K. Krogh-Jespersen and A. S. Goldman, *Journal of the American Chemical Society*, 2007, **129**, 853-866.

75. J. J. Low and W. A. Goddard, *Journal of the American Chemical Society*, 1984, **106**, 8321-8322.
76. J. J. Low and W. A. Goddard, *Journal of the American Chemical Society*, 1986, **108**, 6115-6128.
77. U. Fekl and K. I. Goldberg, *Journal of the American Chemical Society*, 2002, **124**, 6804-6805.
78. G. S. Hill and R. J. Puddephatt, *Organometallics*, 1998, **17**, 1478-1486.
79. A. T. Luedtke and K. I. Goldberg, *Inorganic Chemistry*, 2007, **46**, 8496-8498.
80. J. Procelewska, A. Zahl, G. Liehr, R. van Eldik, N. A. Smythe, B. S. Williams and K. I. Goldberg, *Inorganic Chemistry*, 2005, **44**, 7732-7742.
81. D. Milstein, *Accounts of Chemical Research*, 1984, **17**, 221-226.
82. G. Ujaque, F. Maseras, O. Eisenstein, L. Liable-Sands, A. L. Rheingold, W. Yao and R. H. Crabtree, *New Journal of Chemistry*, 1998, **22**, 1493-1498.
83. S. M. Kloek, D. M. Heinekey and K. I. Goldberg, *Organometallics*, 2006, **25**, 3007-3011.
84. N. W. West, S. Reinartz, P. S. White and J. L. Templeton, *Journal of the American Chemical Society*, 2006, **128**, 2059-2066.
85. E. R. Evitt and R. G. Bergman, *Journal of the American Chemical Society*, 1980, **102**, 7003-7011.
86. K. Sakai, J. Ide, O. Oda and N. Nakamura, *Tetrahedron Letters*, 1972, **13**, 1287-1290.
87. R. H. Crabtree, *New J. Chem*, 1998, **22**, 1493.
88. R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, 3rd edn., John Wiley and Sons, Inc., 2001.
89. T. Seki, T. Nakajo and M. Onaka, *Chemistry Letters*, 2006, **35**, 824-829.
90. T. Andrea, E. Barnea and M. S. Eisen, *Journal of the American Chemical Society*, 2008, **130**, 2454-2455.
91. M. Sharma, T. Andrea, N. J. Brookes, B. F. Yates and M. S. Eisen, *Journal of the American Chemical Society*, 2011, **133**, 1341-1356.
92. M. M. Coulter, P. K. Dornan and V. M. Dong, *Journal of the American Chemical Society*, 2009, **131**, 6932-6933.
93. M. M. Coulter, K. G. M. Kou, B. Galligan and V. M. Dong, *Journal of the American Chemical Society*, 2010, **132**, 16330-16333.
94. S. K. Murphy, M. M. Coulter and V. M. Dong, *Chemical Science*, 2012, **3**, 355-358.
95. S. K. Murphy, D. A. Petrone, M. M. Coulter and V. M. Dong, *Organic Letters*, 2011, **13**, 6216-6219.
96. D. H. T. Phan, B. Kim and V. M. Dong, *Journal of the American Chemical Society*, 2009, **131**, 15608-15609.
97. D. H. T. Phan, K. G. M. Kou and V. M. Dong, *Journal of the American Chemical Society*, 2010, **132**, 16354-16355.
98. Z. Shen, P. K. Dornan, H. A. Khan, T. K. Woo and V. M. Dong, *Journal of the American Chemical Society*, 2009, **131**, 1077-1091.
99. M. R. Crimmin, A. G. M. Barrett, M. S. Hill and P. A. Procopiou, *Organic Letters*, 2006, **9**, 331-333.
100. H. Berberich and P. W. Roesky, *Angewandte Chemie International Edition*, 1998, **37**, 1569-1571.
101. M. R. Bürgstein, H. Berberich and P. W. Roesky, *Chemistry – A European Journal*, 2001, **7**, 3078-3085.
102. K. Fuji, T. Morimoto, K. Tsutsumi and K. Kakiuchi, *Chemical Communications*, 2005, **26**, 3295-3297.
103. F. Shibahara, J. F. Bower and M. J. Krische, *Journal of the American Chemical Society*, 2008, **130**, 14120-14122.
104. S. Omura, T. Fukuyama, J. Horiguchi, Y. Murakami and I. Ryu, *Journal of the American Chemical Society*, 2008, **130**, 14094-14095.
105. M. Imai, M. Tanaka, K. Tanaka, Y. Yamamoto, N. Imai-Ogata, M. Shimowatari, S. Nagumo, N. Kawahara and H. Suemune, *The Journal of Organic Chemistry*, 2004, **69**, 1144-1150.
106. Y. Inui, M. Tanaka, M. Imai, K. Tanaka and H. Suemune, *Chemical and Pharmaceutical Bulletin*, 2009, **57**, 1158-1160.
107. C.-H. Jun, H. Lee, J.-B. Hong and B.-I. Kwon, *Angewandte Chemie*, 2002, **114**, 2250-2251.
108. C.-H. Jun, H. Lee and J.-B. Hong, *The Journal of Organic Chemistry*, 1997, **62**, 1200-1201.
109. C.-H. Jun, D.-Y. Lee, H. Lee and J.-B. Hong, *Angewandte Chemie International Edition*, 2000, **39**, 3070-3072.

110. J. W. Suggs, *Journal of the American Chemical Society*, 1979, **101**, 489-489.
111. A. H. Roy, C. P. Lenges and M. Brookhart, *Journal of the American Chemical Society*, 2007, **129**, 2082-2093.
112. T. Kondo, M. Akazome, Y. Tsuji and Y. Watanabe, *The Journal of Organic Chemistry*, 1990, **55**, 1286-1291.
113. T. Kondo, N. Hiraishi, Y. Morisaki, K. Wada, Y. Watanabe and T.-a. Mitsudo, *Organometallics*, 1998, **17**, 2131-2134.
114. T. B. Marder, D. C. Roe and D. Milstein, *Organometallics*, 1988, **7**, 1451-1453.
115. J. Schwartz and J. B. Cannon, *Journal of the American Chemical Society*, 1974, **96**, 4721-4723.
116. C. P. Lenges and M. Brookhart, *Journal of the American Chemical Society*, 1997, **119**, 3165-3166.
117. C. P. Lenges, P. S. White and M. Brookhart, *Journal of the American Chemical Society*, 1998, **120**, 6965-6979.
118. J. C. Leung and M. J. Krische, *Chemical Science*, 2012, **3**, 2202-2209.
119. D. P. Fairlie and B. Bosnich, *Organometallics*, 1988, **7**, 946-954.
120. C.-H. Jun, *Bull. Korean Chem. Soc.*, 1995, **16**, 1135-1138.
121. K. Kokubo, K. Matsumasa, M. Miura and M. Nomura, *The Journal of Organic Chemistry*, 1997, **62**, 4564-4565.
122. J. W. Suggs, *Journal of the American Chemical Society*, 1978, **100**, 640-641.
123. M. Tanaka, *Organic Letters*, 2003, **5**, 1365-1367.
124. M. C. Willis, H. E. Randell-Sly, R. L. Woodward and G. S. Currie, *Organic Letters*, 2005, **7**, 2249-2251.
125. M. C. Willis, S. J. McNally and P. J. Beswick, *Angewandte Chemie International Edition*, 2004, **43**, 340-343.
126. R. H. Crabtree, *Chemical Reviews*, 1985, **85**, 245-269.
127. D. Milstein, *Journal of the Chemical Society, Chemical Communications* 1982, **23**, 1357.
128. P. K. Wong, M. Madhavarao, D. F. Marten and M. Rosenblum, *Journal of the American Chemical Society*, 1977, **99**, 2823-2824.
129. M. C. Willis, H. E. Randell-Sly, R. L. Woodward, S. J. McNally and G. S. Currie, *The Journal of Organic Chemistry*, 2006, **71**, 5291-5297.
130. M. C. Willis, H. E. Randell-Sly, R. L. Woodward and G. S. Currie, *Organic Letters*, 2005, **7**, 2249-2251.
131. M. C. Willis, S. J. McNally and P. J. Beswick, *Angewandte Chemie International Edition*, 2004, **43**, 340-343.
132. G. L. Moxham, H. Randell-Sly, E. , S. Brayshaw, K., R. L. Woodward, A. S. Weller and M. Willis, C., *Angewandte Chemie International Edition*, 2006, **45**, 7618-7622.
133. A. B. Chaplin, J. F. Hooper, A. S. Weller and M. C. Willis, *Journal of the American Chemical Society*, 2012, **134**, 4885-4897.
134. P. Lenden, D. A. Entwistle and M. C. Willis, *Angewandte Chemie International Edition*, 2011, **50**, 10657-10660.
135. P. Lenden, P. M. Ylioja, C. Gonzalez-Rodriguez, D. A. Entwistle and M. C. Willis, *Green Chemistry*, 2011, **13**, 1980-1982.
136. J. D. Osborne and M. C. Willis, *Chemical Communications*, 2008, **40**, 5025-5027.
137. G. L. Moxham, H. Randell-Sly, S. K. Brayshaw, A. S. Weller and M. C. Willis, *Chemistry - A European Journal*, 2008, **14**, 8383-8397.
138. J. F. Hooper, A. B. Chaplin, C. González-Rodríguez, A. L. Thompson, A. S. Weller and M. C. Willis, *Journal of the American Chemical Society*, **134**, 2906-2909.

2.1 Introduction

Previous research within the Weller group identified the $\{\text{Rh}(\text{DPEphos})\}^+$ system as being a particularly robust catalyst for the hydroacylation reaction.¹ The ligand was chosen for its potential to coordinate in a hemilabile manner² to the metal through the oxygen atom, which was justified as the ligand demonstrated the ability to cycle through bidentate- $\kappa^2_{(\text{PP})}$ -*cis* and tridentate- $\kappa^3_{(\text{POP})}$ -*meridional* coordination modes during the catalytic cycle (Scheme 1.45). This 2nd generation system is particularly successful at attenuating catalyst deactivation through reductive decarbonylation, by the reversible coordination of the DPEphos oxygen group to give a 6-coordinate complex (**i-100**) which cannot undergo decarbonylation; however, it is limited to aldehydes containing the pendant β -sulphur atom.³ Ultimately, the aim is to design a catalyst capable of combining any aldehyde with any alkene or alkyne. The first step towards this is to probe the current system, and understand what effect subtle ligand modifications will have on it. Initial investigations into the role of the ligand focused on maintaining the P-O-P hemilabile ligand motif, while exploring the importance of the ligand's coordinative capability by varying the flexibility of the ligand backbone. The ligands chosen are shown in Figure 2.1.

Suitable stable precursor complexes are necessary in order to access the reactive intermediate species in the hydroacylation cycle. Cationic rhodium(I) complexes of the general formula $[\text{Rh}(\text{L}_2)(\text{NBD})][\text{anion}]$ ($\text{L} = 2$ electron donor) are relatively simple to synthesise, with the strained norbornadiene ligand readily removed by reductive hydrogenation (forming norbornane) to generate the active rhodium(I) precatalyst species $\{\text{Rh}(\text{L}_2)\}^+$. $[\text{BAr}^{\text{F}}_4]^-$ (where $\text{Ar}^{\text{F}} = \text{C}_6\text{H}_3(\text{CF}_3)_2$) is a known weakly coordinating anion,⁴ so the motif $[\text{Rh}(\text{diphosphine})(\text{NBD})][\text{BAr}^{\text{F}}_4]$ was chosen as a suitable precursor complex. Research conducted by William Reilly (Weller group) has shown the very limited influence of the following anions ($[\text{BAr}^{\text{F}}_4]^-$,⁴ $[\text{closo-CB}_{11}\text{H}_6\text{Br}_6]^-$,⁵ $[\text{closo-CB}_{11}\text{H}_{12}]^-$,⁵ $[\text{BAr}^{\text{Cl}}_4]^-$,⁶ $[\text{PF}_6]^-$ and $[\text{CF}_3\text{SO}_3]^-$) on the rates and stability of the catalyst during the hydroacylation reaction.⁷ As a result, the anions have been used interchangeably throughout this thesis, with the insolubility of the carborane and $[\text{BAr}^{\text{Cl}}_4]^-$ anions exploited to obtain single crystals for X-ray crystallography.

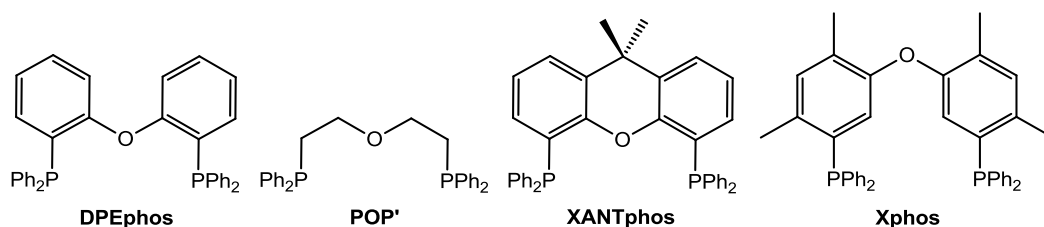


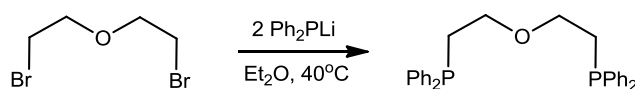
Figure 2.1: Potentially hemilabile ligands used in this study.

The ligand 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (XANTphos, Figure 2.1) was originally developed to enforce a constrained geometry at the metal centre, in the catalysis of the hydroformylation reaction.⁸ However, research since has shown that this ligand is capable of adopting both $\kappa^3_{(\text{POP})}$ -*meridinal* and -*facial* geometries, although $\kappa^2_{(\text{PP})}$ -*cis* and -*trans* are the most common coordination modes.⁹⁻¹¹ This ligand was chosen as an analogue of the DPEphos ligand, but with

restricted flexibility. Conversely, bis(2-diphenylphosphino)ethyl ether (POP', Figure 2.1), with its alkyl instead of aromatic backbone, was chosen to explore the influence of a more flexible ligand backbone. While trying to investigate the effect of using an even more sterically hindered DPEphos analogue than XANTphos, the ligand Xphos (Figure 2.1) was synthesised, which has a different P-O-P geometry compared to the other ligands, and when coordinated to a rhodium centre, showed surprising properties which do not follow on from the DPEphos, XANTphos, POP' series. This chapter will first cover the rhodium complexes formed with these ligands, followed by their activity as hydroacylation catalysts.

2.2 Complexes incorporating POP' and XANTphos

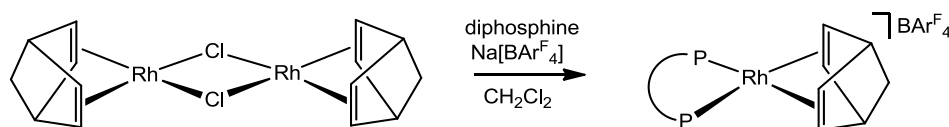
Both the POP' and XANTphos ligands have similar natural bite angles to the DPEphos ligand (108° , 108° and 107° respectively)¹² but different flexibility, which, given the different coordination modes adopted by DPEphos during the catalytic cycle, could affect the resulting catalytic activity in hydroacylation. The POP' ligand was synthesised *via* the published route shown in Scheme 2.1.¹³ ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy confirmed its formation being in agreement with literature values.



Scheme 2.1: Synthesis of POP' ligand.

Synthesis of both precursor complexes $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-POP}')(\text{NBD})][\text{BAR}^{\text{F}}_4]$ (**1**) and $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-XANTphos})(\text{NBD})][\text{BAR}^{\text{F}}_4]$ (**8**) was achieved by addition of the

appropriate ligand to $[\text{Rh}(\text{NBD})\text{Cl}]_2$ in the presence of the chloride abstracting agent $\text{Na}[\text{BAr}^{\text{F}}_4]$ (Scheme 2.2). Complex **1** has been previously reported as a different salt (BF_4^-), and its formation was confirmed by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, by comparison with literature data.^{14, 15}



Scheme 2.2: Synthesis of rhodium(I) norbornadiene precursors.

Somewhat surprisingly, complex **8** is unknown with any counterion. Complex **8** was characterised by NMR spectroscopy, ESI-MS and elemental analysis. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **8** shows a doublet at δ 9.74 [$J(\text{RhP}) = 142$] suggesting a rhodium(I) oxidation state.¹⁶ The ^1H NMR spectrum shows three environments (4:2:2) for the eight protons of the norbornadiene ligand, and one integral 6H environment for the XANTphos methyl groups at δ 1.70. ESI-MS of complex **8** in acetone confirms the empirical formula with a signal at $m/z = 773.15$ (calc. 773.16), showing the correct isotope pattern. A crystal structure of the complex was obtained by Romaeo Dallanegra (Weller group) who used related XANTphos complexes in his research into chelating phosphine alkene ligands; it is reported here for the first time (Figure 2.2).¹⁷ The solid state structure of **8** shows C_s symmetry, and is equivalent to those observed with POP' (**1**)¹⁸ and DPEphos (**98**), with a pseudo-square planar environment about the rhodium centre, the phosphine ligand adopting a $\kappa^2(\text{PP})$ -*cis* coordination mode and the norbornadiene coordinated η^2 - η^2 through the two alkene groups. The ligand bite angle, on complexation to rhodium, has reduced from 108° to 101° . A similar reduction in ligand bite angle is seen in the solid state structure of **1** [from 108° to

99.017(14)°],¹⁸ and $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-DPEphos})(\text{NBD})][\text{BAR}^{\text{F}}_4]$ (**i-98**) [from 107° to 100.12(5)°].³

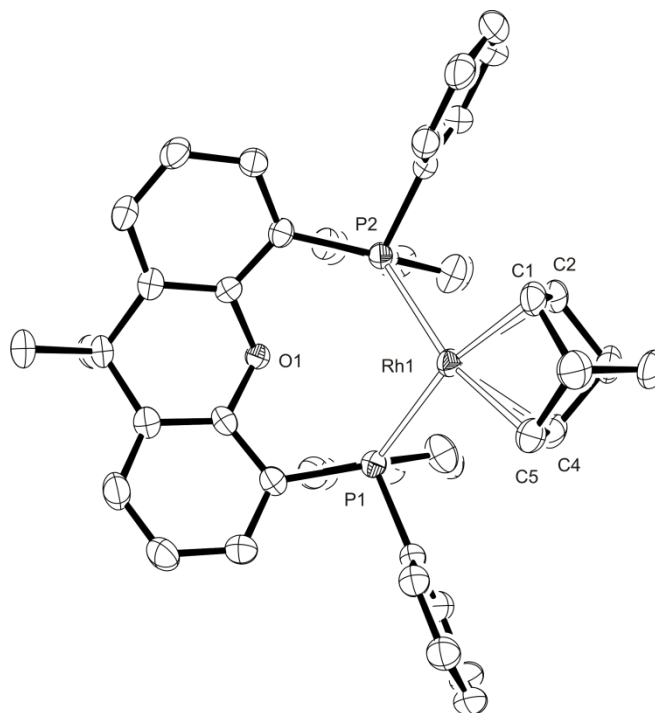
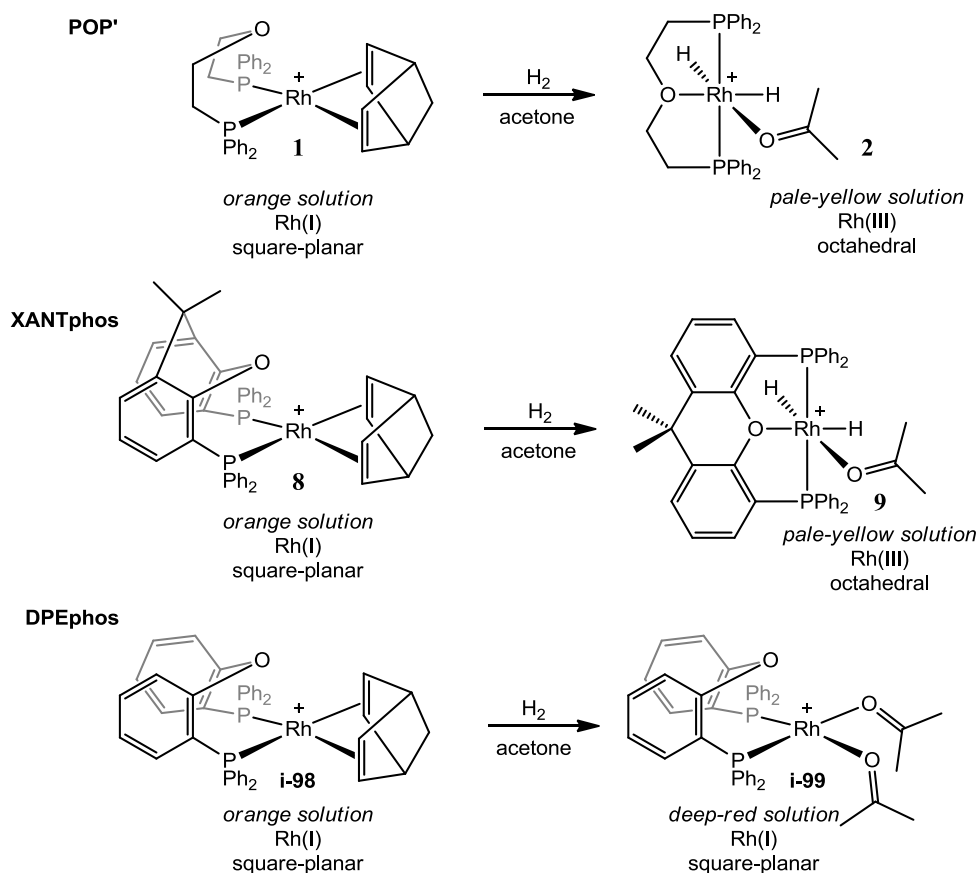


Figure 2.2: Molecular structure of the cationic portion of $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-XANTphos})(\text{NBD})][\text{BAR}^{\text{F}}_4]$ (**8**). Displacement ellipsoids are drawn at the 50% probability level. The anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Rh1-P1, 2.4023(9); Rh1-P2, 2.3946 (9); Rh1-C1, 2.206(4); Rh1-C2, 2.193(4); Rh1-C5, 2.206(4); Rh1-C4, 2.185(4); C1-C2, 1.379(6); C4-C5, 1.385(6). Selected bond angles [°]: P1-Rh1-P2, 101.04(3).

Previous work has shown the addition of hydrogen (4 atm) to the DPEphos precursor complex $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-DPEphos})(\text{NBD})][\text{BAR}^{\text{F}}_4]$ (**i-98**) in acetone solution, results in a deep-red solution of $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-DPEphos})(\text{acetone})_2][\text{BAR}^{\text{F}}_4]$ (**i-99**).¹ It was expected that the analogous POP' and XANTphos rhodium(I) bis-acetone complexes would form on addition of hydrogen (4 atm) to **1** and **8** in acetone solution. However, the reactions instead yielded pale yellow solutions of the rhodium(III) complexes $[\text{Rh}(\kappa^3_{\text{(POP)}}\text{-POP}')(\text{H})_2(\text{acetone})][\text{BAR}^{\text{F}}_4]$ (**2**) and $[\text{Rh}(\kappa^3_{\text{(POP)}}\text{-XANTphos})(\text{H})_2(\text{acetone})][\text{BAR}^{\text{F}}_4]$ (**9**) (Scheme 2.3).



Scheme 2.3: Activation of the precursor complexes **1** and **8** by addition of hydrogen in acetone, to give **2** and **9**. DPEphos complexes shown for comparison. $[\text{BAR}^{\text{F}}_4]^-$ anions not shown.

The characterisation of complexes **2** and **9** was achieved by *in situ* NMR spectroscopy and ESI-MS, resulting in very similar data. Both complexes display signals (integral 2H, relative to the aryl regions of 32H and 38H respectively for **2** and **9**) in the hydride region of the 295 K ^1H NMR spectrum, at δ -19.84 (**2**) and -18.89 (**9**). Hydrides appear further upfield than dihydrogen ligands in the NMR spectrum, as demonstrated by the dihydride-dihydrogen complex $[\text{Rh}(\text{PCy}_3)_2(\text{H})_2(\eta^2\text{-H}_2)_2][\text{BAR}^{\text{F}}_4]$ in which, at 190 K, the dihydrogen signal appears at δ -1.41, and the dihydride at δ -14.14;¹⁹ on this basis the ligands are assigned as dihydrides not coordinated dihydrogen. For complex **2** the signal is a broad singlet, while for complex **9** the signal appears to be a broad doublet (*vide infra*)

and the methyl groups of the XANTphos ligand are observed in the ^1H NMR spectrum as a broad integral 6H singlet between δ 2.25-1.54. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at 295 K of **2** and **9** both show a single phosphorus environment as a doublet with ^{103}Rh - ^{31}P coupling constant of 121 Hz, at δ 48.4 (**2**) and 45.4 (**9**) indicative of rhodium(III) environments.¹⁶ The room temperature NMR data is suggestive of structures which are undergoing a fluxional process to make the hydrides equivalent on the NMR time-scale. Cooling solutions of **2** and **9** in d_6 -acetone to 225 K results in a loss of time-averaged symmetry in the two molecules; in both complexes the hydride signals resolve into two, integral 1H, sharp multiplet signals at δ -19.25 [$J(\text{RhH}) = 24.5$, $J(\text{PH}) = 13.9$, $J(\text{HH}) = 10.7$] and -20.27 [$J(\text{RhH}) = 24.3$, $J(\text{PH}) = 13.4$, $J(\text{HH}) = 10.7$] (**2**); and δ -18.44 [$J(\text{RhH}) = 22.1$, $J(\text{PH}) = 12.8$, $J(\text{HH}) = 9.5$] and -19.17 [$J(\text{RhH}) = 31.4$, $J(\text{PH}) = 14.5$, $J(\text{HH}) = 9.5$] (**9**) (Figure 2.3). Further evidence of a loss of symmetry is observed on cooling the solutions to 225 K: the two integral 4H proton environments for the POP' ligand backbone in **2** separate out into four integral 2H proton environments, and the XANTphos ligand methyl groups separate out into two integral 3H singlets in **9**. No significant change is observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of either complex, which remain doublets at low temperature. The hydride signals of both complexes observed at 225 K were simulated using the program gNMR,²⁰ which demonstrated that the coupling in each set of multiplets is best described as overlapped doublet of triplet of doublets, suggestive of a hydride coupling to one rhodium atom, two equivalent phosphorus atoms, and the other hydride (Figure 2.3).

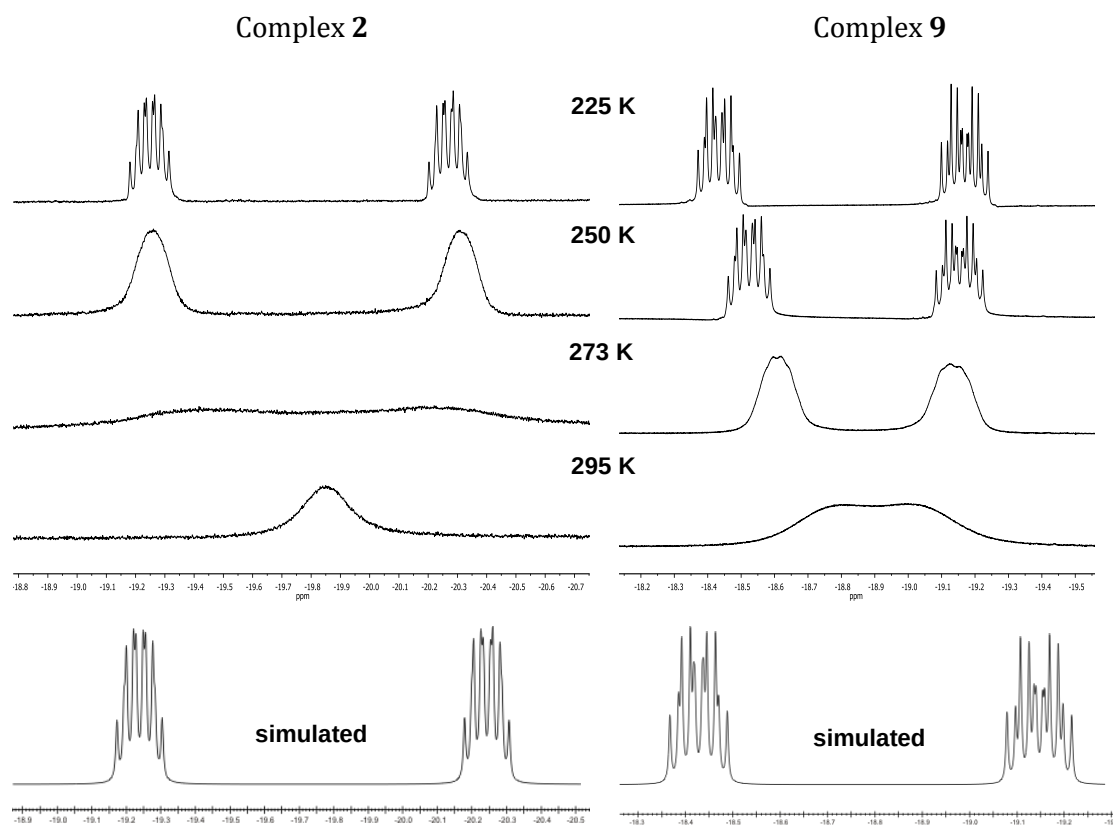


Figure 2.3: ^1H NMR variable temperature spectra and simulated spectra of complexes **2** and **9**.

$^1\text{H}\{^{31}\text{P}\}$ NMR experiments demonstrated the collapse of these multiplets into two doublet of doublets, confirming the triplet coupling is due to two equivalent phosphorus nuclei. The size of the coupling of the hydrides to each other and to the phosphines places them all mutually *cis*. ^{31}P - ^1H and ^1H - ^1H *trans* coupling constants in rhodium complexes are usually in the region of 90-160 Hz, while *cis* coupling constants are usually in the region of 10-30 Hz.²¹ The low-temperature NMR data precludes the possibility of the structures being pseudo-trigonal-bipyramidal with equivalent hydride ligands, as this would show one integral 2H hydride signal (Figure 2.4a); likewise a five-coordinate square-based pyramid structure with a vacant site *trans* to a hydride (Figure 2.4b) is discounted as the chemical shift of the hydride would be expected to be shifted significantly upfield

from that observed, such as is seen in $[\text{Ir}(\text{PCy}_2\text{Ph})_3(\text{H})_2][\text{BAR}^{\text{F}}_4]$ in which the hydride signals are observed at δ -5.4 and -44.8 for the hydride *trans* to a phosphine and *trans* to a vacant site respectively.²² A final alternative structure, with hydrides which are mutually *trans* (Figure 2.4c), is also discounted, as the hydrides would be significantly deshielded, resulting in a downfield chemical shift, as seen in the complex $[\text{Ru}(\text{H})_2\{\text{PCyp}_2(\eta^2\text{-C}_5\text{H}_7)\}_2]$, where the hydrides are observed at δ -5 in the ^1H NMR spectrum, and would also display a large *trans* ^1H - ^1H coupling if the hydride environments were inequivalent.²³

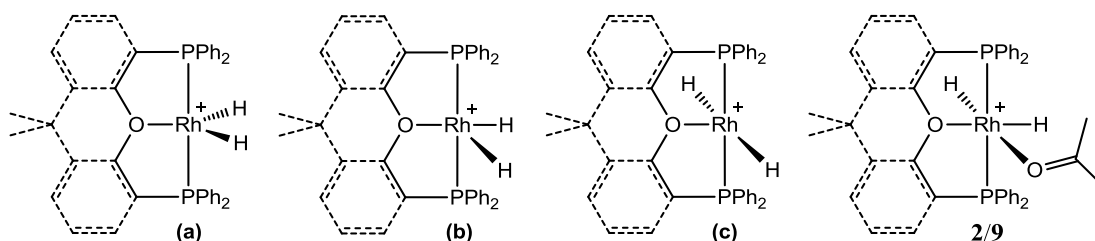
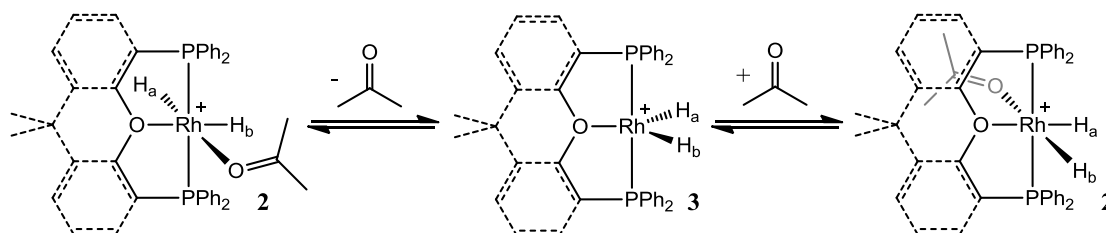


Figure 2.4: (a) Five-coordinate structure with a hydride *trans* to a vacant site; (b) pseudo-trigonal-bipyramidal structure; (c) five-coordinate structure with *trans* hydrides; complex **2/9**. $[\text{BAR}^{\text{F}}_4]^-$ anions not shown.

The methanol analogue of **2**, $[\text{Rh}(\kappa^3(\text{POP})\text{-POP}')(\text{H})_2(\text{MeOH})][\text{BF}_4]$ has been reported by Brown.¹⁴ The NMR spectroscopy data for this complex is very similar to **2** (and **9**), with a signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 45.1 [$J(\text{RhP}) = 120$], and two hydride environments observed at δ -19.2 and -21.6 [$J(\text{RhH}) = 27$, $J(\text{PH}) = 14$, $J(\text{HH}) = 14$] in the ^1H NMR spectrum. From this combined data the structures of **2** and **9** are assigned as octahedral rhodium(III) complexes, with the POP' and XANTphos ligands both coordinated through the oxygen atoms in a *meridinal* arrangement, one hydride *trans* to the ether linkage and the other hydride *cis* to both. The sixth coordination site is likely to be occupied by acetone. ESI-MS

supports the formulation of **2** and **9** with a minor signal observed in the ESI-MS spectrum of **2**, at $[M]^+ m/z = 605.11$ (calc. 605.12), and a major signal at $[M\text{-acetone}]^+ m/z = 547.07$ (calc. 547.08); and for complex **9** a minor signal at $[M]^+ m/z = 741.15$ (calc. 741.16) and a major signal at $[M\text{-acetone}]^+ m/z = 683.11$ (calc. 683.11); all with the correct isotope patterns.



Scheme 2.4: Suggested mechanism for fluxionality in complexes **2** and **9**. $[\text{BAR}^{\text{F}}_4]^-$ anions not shown.

The observed fluxionality of **2** and **9** in the room temperature NMR spectra is likely to be due to a mechanism whereby dissociation of the acetone ligand allows the formation of a five-coordinate trigonal bipyramidal intermediate (**3**) in which the hydrides are equivalent, while re-coordination of the acetone ligand interchanges the hydrides, making them equivalent on the NMR time scale (Scheme 2.4). The variable-temperature ^1H NMR spectroscopic data of complexes **2** and **9** were of sufficient quality to allow line-shape analysis using gNMR, which provided rates of exchange for this process at each temperature. The data was analysed using an Eyring plot from which the activation parameters for complex **2**, of $\Delta H^\ddagger = +60 \pm 5 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = +30 \pm 20 \text{ J K}^{-1} \text{ mol}^{-1}$ were calculated, as well as the free energy of activation: $\Delta G^\ddagger_{295} = +50 \pm 10 \text{ kJ mol}^{-1}$; these were also calculated for complex **9**: $\Delta H^\ddagger = +61 \pm 2 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = +13 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta G^\ddagger_{295} = +57 \pm 4 \text{ kJ mol}^{-1}$ (Figure 2.5). The mechanisms for reorganisation of the two molecules

would be expected to be similar for both complexes; therefore the free energies of activation should also be similar. From this data it can be seen that the free energy for activation of the XANTphos complex is slightly greater than that of the POP' complex, but the two values are within error of each other. The intermediate species is not observed, but the positive $\Delta S^\ddagger$ values are consistent with a dissociative mechanism, suggesting an I_d activation mode.^{24, 25}

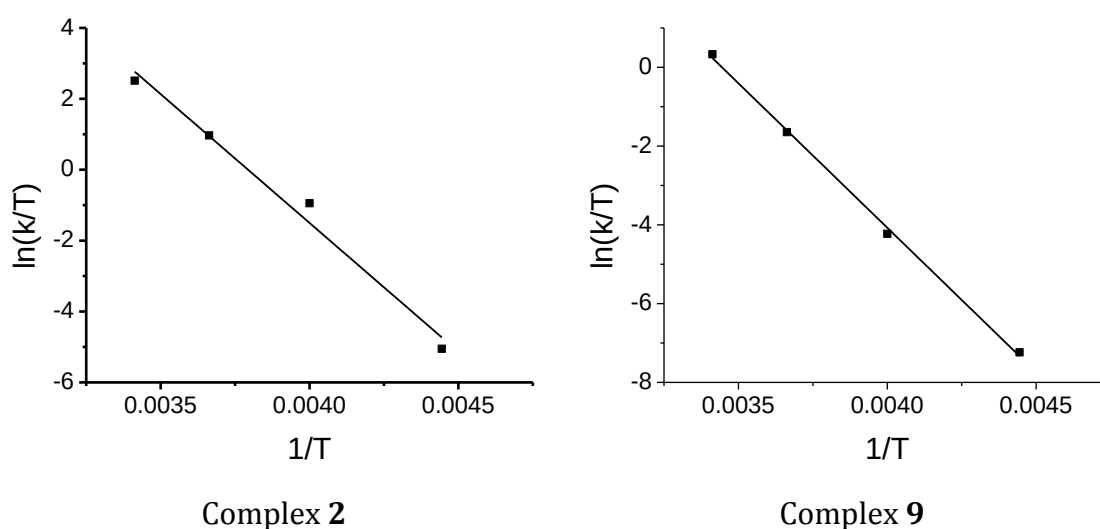
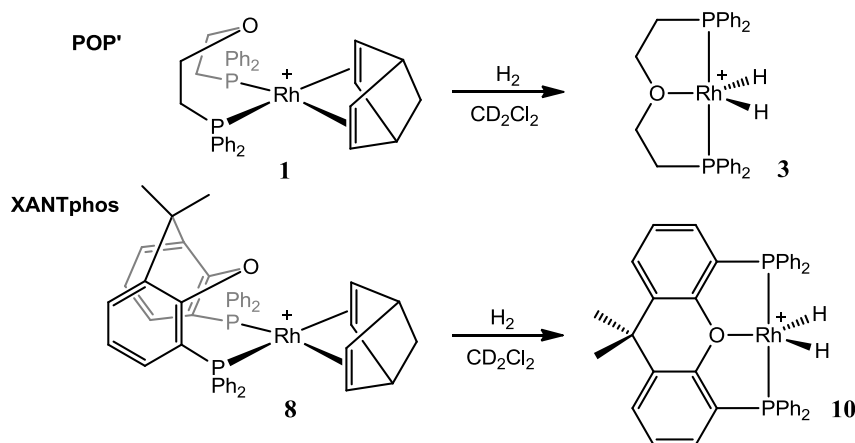


Figure 2.5: Eyring plots for the rate of exchange in **2** and **9**.

Activation parameters for solvent exchange in rhodium(III) complexes vary enormously depending on solvent and spectator ligands. However, the activation parameters for this exchange are similar to those observed for $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{DMSO})_3]^{2+}$ ($\Delta H^\ddagger = +54.6 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = +6.4 \text{ J K}^{-1} \text{ mol}^{-1}$), and exchange is said to occur *via* a dissociative mechanism,²⁴ as has been suggested here for the POP' and XANTphos systems (Scheme 2.4). Evidence for the formation of a five coordinate pseudo-trigonal-bipyramidal intermediate (Scheme 2.4) is provided when complexes **1** and **8** are hydrogenated in a non-coordinating solvent such as CD_2Cl_2 rather than acetone. The NMR data is different and strongly suggests the

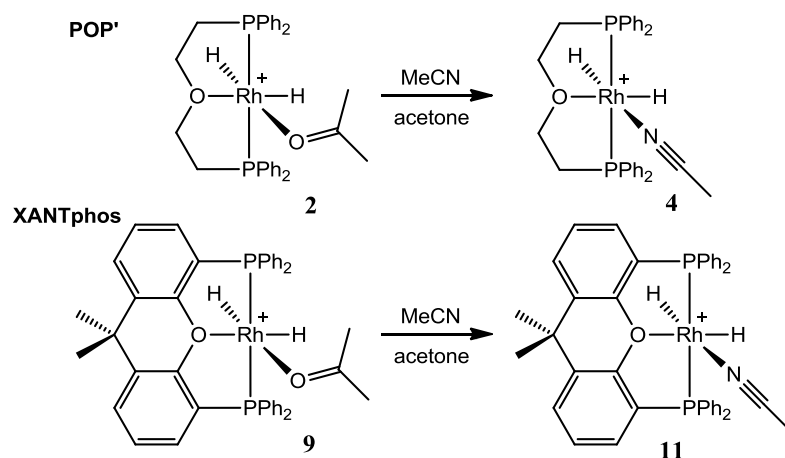
formation of the pseudo-trigonal-bipyramidal 16 electron complexes: $[\text{Rh}(\kappa^3(\text{POP})\text{-POP}')(\text{H})_2][\text{BAR}^{\text{F}}_4]$ (**3**) and $[\text{Rh}(\kappa^3(\text{POP})\text{-XANTphos})(\text{H})_2][\text{BAR}^{\text{F}}_4]$ (**10**) (Scheme 2.5). These are the postulated intermediate species in the fluxional mechanism of **2** and **9**.



Scheme 2.5: Hydrogenation of complexes **1** and **8** in CD_2Cl_2 . $[\text{BAR}^{\text{F}}_4]^-$ anions not shown.

The room temperature ^1H NMR spectra of **3** and **10** both show integral 2H hydride signals with doublet of triplet multiplicity at δ -19.10 [$J(\text{RhH}) = 32$, $J(\text{PH}) = 12$] for complex **3**, and δ -18.28 [$J(\text{RhH}) = 33$, $J(\text{PH}) = 12$] for complex **10**; which are consistent with two equivalent hydrides coupling to one rhodium centre and two equivalent phosphorus atoms. Doublets at δ 44.04 [$J(\text{RhP}) = 119$] (**3**) and 41.50 [$J(\text{RhP}) = 117$] (**10**) are observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, indicating equivalent phosphines coupling to a rhodium(III) centre. ESI-MS of both complexes are consistent with their empirical formulae, with signals at $[\text{M}]^+ m/z = 547.09$ (calc. 547.08) (**3**) and $[\text{M}]^+ m/z = 683.13$ (calc. 683.11) (**10**). Addition of 10 equivalents of acetone to complex **3** in CD_2Cl_2 solution quantitatively forms complex **2**, consistent with its role in the fluxional process. Interestingly, hydrogenation of $[\text{Rh}(\kappa^2(\text{PP})\text{-DPEphos})(\text{NBD})][\text{BAR}^{\text{F}}_4]$ (**i-98**) in CD_2Cl_2 forms an

unstable species which rapidly decomposes in the absence of a coordinating ligand.



Scheme 2.6: Formation of complexes **4** and **11**. $[\text{Bar}^{\text{F}}_4]^-$ anions not shown.

Attempts to isolate solid material of complexes **2**, **3**, **9** and **10** all failed due to decomposition over the timescales required. However, addition of acetonitrile to acetone solutions of **2** and **9** cleanly affords the acetonitrile adducts $[\text{Rh}(\kappa^3_{\text{POP}}\text{-POP}')(\text{H})_2(\text{MeCN})][\text{Bar}^{\text{F}}_4]$ (**4**) and $[\text{Rh}(\kappa^3_{\text{POP}}\text{-XANTphos})(\text{H})_2(\text{MeCN})][\text{Bar}^{\text{F}}_4]$ (**11**) (Scheme 2.6). The room temperature ^1H NMR spectra of **4** and **11** both show two integral 1H doublet of triplet of doublet hydride environments at δ -16.69 [$J(\text{RhH}) = 21$, $J(\text{PH}) = 12$, $J(\text{HH}) = 8.9$] and -19.39 [$J(\text{RhH}) = 22$, $J(\text{PH}) = 13$, $J(\text{HH}) = 8.9$] for complex **4**, and δ -15.36 [$J(\text{RhH}) = 20.3$, $J(\text{PH}) = 12.3$, $J(\text{HH}) = 7.8$] and -19.36 [$J(\text{RhH}) = 30.8$, $J(\text{PH}) = 13.9$, $J(\text{HH}) = 7.8$] for complex **11** (Figure 2.6); which are similar to the ^1H NMR spectra of complexes **2** and **9** at 225 K (Figure 2.3). Two signals are observed in the ^1H NMR spectrum of complex **11** for the XANTphos ligand methyl groups at δ 1.91 and 1.51 indicating they are inequivalent at room temperature. This data supports the proposed fluxional mechanism in complexes **2** and **9**, as acetonitrile is a more strongly coordinating ligand than acetone, and

therefore presents a large barrier to fluxionality through any mechanism requiring dissociation of the acetonitrile ligand.

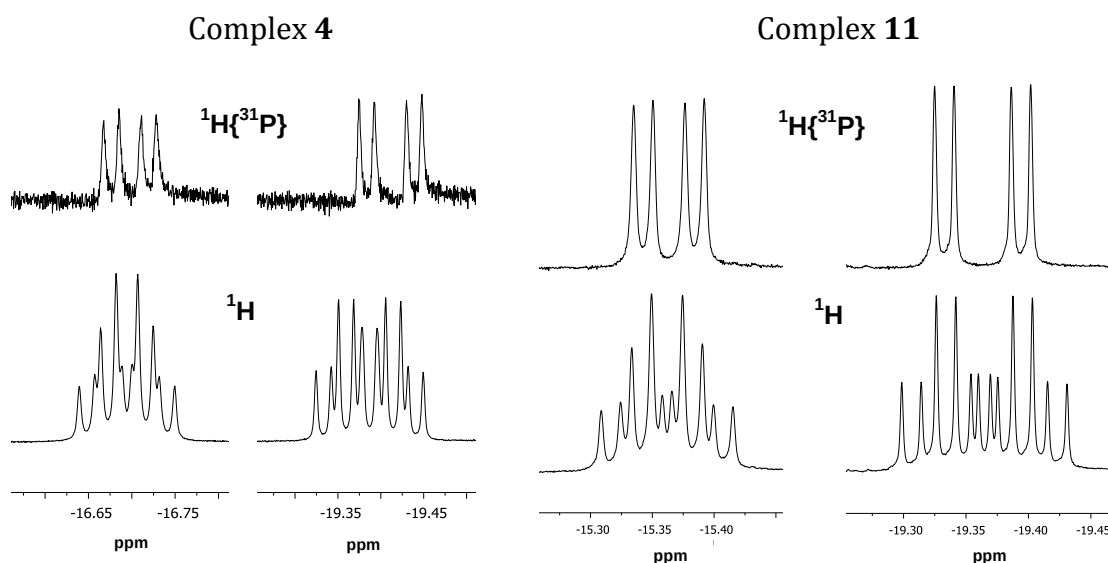


Figure 2.6: $^1\text{H}\{^{31}\text{P}\}$ and ^1H NMR spectra of complexes **4** and **11**.

$^1\text{H}\{^{31}\text{P}\}$ NMR experiments remove the triplet coupling, indicating that the hydrides are coupling to two equivalent phosphine environments. ESI-MS analysis of complexes **4** and **11** confirm the empirical formulae, with a minor signal at $[\text{M}]^+$ $m/z = 588.09$ (calc. 588.11), and a major signal at $[\text{M} - \text{CH}_3\text{CN}]^+$ $m/z = 547.07$ (calc. 547.08) for complex **4**; and a minor signal at $[\text{M}]^+$ $m/z = 724.09$ (calc. 724.14), and a major signal at $[\text{M} - \text{MeCN}]^+$ $m/z = 683.07$ (calc. 683.11) (**11**). Single crystals of **4** and **11**, suitable for X-ray diffraction, were obtained by diffusion of hexane or pentane into a solution of the respective complex in $\text{C}_6\text{H}_5\text{F}$. The resulting structures show *meridinal* coordination of the POP' and XANTphos ligands, *cis* hydrides and coordinated MeCN ligands, confirming the solution NMR data (Figure 2.7). The Rh1-P1 and Rh1-P2 bond lengths are (within 3 st. dev.) the same in complex **4**, while the Rh1-P1 bond length in complex **11** is within three

standard deviations of the Rh-P bond lengths observed in **4**, but is slightly longer than the Rh1-P2 bond length. The Rh1-O1 and Rh1-N1 bond lengths are (within 3 st. dev.) the same in both complexes. The P1-Rh1-P2 bond angles show little difference between the two complexes [$164.95(4)^\circ$ in complex **4**, $164.31(3)^\circ$ in **11**], and are similar to the P-Rh-P bond angles observed in the complexes $[\text{Rh}(\text{POP}')(\text{CO})][\text{PF}_6]$ $165.9(1)^\circ$,²⁶ and $[\text{Rh}(\text{XANTphos})(\text{CO})][\text{BF}_4]$ $164.42(4)^\circ$.²⁷

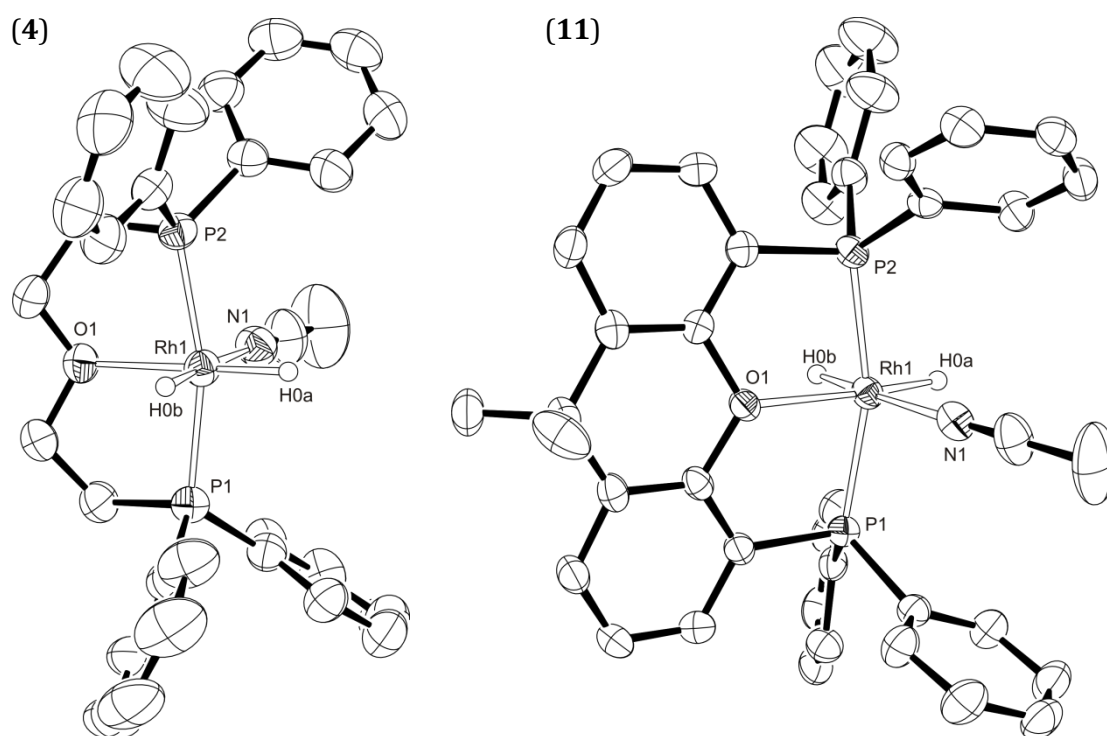
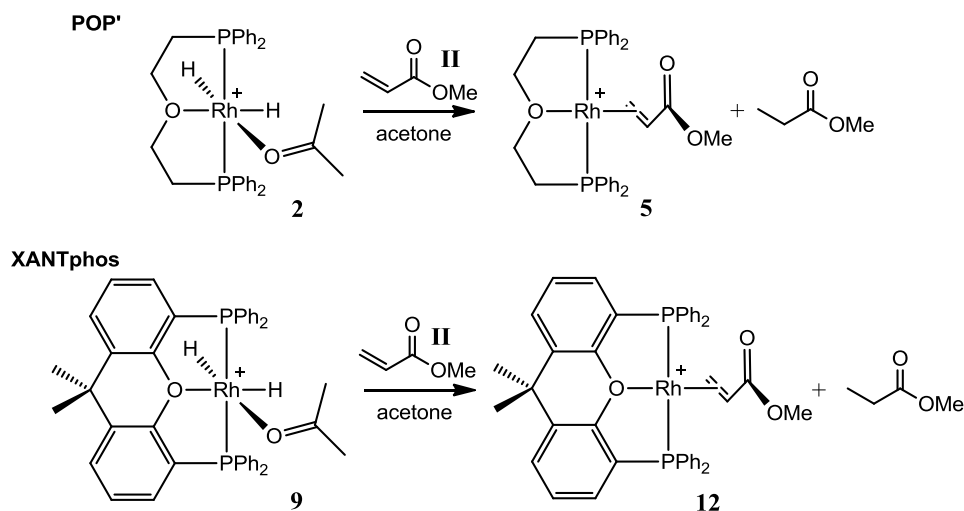


Figure 2.7: Molecular structures of the cationic portions of $[\text{Rh}(\kappa^3\text{-POP}')(\text{H})_2(\text{MeCN})][\text{BAR}^{\text{F}}_4]$ (**4**) and $[\text{Rh}(\kappa^3(\text{POP})\text{-XANTphos})(\text{H})_2(\text{MeCN})][\text{BAR}^{\text{F}}_4]$ (**11**). Displacement ellipsoids are drawn at the 50% probability level. The anion and hydrogen atoms, apart from H0a and H0b, are omitted for clarity. (**4**) Selected bond lengths [$\text{\AA}$]: Rh1-P1, 2.2765(10); Rh1-P2, 2.2778(10); Rh1-O1, 2.232(3); Rh1-N1, 2.134(4). Selected bond angles [$^\circ$]: P1-Rh1-P2, $164.95(4)$; N1-Rh1-O1, $89.97(12)$. (**11**) Selected bond lengths [$\text{\AA}$]: Rh1-P1, 2.2748(8); Rh1-P2, 2.2584(8); Rh1-O1, 2.233(2); Rh1-N1, 2.128(3). Selected bond angles [$^\circ$]: P1-Rh1-P2, $164.31(3)$; N1-Rh1-O1, $95.98(9)$.



Scheme 2.7: Removal of the hydrides in complexes **2** and **9**. $[\text{BAr}^{\text{F}}_4]^-$ anions not shown.

For the rhodium complexes **2**, **3**, **9** or **10** to enter the hydroacylation catalytic cycle they must be able to undergo oxidative addition of an aldehyde molecule. The complexes are in +3 oxidation states, and are 5 or 6 coordinate. The hydrides in complexes **2**, **3**, **9** or **10** do not readily reductively eliminate in solution and addition of aldehyde (10 eq.) to complexes **2**, **3**, **9** and **10** leaves the complexes unchanged. Therefore, in order to generate an active precatalyst it is necessary for the metal to reform a rhodium(I) oxidation state, and reduce the coordination number by two, through reductive elimination of the hydrides. To encourage this process two equivalents of methyl acrylate (**II**) were added to **2** and **9**, resulting in the hydrogenation of 1 equivalent of the olefin and formation of new rhodium(I) complexes $[\text{Rh}(\kappa^3(\text{POP})\text{-POP}')(\eta^2\text{-H}_2\text{C=CHCO}_2\text{Me})][\text{BAr}^{\text{F}}_4]$ (**5**) and $[\text{Rh}(\kappa^3(\text{POP})\text{-XANTphos})(\eta^2\text{-H}_2\text{C=CHCO}_2\text{Me})][\text{BAr}^{\text{F}}_4]$ (**12**) (Scheme 2.7). Complexes **5** and **12** were isolated by the slow addition of concentrated solutions of **5** and **12** formed *in situ*, to stirring pentane. The ^1H NMR spectrum of complex **12** in CD_2Cl_2 clearly shows three sharp integral ^1H multiplet proton environments for co-ordinated

alkene at δ 3.97, 3.45 and 2.91 and an integral 3H singlet at δ 3.24 for the O-CH₃ group. The ¹H NMR spectrum of complex **5** is slightly more ambiguous: two integral 1H signals and an integral 3H singlet at δ 3.33 (O-CH₃) are observed, which are due to the coordinated alkene. The final integral 1H signal of the coordinated alkene is masked by the P-CH₂ signal of the ligand backbone at δ 2.76, and another three integral 2H signals are observed for the ligand backbone. A ¹³C-¹H HSQC NMR experiment allows for the unequivocal assignment of the signals in the ¹H NMR spectrum of **5** as δ 3.66 (CH=CH₂), 3.33 (O-CH₃), 3.20 (CH=CH₂), and 2.76 (CH=CH₂') (Figure 2.8).

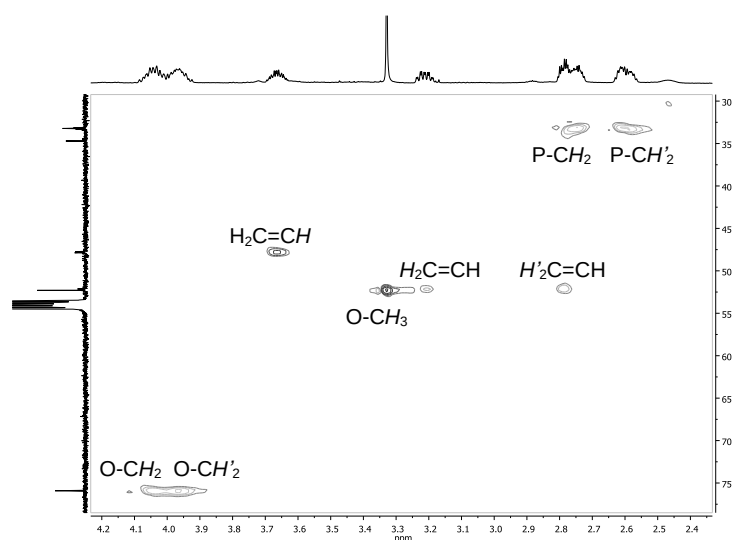


Figure 2.8: 295 K ¹³C-¹H HSQC NMR spectrum of complex **5**, aliphatic region only.

No hydride signal is observed for either complex, indicating the hydrides in complexes **2** and **9** have been successfully removed. For the complex [Rh(triphos)(H)(η^2 -H₂C=CHCO₂Me)] [triphos = MeC(CH₂PPh₂)₃] signals for bound methyl acrylate are observed at δ 3.4 and δ 2.9 in the ¹H NMR spectrum in CD₂Cl₂,²⁸ which supports the assignment of these high field signals as the coordinated alkene ligand. Both complexes show only one doublet signal in the

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 38.86 [$J(\text{RhP}) = 133$] (**5**), and 32.66 [$J(\text{RhP}) = 124$] (**12**), which indicate that a fluxional mechanism must be occurring to make the phosphine environments equivalent on the NMR timescale, given the inherent asymmetry of the alkene. The coupling constant for the rhodium(I) complex, **12**, is similar to the coupling observed in the rhodium(III) complex. However, other rhodium(I) complexes of XANTphos have demonstrated small ^{103}Rh - ^{31}P coupling constants, such as $\text{Rh}(\text{CO})\text{Cl}(\text{XANTphos})$ [$J(\text{RhP}) = 123.5$]²⁹ and $[\text{Rh}(\text{XANTphos})(\text{CO})][\text{BF}_4]$ [$J(\text{RhP}) = 121.2$]¹⁰. ESI-MS of complexes **5** and **12** confirm the empirical formulae, with a signal at $[\text{M}]^+ m/z = 631.13$ (calc. 631.10) corresponding to the cationic portion of **5**, and a signal at $[\text{M}]^+ m/z = 767.09$ (767.14) for complex **12**, of the correct isotope pattern.

To understand the mechanism which could be making the phosphine environments equivalent on the NMR timescale, the solution NMR behaviour of complex **5** was studied in detail. Cooling a CD_2Cl_2 solution of complex **5** progressively from 295 K to 200 K resulted in a $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 200 K which shows two clearly resolved ABX doublet of doublets at δ 40.70 [$J(\text{PP}) = 384$, $J(\text{RhP}) = 119$] and 32.91 [$J(\text{PP}) = 384$, $J(\text{RhP}) = 127$] (Figure 2.9), indicating *trans* inequivalent phosphines. At this temperature, in the ^1H NMR spectrum, the methylene signals of the ligand are broad and do not offer any extra information. This NMR data suggests that a fluxional process must be occurring which is arrested at 200 K resulting in inequivalent mutually *trans* phosphine environments.

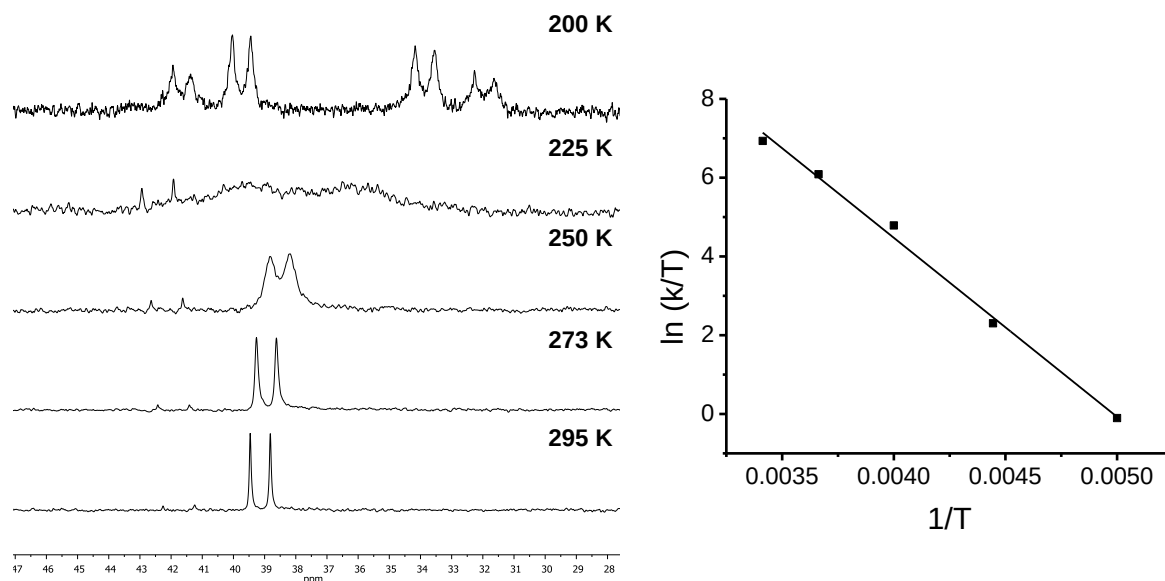
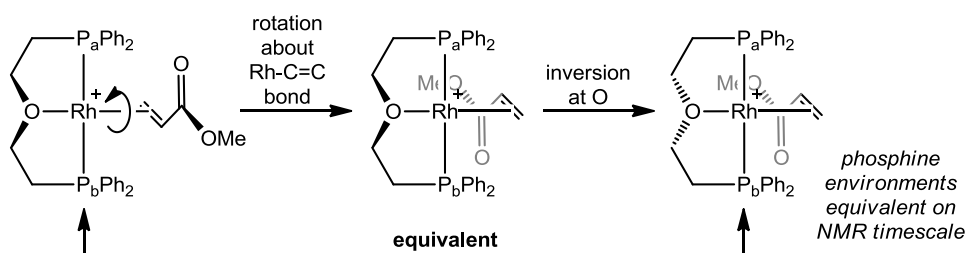


Figure 2.9: $^{31}\text{P}\{^1\text{H}\}$ variable temperature NMR spectra of complex **5** (the signal at $\delta \approx 42$ is an unidentified minor impurity) and Eyring analysis for the rate of exchange in **5**.

The variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic data was of sufficient quality to allow a line-shape analysis using gNMR which afford rates of exchange for each temperature. The data was analysed using an Eyring plot, from which the activation parameters of $\Delta H^\ddagger = +38 \pm 2 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -9 \pm 7 \text{ J K}^{-1} \text{ mol}^{-1}$ were calculated, as well as the free energy of activation for the process: $\Delta G^\ddagger_{295} = +41 \pm 4 \text{ kJ mol}^{-1}$ (Figure 2.9). The small $\Delta S^\ddagger$ value suggests an intramolecular fluxional process, and the value for the free energy of activation is in line with a relatively low energy process. Systematic studies of the rotation of olefins bound to square-planar rhodium(I) complexes have been reported,^{30, 31} and typical values for the free energy of activation for such processes are in the range 29-79 kJ mol^{-1} (7-19 kcal mol^{-1} as reported), depending on the nature of the bound alkene, and the ligand set involved.³²



Scheme 2.8: A fluxional process which would give time-averaged C_{2v} symmetry. $[\text{BAr}^{\text{F}}_4]^-$ anions not shown.

A simple rotation of the alkene around the Rh-C=C (Rh1-C33/C34 *vide infra*) vector would make the phosphines equivalent, and give time-averaged C_{2v} symmetry, but only if it were followed by a low-energy inversion of the stereochemistry at the ether linkage in the ligand backbone (Scheme 2.8). However, this process would give a structure with equivalent environments for the four P-CH₂ protons, and the four CH₂-O protons: i.e. two integral 4H environments would be observed for the ligand backbone protons in the ¹H NMR spectrum. Instead, four integral 2H proton environments are observed for the ligand backbone in the 295 K ¹H NMR spectrum of **5**; the ¹³C-¹H HSQC NMR spectrum (Figure 2.8) shows that the protons are inequivalent across the ligand backbone (both O-CH₂ proton signals correlate with one carbon signal at δ 75.74, likewise the two P-CH₂ proton signals correlate with one carbon signal at δ 33.03), and therefore must be inequivalent within each methylene group, to give rise to four integral 2H signals (Figure 2.10).

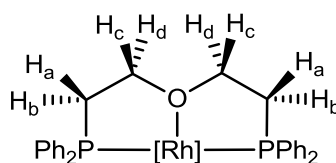
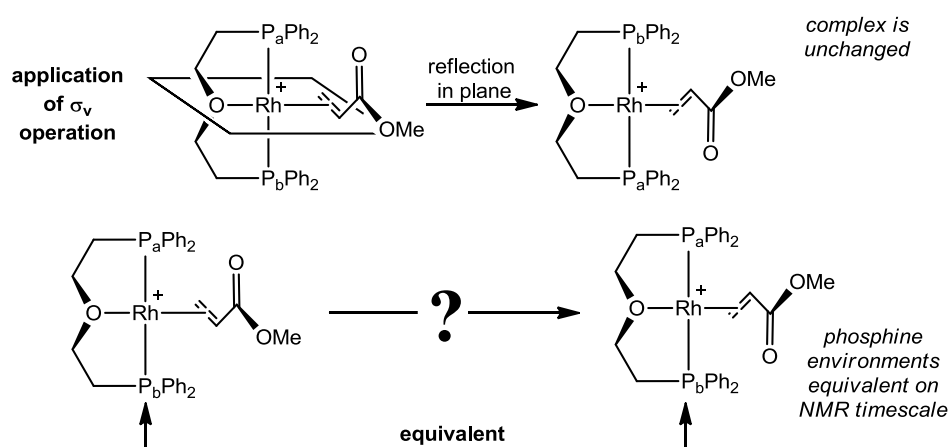


Figure 2.10: Diagram of ligand backbone in complex **5** showing four proton environments, which are inequivalent across the ligand backbone. $[\text{BAr}^{\text{F}}_4]^-$ anion not shown.

As four 2H proton environments are observed for the ligand backbone, this indicates that time-averaged C_s symmetry is present, i.e. a σ_v symmetry element is present on the NMR time-scale, and thus inversion at the ether group is not occurring (Scheme 2.9). Therefore, to obtain the observed equivalence of the phosphines and ^1H NMR pattern, some fluxional process must be occurring, other than a simple alkene rotation/ligand inversion.



Scheme 2.9: (top) Application of σ_v symmetry operation to complex **5**, complex remains unchanged. (bottom) A fluxional process is required which gives time-averaged C_s symmetry. $[\text{BAR}^{\text{F}}_4]^-$ anions not shown.

Research by Sebastian Pike (Weller group) investigated complexes containing the related ligand $(\text{PPh}_2\text{CH}_2\text{CH}_2)_2\text{PPh}$ (PPP' , Figure 2.11).³³ The methyl acrylate complex $[\text{Rh}(\kappa^3_{(\text{PPP})}\text{-PPP}')(\eta^2\text{-H}_2\text{C}=\text{CHCO}_2\text{CH}_3)][\text{BAR}^{\text{F}}_4]$ (**i-110**) (Figure 2.11) showed similar spectroscopic properties to **5**, i.e. equivalent phosphine environments (for the terminal phosphines of the ligand backbone) and four integral 2H proton environments for the methylene groups of the ligand backbone.³⁴ As this complex is unlikely to undergo inversion of the backbone at the PPh group, and it is proposed on the basis of the NMR data that this inversion also is not occurring in complex **5**, **i-110** provides a useful comparison to **5**.

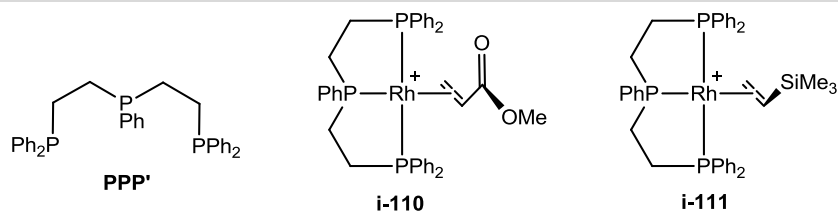
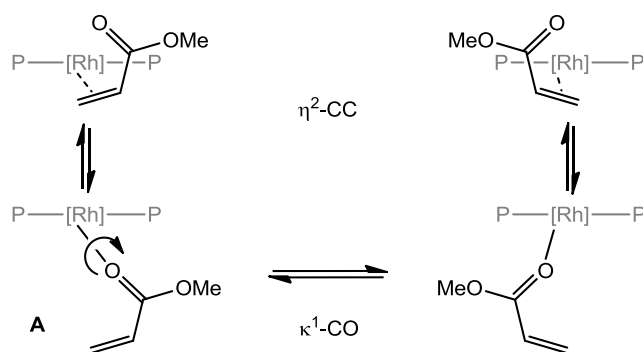


Figure 2.11: Ligand PPP' and coordinated alkene complexes formed with PPP'. [BAR^F₄]⁻ anions not shown.

To explore the fluxional process occurring in this complex and in complex **5**, the vinylmethylsilane complex [Rh(κ^3 _(PPP)-PPP')(η^2 -H₂C=CHSiMe₃)] [BAR^F₄] (**i-111**) was also investigated (Figure 2.11). The related POP' complex could not be prepared, so the results for the PPP' complex are briefly discussed here, to explain the reasoning behind the proposed mechanism for the fluxional process which makes the phosphines equivalent in complex **5**. The incorporation of a SiMe₃ group into the alkene, has a significant effect on the fluxional process: instead of four integral 2H proton environments (as observed in complex **5** and the related PPP' methyl acrylate complex), eight methylene environments are observed in the ¹H NMR spectrum, alongside three sharp integral 1H signals for the alkene protons. Three separate environments are observed in the room temperature ³¹P{¹H} NMR spectrum which all couple to one another, with two showing *trans* ³¹P-³¹P coupling [*J*(PP) = 331 Hz]. This data indicates that there is no fluxional process occurring in this complex to make the terminal phosphines equivalent; unlike in **5** and **i-110**.

Therefore, there is a process occurring in complexes **5** and **i-110** whereby the alkene flips, but which does not occur in complex **i-111**. This process must be mediated by the acrylate group, as the SiMe₃ group effectively halts the process. A

possible mechanism for this process is shown in Scheme 2.10, whereby coordination of the alkene through the oxygen (intermediate **A**, Scheme 2.10) is followed by the alkene flipping, and then re-coordinating to the metal centre through the double bond, to give the other enantiomeric complex.



Scheme 2.10: Suggested mechanism for the fluxional process in complexes **5** and **i-110**. $[\text{BAR}^{\text{F}}_4]^-$ anions not shown.

Alternative coordination modes of the alkene complex in the intermediate species **A**, such as $\eta^2\text{-CO}:\eta^2\text{-CC}$ as seen in the complex $\{\text{Ru}(\text{PPh}_3)_2(\eta^2\text{-H}_2\text{C}=\text{CHCO}_2\text{CH}_3)(\eta^2\text{-H}_2\text{C}=\text{CHCO}_2\text{CH}_3)\}$, or a metallacyclic structure as seen in the complex $\{\text{Cp}^*\text{TaCl}_2(\text{H}_2\text{C}=\text{CHCO}_2\text{CH}_3)\}$ (Figure 2.12),^{35, 36} have been discounted as they do not account for the observed inequivalence of the geminal alkene protons.

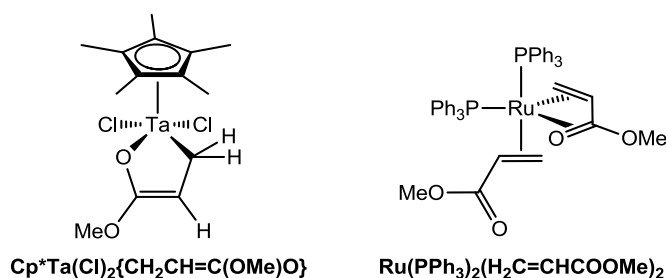


Figure 2.12: Possible alternative coordination modes of the alkene complex.

Yellow crystals of complex **5** suitable for X-ray diffraction were obtained by diffusion of pentane into a solution of the crude complex in CD_2Cl_2 . The solid state

structure of **5** (Figure 2.13) has a pseudo-square-planar environment about the rhodium atom, with an η^2 -coordinated alkene. The alkene is disordered over two positions in a 70:30 ratio which are related to each other by an approximate reflection in the O-Rh-C=C plane, to give an enantiomeric pair of cations. The C-C distance in the alkene [1.405(7) Å, major; 1.411(9) Å, minor] lies within the range found for later transition metals with coordinated methyl acrylate (≈ 1.3 -1.43 Å).³⁷⁻³⁹ The two components of disorder observed in the solid state for complex **5** are effectively represented by the two η^2 -CC structures shown in Scheme 2.10. This further supports the hypothesised fluxional mechanism.

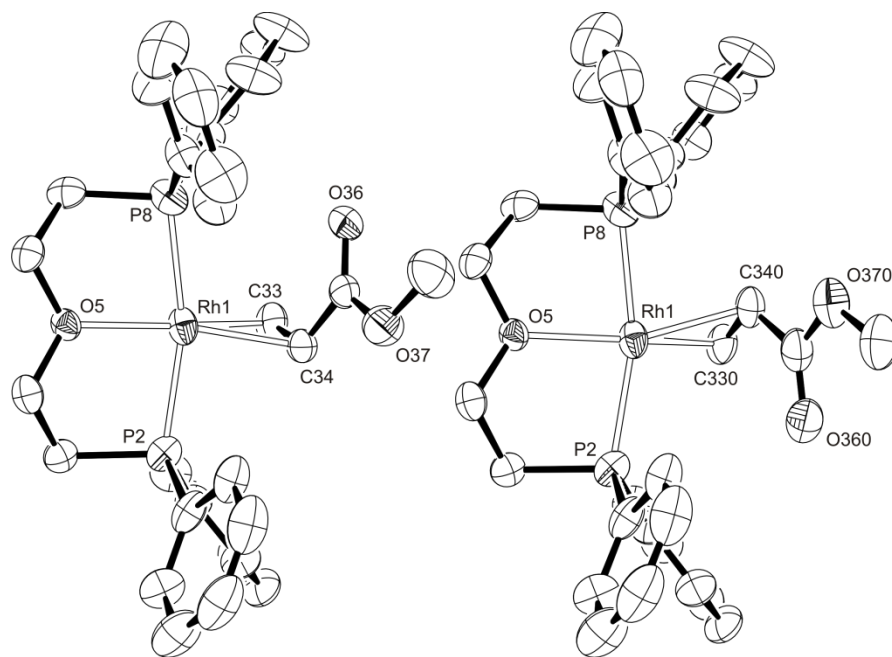
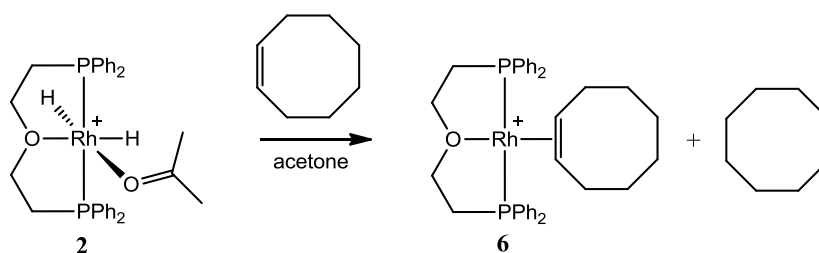


Figure 2.13: Solid-state structure of the cationic portion of [Rh(POP')(η^2 -H₂C=CHCO₂Me)][BARF₄] (**5**) (minor component shown to the right, ratio 70:30, respectively). Displacement ellipsoids are drawn at the 50% probability level. The anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Rh1-P2, 2.2917(16); Rh-P8, 2.2982(16); Rh-O5, 2.2100(3); C33-C34, 1.405(7); Rh-C33, 2.074(16); Rh-C34, 2.144(7); C330-C340, 1.411(9); Rh-C330, 2.11(4); Rh-C340, 2.148(17). Selected bond angles [°], (dihedral): C33-C34-C35-O36, 12.4(11); C330-C340-C350-O360, -11(3); (planes): O5Rh1P8P2/Rh1C33C34, 76.9(5); O5Rh1P8P2/Rh1C330C, 340 69.6(12).

There is significant literature on the orientation of alkene ligands coordinated to transition-metal centres, and studies indicate that the preferred conformation for a metal-bonded alkene can be explained by a combination of the electronic effect of back-donation from metal *d* orbitals into the alkene π^* orbital, and the steric effect of other ligands.⁴⁰ This leads to an upright alkene orientation in d^8 ML_3 fragments, with a small barrier to rotation of the alkene around the metal-alkene axis.⁴¹ In-plane orientations of the alkene are known where the environment around the metal-complex hinders or prevents the coordination of the alkene in an upright orientation.⁴² In the solid state structure obtained of complex **5**, the alkene adopts the more common upright orientation observed for d^8 ML_3 fragments.

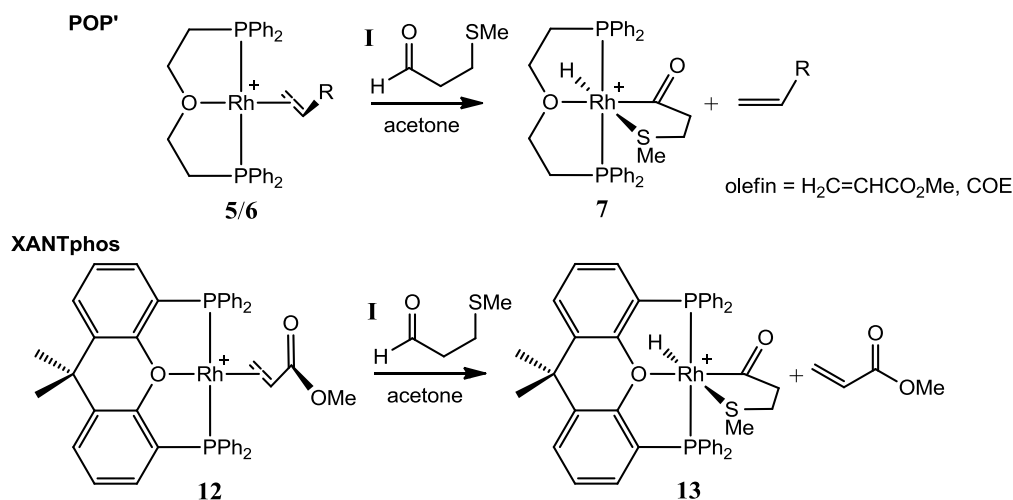
Other rhodium(I) complexes with coordinated alkenes related to **5** were explored. The complex $[Rh(\kappa^3_{(POP)}-POP')(\eta^2-COE)][BAR^F_4]$ (COE = cyclooctene) (**6**, Scheme 2.11) was prepared in a similar manner to complex **5**. In the ^1H NMR spectrum of complex **6** in CD_2Cl_2 , the coordinated alkene protons were observed as a broad integral 2H signal at δ 3.66, while the other methylene signals of the COE ligand were observed at δ 2.02 (integral 2H) and 1.35-0.76 (integral 6H + 2H + 2H). Unlike complex **5**, two environments of integral 4H each are observed in the ^1H NMR spectrum for the ligand backbone at δ 3.74 and 2.61 indicating C_2 symmetry. The $^{31}P\{^1H\}$ NMR spectrum shows a single environment at δ 35.9 [$J(RhP) = 143$] indicating a rhodium(I) environment. ESI-MS in C_6H_5F of complex **6** gives a signal at $[M]^+ m/z = 655.19$ (calc. 655.18). This NMR data is consistent with the related neutral complex $\{Rh(PNP^{Ph})(COE)\}$ (where $PNP^{Ph} = [N\{2-PPh_2-4-Me-C_6H_3\}_2]^-$) in

which the alkene protons are observed as a broad doublet at 3.60 ppm in the ^1H NMR spectrum, and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the complex shows a doublet at δ 38 [$J(\text{RhP}) = 149$ Hz].⁴³ The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **6** displays a signal at δ 69.5 that correlates to the ^1H alkene signals in the HSQC NMR spectrum.



Scheme 2.11: Formation of $[\text{Rh}(\kappa^3(\text{POP})\text{-POP}')(\eta^2\text{-COE})][\text{BAr}^{\text{F}}_4]$ (**6**). $[\text{BAr}^{\text{F}}_4]^-$ anions not shown.

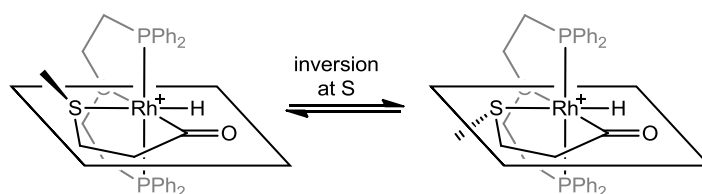
Ultimately the aim of this research is to explore the properties of these complexes as catalysts for hydroacylation and to elucidate the catalytic cycle for each system, and therefore stoichiometric reactions mimicking the first step of the catalytic cycle were undertaken: the activation of the aldehyde C-H bond. The aldehyde chosen was the β -S-substituted pentanal (**I**) used in earlier studies by the Weller group.³ The alkene groups proved to be labile ligands, easily displaced by the incoming aldehyde. On addition of 1 equivalent of aldehyde **I** to a solution of complex **5**, **6** or **12** in acetone, there was an immediate (on mixing) colour change from bright yellow to nearly colourless, to form the new rhodium(III) acyl-hydride complexes $[\text{Rh}(\kappa^3(\text{POP})\text{-POP}')(\text{H})(\kappa^1_{(\text{S})}\text{-}\sigma^1_{(\text{C})}\text{-COC}_2\text{H}_4\text{SCH}_3)][\text{BAr}^{\text{F}}_4]$ (**7**) and $[\text{Rh}(\kappa^3(\text{POP})\text{-XANTphos})(\text{H})(\kappa^1_{(\text{S})}\text{-}\sigma^1_{(\text{C})}\text{-COC}_2\text{H}_4\text{SCH}_3)][\text{BAr}^{\text{F}}_4]$ (**13**) (Scheme 2.12).



Scheme 2.12: Addition of aldehyde **I** to rhodium(I) alkene complexes, to form complexes **7** and **13**. $[\text{BAR}^{\text{F}}_4]^-$ anions not shown.

Complexes **7** and **13** were analysed by NMR spectroscopy and for both, integral ^1H hydride signals were observed as broad doublets in the ^1H NMR spectra at δ -9.58 [$J(\text{RhH}) = 24$] (**7**) and -8.72 [$J(\text{RhH}) = 23$] (**13**). Two broad integral 2H signals were observed for the aldehyde methylene backbone in complex **13**, as well as two integral 3H inequivalent environments for the XANTphos methyl groups. A doublet signal at δ 1.47 [$J(\text{HH}) = 1.8$] is assigned as the SMe protons in **13**, and an equivalent doublet signal is observed for complex **7** at δ 1.79 ppm [$J(\text{HH}) = 1.8$]. ESI-MS confirms the mass of the parent ions with a signal observed at $[\text{M}]^+ m/z = 785.12$ (calc. 785.13) in the spectrum for complex **13**, and a signal at $[\text{M}]^+ m/z = 649.10$ (calc. 649.10) for complex **7**. The 295 K $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **7** and **13** both show broad signals at δ 31.1 and 32.8; however, cooling the solutions (to 225 K for complex **7** and 240 K for complex **13**) ultimately resolves these signals into an ABX second order doublet of doublets at δ 34.30 [dd, $J(\text{PP}) = 308$, $J(\text{RhP}) = 127$] and 28.19 [$J(\text{PP}) = 308$, $J(\text{RhP}) = 130$] (**7**); and δ 35.22 [$J(\text{PP}) = 300$, $J(\text{RhP}) = 124$] and 32.04 [$J(\text{PP}) = 300$, $J(\text{RhP}) = 127$] (**13**), which both show *trans* ^{31}P - ^{31}P

coupling. The ^{103}Rh - ^{31}P coupling is indicative of a rhodium(III) oxidation state; this, combined with the quantitative formation of free alkene observed in the ^1H NMR spectra along with integral 1H hydride signals that show coupling to rhodium, suggests the incoming aldehyde has displaced the alkene ligands and undergone oxidative addition to the rhodium(I) metal centres. It is also worth mentioning that the free alkene shows no sign of reacting with the acyl hydride formed in complex **7** and **13**. The *trans* coupling of the phosphines locates the ligand in a *meridinal* geometry, while a correlation between the hydride signal and the SMe protons in the ^1H - ^1H COSY NMR spectra of both complexes suggests the hydride is orientated *trans* to the thioether. The inequivalence of the phosphines at low temperature is a result of the stereochemistry about the sulphur, which causes the methyl group to be canted to one side of the central mirror plane (Scheme 2.13).



Scheme 2.13: Inversion at sulphur gives time-averaged C_s symmetry (i.e. σ_v symmetry element is present on the NMR time scale), proposed to occur in complexes **7** and **13**. $[\text{BAr}^{\text{F}}_4]^-$ anions not shown.

However, at room temperature it is proposed that a fluxional process is occurring involving an inversion at the sulphur group, possibly *via* an sp^2 -hybridised intermediate at the sulphur, which makes the phosphines equivalent. A fluxional process involving the decoordination of the sulphur group is discounted as coupling of the SMe protons to the hydride is observed at 295 K. The equivalent

complex $[\text{Rh}(\kappa^3_{\text{(POP)}}\text{-DPEphos})(\text{H})(\kappa^1_{\text{(S)}}\text{-}\sigma^1_{\text{(C)}}\text{-COC}_6\text{H}_4\text{SCH}_3)][\text{BAR}^{\text{F}}_4]$ (**i-100a**) (with an aromatic acyl group) undergoes a related fluxional process, involving inversion at the thioether.¹ Inversion at coordinated thioethers is a well-documented process;⁴⁴⁻⁵⁰ $\Delta G^\ddagger_{298}$ for the fluxional process in **i-100a** ($+32 \pm 2.3 \text{ kJ mol}^{-1}$) is consistent with reported barriers, and $\Delta S^\ddagger = +5 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$ suggests an intramolecular process. **i-100a** was reported as having a hydride signal at δ -8.75, which showed doublet of triplet multiplicity [$J(\text{RhH}) = 23$, $J(\text{PH}) = 1$], and a broadened signal for the SMe group at δ 1.56, which is consistent with the observed data in **7** and **13**, and supports the proposed structures.¹

Crystals suitable for X-ray diffraction were obtained by slow diffusion of solutions of complexes **7**⁵¹ and **13** in $\text{C}_6\text{H}_5\text{F}$, into hexane or pentane. The solid-state structures are displayed in Figure 2.14, and are consistent with the solution data. Both complexes show rhodium in pseudo-octahedral environments with the ligands adopting a *meridinal* coordination mode, and the C-H activated aldehyde occupying the other *meridinal* plane as proposed, with the hydride *trans* to the sulphur group, and the acyl *trans* to the ether of the ligand. Unlike $[\text{Rh}(\kappa^3_{\text{(POP)}}\text{-DPEphos})(\text{H})(\kappa^1_{\text{(S)}}\text{-}\sigma^1_{\text{(C)}}\text{-COC}_6\text{H}_4\text{SCH}_3)][\text{BAR}^{\text{F}}_4]$ (**i-100a**) (aromatic acyl group) and $[\text{Rh}(\kappa^3_{\text{(POP)}}\text{-DPEphos})(\text{H})(\kappa^1_{\text{(S)}}\text{-}\sigma^1_{\text{(C)}}\text{-COC}_2\text{H}_4\text{SCH}_3)][\text{BAR}^{\text{F}}_4]$ (**i-100b**) (aliphatic acyl group), which both undergo reductive decarbonylation (with first order kinetics) in solution over the course of 7 days,¹ complex **7** is stable to decarbonylation in solution, and remains unchanged over the course of 7 days as monitored by NMR spectroscopy and ESI-MS at room temperature (Scheme 2.14). This suggests that oxygen decoordination is disfavoured, preventing access to the 5-coordinate

intermediate required for reductive elimination (and specifically reductive decarbonylation) to occur.⁵²⁻⁵⁴

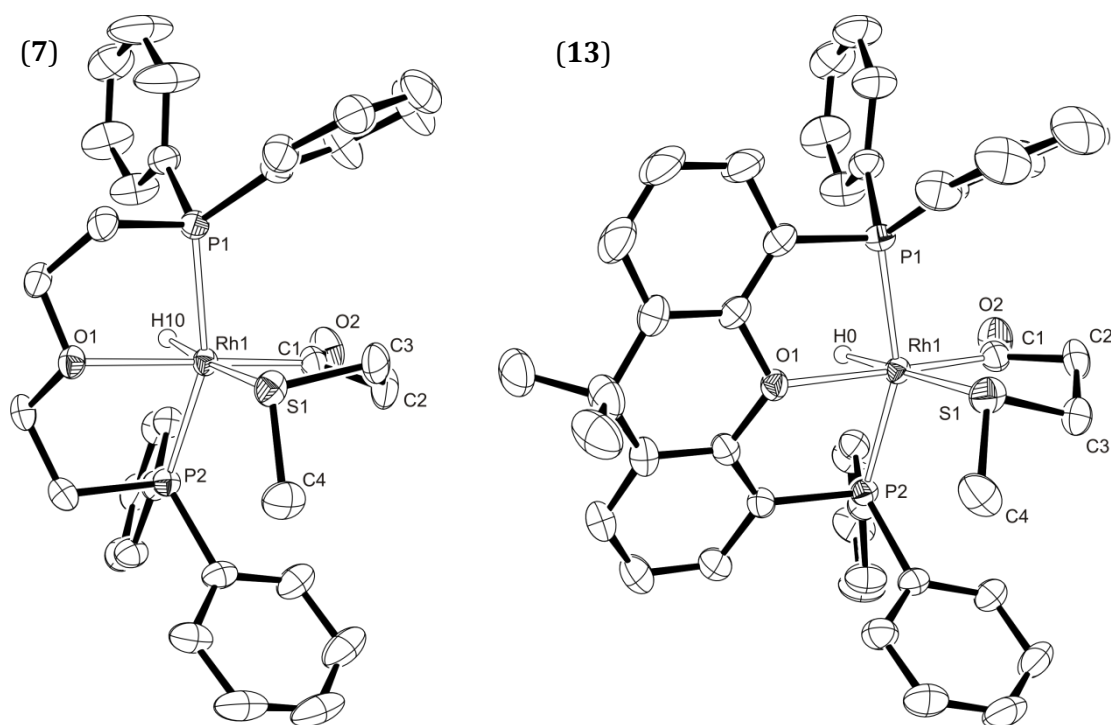
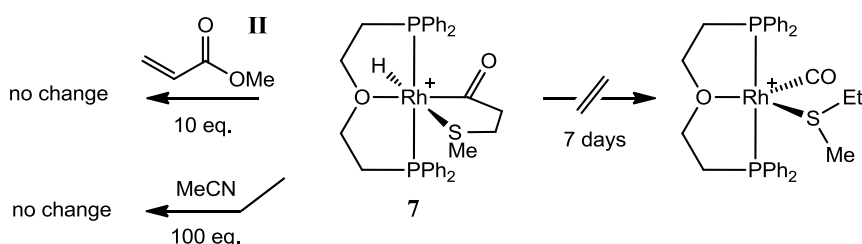


Figure 2.14: Molecular structures of the cationic portions of $[\text{Rh}(\kappa^3(\text{POP})\text{-POP}')(\text{H})(\kappa^1(\text{S})\text{-}\sigma^1(\text{C})\text{-COC}_2\text{H}_4\text{SCH}_3)][\text{BARF}_4]$ (**7**) $[\text{Rh}(\kappa^3(\text{POP})\text{-XANTphos})(\text{H})(\kappa^1(\text{S})\text{-}\sigma^1(\text{C})\text{-COC}_2\text{H}_4\text{SCH}_3)][\text{BARF}_4]$ (**13**) (major disordered component shown). Displacement ellipsoids are drawn at the 50% probability level. The anion and hydrogen atoms, apart from H10 and H0, are omitted for clarity. (**7**) Selected bond lengths [Å]: Rh1-H10, 1.51(2); Rh1-C1, 1.969(2); Rh1-P2, 2.2938(4); Rh1-P1, 2.2971(5); Rh1-O1, 2.302(1); Rh1-S1, 2.4369(4). Selected bond angles [°]: P2-Rh1-P1, 156.21(2); C1-Rh1-S1, 87.57(6); H10-Rh1-S1, 174.5(9); C1-Rh1-O1, 177.18(7); (dihedral): C4-S1-Rh1-O1, 88.46(9). (**13**) Selected bond lengths [Å]: Rh1-H0 1.58(2), Rh1-C1, 1.981(3); Rh1-P2, 2.2841(8); Rh1-P1, 2.2896(8); Rh1-O1, 2.308(2); Rh1-S1, 2.4431(9). Selected bond angles [°]: P2-Rh1-P1, 157.60(3); C1-Rh1-S1, 86.60(11); H0-Rh1-S1, 180(2); C1-Rh1-O1, 176.31(12); (dihedral): C4-S1-Rh1-O1, 58.6(5).

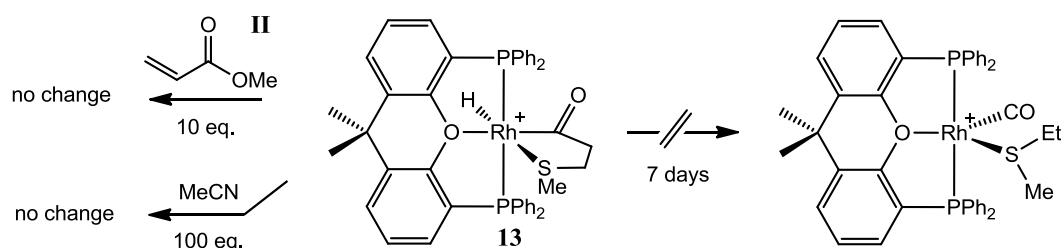
In an attempt to step around the catalytic cycle, 1 equivalent of methyl acrylate (**II**) was added to a solution of **7** in d_6 -acetone (Scheme 2.14). Given that aldehyde **I** easily and quickly displaces **II** when added to a solution of **6**, it is perhaps unsurprising that this resulted in no observable change, returning **7** unchanged. Research by Sebastian Pike (Weller group) indicated the PPP' and PSP' complexes

preferentially coordinate aldehyde **I**>alkene **II**>pentanal, although no binding energies were obtained.³³ In the cases of both **i-100a** and **i-100b**, addition of methyl acrylate (**II**) to solutions of these complexes results in rapid formation of the hydroacylation product and the rhodium(I) precursor. Addition of a large excess of **II** to **7** has no effect however, suggesting oxygen decoordination is disfavoured.



Scheme 2.14: Attempted reactivity of complex **7**. [BAr^F₄]⁻ anions not shown.

Addition of 100 equivalents of acetonitrile to a solution of complex **7** in acetone does not result in the displacement of the ether (as measured by ESI-MS and NMR spectroscopy). This is again in contrast to both **i-100a** and **i-100b**, in which the ether is immediately displaced by acetonitrile to form the corresponding acetonitrile adducts **i-100a** and **i-100b**. The stability of complex **7** must be related to the strong binding of the oxygen in the POP' ligand to the metal centre; it appears the ether cannot dissociate and so occupies the vacant site, preventing decarbonylation and coordination of the incoming alkene (or acetonitrile).

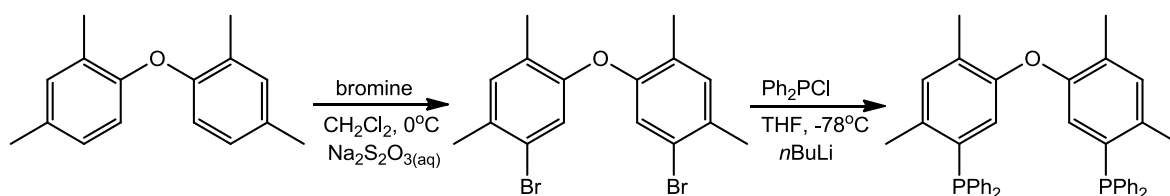


Scheme 2.15: Attempted reactivity of complex **13**. [BAr^F₄]⁻ anions not shown.

Given the similarities displayed between the equivalent complexes formed with POP' and XANTphos, it is unsurprising to find that complex **13** exhibits the same lack of reactivity as complex **7**. It remains stable to reductive decarbonylation over the course of 7 days in solution, as monitored by NMR spectroscopy and ESI-MS, addition of 10 equivalents of methyl acrylate results in no observable change or reactivity, and 100 equivalents of acetonitrile do not displace the coordinated ether linkage of the XANTphos ligand (Scheme 2.15).

2.3 Complexes incorporating Xphos

The ligand Xphos is unknown, and was synthesised by Joel Hooper (Willis group) according to the scheme shown in Scheme 2.16. The ligand initially targeted was Me₄-DPEphos (Figure 2.15), chosen as a more sterically hindered analogue of DPEphos, which had the potential to show a different flexibility to XANTphos, with the ability to pivot around the ether group. Instead however, due to experimental limitations, the ligand Xphos was synthesised and initial screening indicated significantly different reactivity and selectivity to that observed with the DPEphos system, warranting further study. Two integral 2H signals for the aryl-protons of the ligand backbone are observed as doublets at δ 7.00 [J = 4.9] and 5.91 [J = 4.2] in the ¹H NMR spectrum, which shift considerably on complexation to rhodium.



Scheme 2.16: Synthesis of Xphos ligand.

Xphos proved to be a particularly difficult ligand to work with when complexed to a metal centre, forming oily materials with the $[\text{BAR}^{\text{F}_4}]^{-4}$ and $[\text{BAR}^{\text{Cl}_4}]^{-55}$ salts, which were difficult to purify and often poorly soluble in common solvents. However, the use of $[\text{closo-CB}_{11}\text{H}_{12}]^{-5}$ and $[\text{closo-CB}_{11}\text{H}_6\text{Br}_6]^{-5}$ anions afforded clean isolable solids, and these anions have been used interchangeably. Following the standard synthetic route (Scheme 2.2, p.71) the norbornadiene precursor $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-Xphos})(\text{NBD})]_2[\text{BAR}^{\text{F}_4}]_2$ (**14**) was prepared (Figure 2.15).

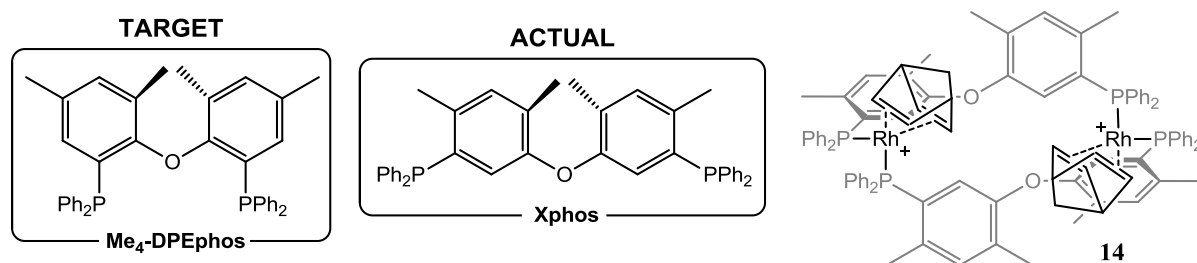


Figure 2.15: $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-Xphos})(\text{NBD})]_2[\text{BAR}^{\text{F}_4}]_2$, **14** (complex of actual ligand). $[\text{BAR}^{\text{F}_4}]^{-}$ anions not shown.

The *meta* location of the phosphines relative to the central ether group prevents the ligand from coordinating both phosphine groups to the same metal centre, forming instead a bimetallic bridging complex. The ^1H NMR spectrum of the complex **14** in d_6 -acetone shows six integral ^1H environments for the coordinated norbornadiene $\text{HC}=\text{CH}$ protons and the bridging norbornadiene CH protons, and the CH_2 protons appear as an integral 2H multiplet (1H + 1H coincidence by ^1H - ^1H COSY NMR experiment). Four integral 3H singlets are observed for the ligand methyl groups. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum two doublet of doublet signals at δ 36.06 [$J(\text{RhP}) = 162.3$, $J(\text{PP}) = 28.8$] and 24.22 [$J(\text{RhP}) = 156.7$, $J(\text{PP}) = 28.8$] are observed indicating two inequivalent, mutually *cis*, phosphine environments and a rhodium(I) centre. Two low field doublets are observed in the ^1H NMR spectrum

at δ 9.20 [$J(\text{PH}) = 15.5$] and 8.95 [$J(\text{PH}) = 18.4$], which collapse to singlets on selective decoupling of the proton spectrum to the signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 36.06 and 24.22 respectively. These are assigned as the Ar-H protons between the PPh_2 groups and the ether in the ligand, having shifted downfield from the free ligand. Both show weak four bond coupling to two each of the ligand methyl carbons in the ^1H - ^{13}C HMBC NMR spectrum. The NMR data for **14** is significantly different to that observed for the rhodium(I) norbornadiene complexes **1** and **8**, indicating a loss of symmetry, and clearly showing that a different structure is observed in solution to that of complexes **1** and **8**. ESI-MS of the complex showed the indicative incremental $m/z = 0.5$ increase in mass between the signals of the isotopic distribution pattern signifying a parent ion with a 2+ charge (Figure 2.16). This suggests formation of a $[\text{M}]_2^{2+}$ dimer.

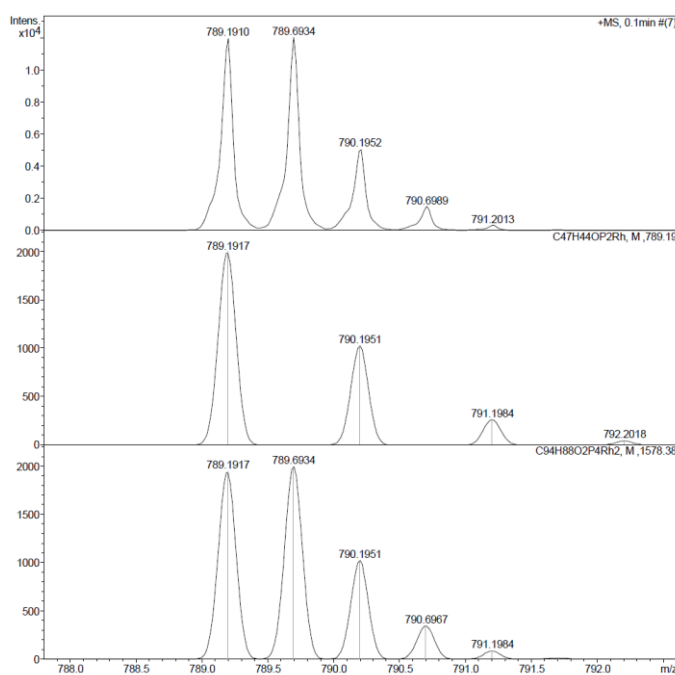


Figure 2.16: Mass spectrum of complex **14** (top); calculated mass spectra of $[\text{M}]^+$ (middle) and $[\text{M}]_2^{2+}$ (bottom).

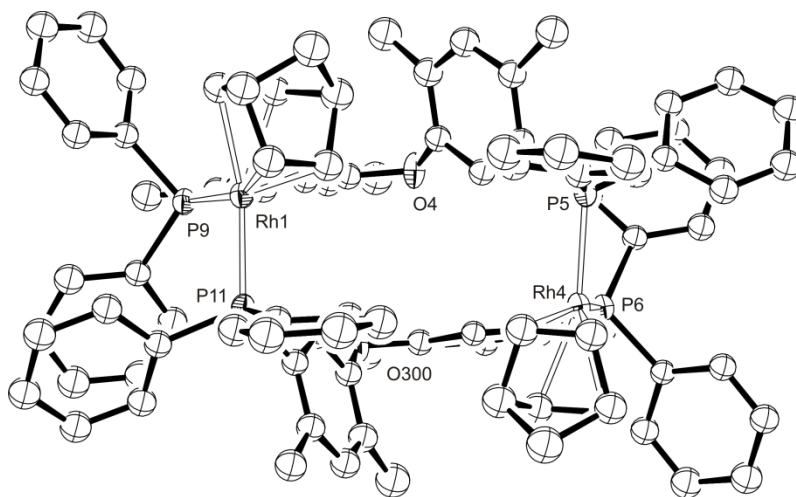


Figure 2.17 Molecular structure of the cationic portion of $[\text{Rh}(\kappa^2(\text{pp})\text{-Xphos})(\text{NBD})]_2[\text{closo-CB}_{11}\text{H}_{12}]_2$ (**14**). Isotropic refinement. The anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Rh1-P9, 2.36(15); Rh1-P11, 2.33(14); Rh1-C17, 2.25(14); Rh1-C60, 2.20(15); Rh1-C170, 2.23(14); Rh1-C210, 2.17(13); C17-C170, 1.37(7); C60-C210, 1.38(7); Rh4-P5, 2.34(16); Rh4-P6, 2.37(16); Rh4-C53, 2.16(14); Rh4-C666, 2.20(17); Rh4-C26, 2.22(14); Rh4-C159, 2.24(13); C26-C159, 1.39(8); C53-C666, 1.39(7). Selected bond angles [°]: P5-Rh4-P6, 99(6); P11-Rh1-P9, 99(6). Selected atom distances [Å]: Rh1-Rh4, 7.253; O4-O300, 3.572.

After switching to the $[\text{closo-CB}_{11}\text{H}_{12}]^-$ anion,⁵ crystals suitable for X-ray diffraction were grown from diffusion of pentane into a solution of the **14** in CH_2Cl_2 at room temperature (Figure 2.17). The solid state crystal structure of **14** indeed demonstrates a dimeric motif. The cation shows a C_2 rotational axis, making one half of the dimer equivalent to the other. The phosphine ligands bridge the two rhodium centres, forming a ligand environment around each rhodium metal centre that is pseudo square planar. The coordinated phosphine groups on each rhodium are *cis* to each other, and the P9-Rh1-P11 and P5-Rh4-P6 bond angles are both $99(6)^\circ$. The distance between the two rhodium centres is 7.253 Å, and the distance between the oxygen groups of the two ligands is 3.572 Å. These distances delineate a cavity within the dimeric molecule, formed by the planes of the bridging phosphine ligands, and ‘capped’ at the ends by the square-planar rhodium centres. Certain features of the NMR spectra can now be

explained: the four phosphines are in two different environments, on each rhodium. The Xphos methyl groups are inequivalent across each ligand, but have a symmetry counterpart on the other ligand leading to only four resonances. The protons of the norbornadiene ligand are all inequivalent to each other within the ligand, but equivalent by symmetry to the norbornadiene protons in the second half of the molecule. The inequivalent CH₂ protons of the norbornadiene can now be understood as one proton points away from the centre of the molecule, while the other points towards it.

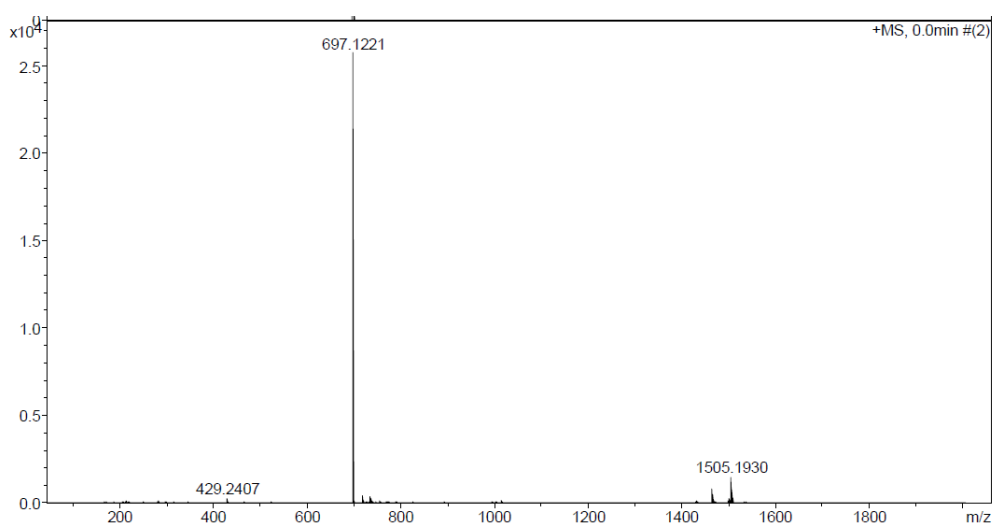
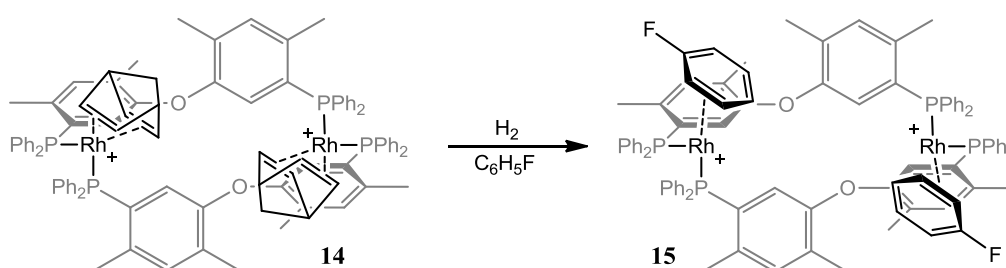


Figure 2.18: Mass spectrum of complex **14** hydrogenated in d₆-acetone.

Activation of complex **14** by addition of hydrogen (4 atm) in d₆-acetone solution forms a complex which was difficult to characterise. Broad hydride signals are observed in the ¹H NMR spectrum at δ -21.11 and -21.89 which separate out at low temperature (200 K) to give roughly 12 overlapping hydride environments of varying intensities. The alkyl and aromatic regions of the ¹H NMR spectrum show many signals of varying intensities which could not be resolved, and do not give any conclusive evidence for a possible structure. The room temperature ³¹P{¹H} NMR spectrum also shows two broad signals which separate out at low

temperature into two regions of roughly 18 overlapping doublets of various intensities. However, ESI-MS of the complex in solution gives only one signal at $[M]^{2+}$ $m/z = 697.12$, which is indicative of dimeric $[\text{Rh}(\text{Xphos})]_2^{2+}$ (calc = 697.13) (Figure 2.18). It is tentatively believed that the complex formed is a mixture of isomers of dimeric $[\text{Rh}(\text{Xphos})(\text{H})_2]_2[\text{BAR}^{\text{F}}_4]_2$, possibly with acetone also coordinated. However, as the complex could not be irrefutably characterised, a different route was taken to form an active catalyst precursor.



Scheme 2.17: Activation of Xphos precatalyst (**14**) in $\text{C}_6\text{H}_5\text{F}$. $[\text{BAR}^{\text{F}}_4]^-$ anions not shown.

Complex **14** is only sparingly soluble in $\text{C}_6\text{H}_5\text{F}$, but when hydrogenated in $\text{C}_6\text{H}_5\text{F}$, a single complex forms (by NMR spectroscopy) which dissolves completely into solution, $[\text{Rh}(\kappa^2(\text{PP})\text{-Xphos})(\eta^6\text{-C}_6\text{H}_5\text{F})]_2[\text{BAR}^{\text{F}}_4]_2$ (**15**) (Scheme 2.17). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **15** is similar to that observed for complex **14**. Two doublet of doublet signals are observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 49.00 [$J(\text{RhP}) = 218.4$, $J(\text{PP}) = 33.9$] and 38.79 [$J(\text{RhP}) = 208.3$, $J(\text{PP}) = 33.9$], indicating two inequivalent phosphorus environments which are not *trans* to each other, and couple to each other and the rhodium, while the large ^{103}Rh - ^{31}P coupling is suggestive of a rhodium centre with an η^6 coordinated arene.⁵⁶ The ^{19}F NMR spectrum shows a large signal for free $\text{C}_6\text{H}_5\text{F}$ (solvent), a smaller signal at δ -64.78 for the $[\text{BAR}^{\text{F}}_4]^-$ anion, and another small signal at δ -124.28 which has been

assigned as the coordinated $\text{C}_6\text{H}_5\text{F}$.⁵⁷ The doublet signals in the ^1H NMR spectrum which come at δ 9.20 and 8.95 in complex **14** – and are diagnostic of this dimeric complex – have shifted to δ 8.92 and 8.85 in complex **15**. The four Xphos methyl groups remain inequivalent in the ^1H NMR spectrum. The aryl region of the ^1H NMR spectrum of complex **15** in $\text{C}_6\text{H}_5\text{F}$ is largely obscured by the residual protio solvent signal. However, integral ^1H multiplet signals at δ 6.16, 5.56, 5.42, 4.79 and 4.52 are characteristic of a coordinated arene group,⁵⁸⁻⁶¹ and show coupling to each other in the COSY NMR spectrum, which allows them to be assigned as H^2 , H^4 , H^5 , H^1 and H^3 respectively, of the coordinated $\text{C}_6\text{H}_5\text{F}$ group (Figure 2.19).

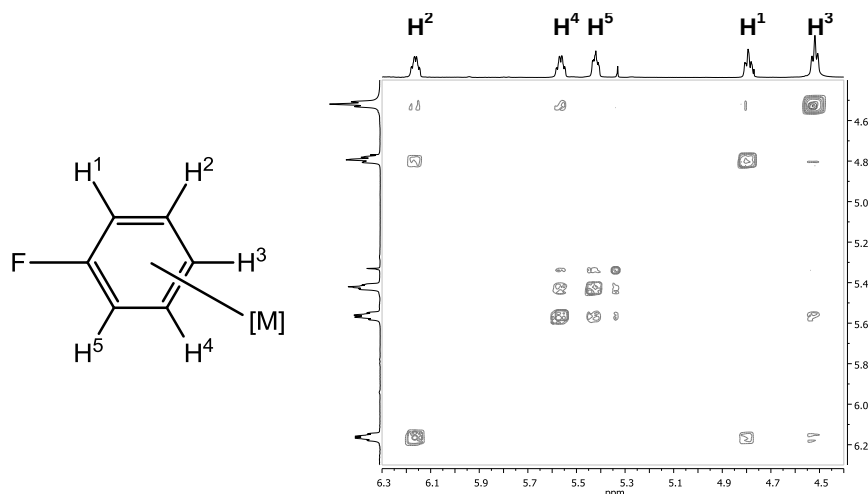
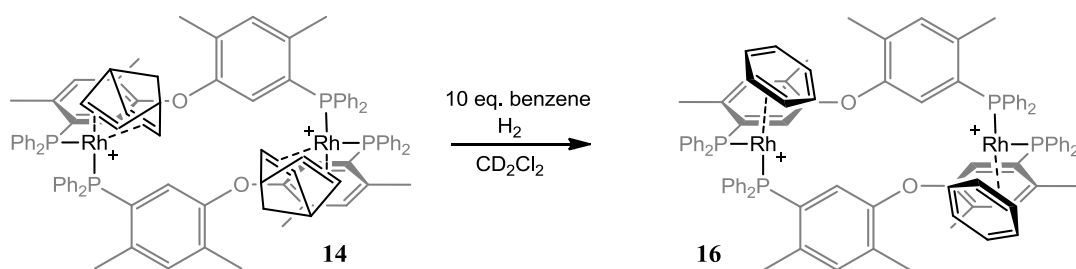


Figure 2.19: Assignment of the coordinated $\text{C}_6\text{H}_5\text{F}$ protons. ^1H - ^1H COSY NMR spectrum (selected region).

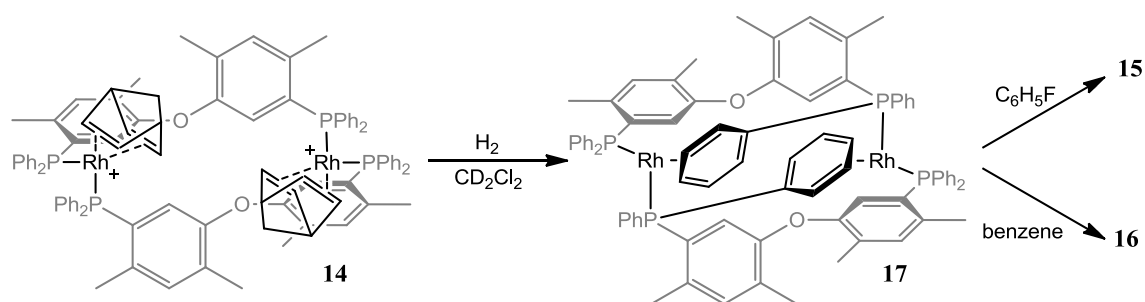
A $^1\text{H}\{^{31}\text{P}\}$ selective decoupling experiment shows the doublets at δ 8.92 and δ 8.85 collapse into singlets, suggesting these signals are the Ar-H protons of the ligand which are located between the PPh_2 group and the ether group. ESI-MS of the complex confirms the empirical formula of $[\text{Rh}(\kappa^2(\text{PP})\text{-Xphos})(\eta^6\text{-C}_6\text{H}_5\text{F})]_2^{2+}$ with a major signal at $[\text{M}]_2^{2+}$ $m/z = 793.69$ (calc. 793.67), and a minor signal at $[(\text{M}-\text{C}_6\text{H}_5\text{F})]_2^{2+}$ $m/z = 697.14$ (calc. 697.13), showing the $m/z = 0.5$ incremental increase between isotopomers, diagnostic of a $[\text{M}]_2^{2+}$ ion.



Scheme 2.18: Formation of complex **16**. [BAr^F₄]⁻ anions not shown.

Addition of hydrogen to complex **14** in the presence of 10 equivalents of benzene leads to the formation of a new complex [Rh($\kappa^2_{(PP)}$ -Xphos)(η^6 -benzene)]₂[BAr^F₄]₂ (**16**) (Scheme 2.18). ¹H NMR spectroscopy of the reaction mixture showed a singlet signal at δ 5.46 indicative of coordinated benzene, alongside a large signal for free benzene. The ³¹P{¹H} NMR spectrum showed two doublet of doublet signals at δ 48.37 [*J*(RhP) = 211.8, *J*(PP) = 33.2] and 38.74 [*J*(RhP) = 202.9, *J*(PP) = 33.3], indicating two inequivalent phosphorus environments coupling to a rhodium centre. The large ¹⁰³Rh-³¹P coupling which is indicative of a coordinated arene group was also observed. ESI-MS of this complex showed the species to be dimeric with a signal observed at [M]₂²⁺ *m/z* = 775.72 (calc. 775.68) indicating the formation of [Rh($\kappa^2_{(PP)}$ -Xphos)(η^6 -benzene)]₂²⁺.

As the use of C₆H₅F as a solvent means that large areas of the ¹H NMR spectrum are obscured, and Rh(η^6 -benzene) coordination is relatively strong, a different method for isolating the activated catalyst precursor was pursued. The precatalyst (**14**) was hydrogenated in CD₂Cl₂ to remove the norbornadiene ligand, resulting in a single complex by NMR spectroscopy, [Rh($\kappa^2_{(PP)}$ -Xphos)]₂[BAr^F₄]₂ (**17**) (Scheme 2.19).



Scheme 2.19: Activation of Xphos precatalyst in CD_2Cl_2 . $[\text{BAR}^{\text{F}}_4]^-$ anions not shown.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **17** at 295 K shows two apparent doublet of doublets at δ 51.13 [$J(\text{RhP}) = 227.67$, $J(\text{PP}) = 31.2$] and 42.15 [$J(\text{RhP}) = 208.8$, $J(\text{PP}) = 31.2$], indicating inequivalent phosphorus environments, and again rhodium with a coordinated arene group. The observed doublet of doublets at δ 51.13 shows further fine coupling, indicating that this phosphine is also coupling to an additional nucleus. The ^1H NMR spectrum shows five characteristic integral 1H signals of a coordinated arene group; four inequivalent ligand methyl groups, and the two doublets at δ 9.82 and 8.69 for the Ar-H protons located between the PPh_2 and ether groups of the Xphos ligand. Two of the coordinated arene signals collapse on decoupling of the ^1H NMR spectrum to the signal at δ 51.13 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum indicating it is one of the phenyl groups on this phosphine which is coordinated to the rhodium. This suggests that the fine coupling seen in the signal at δ 51.13 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, is due to the bridging phosphine coupling to the second rhodium centre. Characterisation by ESI-MS in $\text{C}_6\text{H}_5\text{F}$ indicated the complex was flying as $[\text{M}]_2^{2+}$ dimer, with $m/z = 697.17$ (calc. 697.13) confirming the empirical formula for $[\text{Rh}(\text{Xphos})]_2^{2+}$, while a second signal was observed for $[\text{Rh}(\text{Xphos})(\eta^6\text{-C}_6\text{H}_5\text{F})]_2^{2+}$, presumably formed *in situ*.

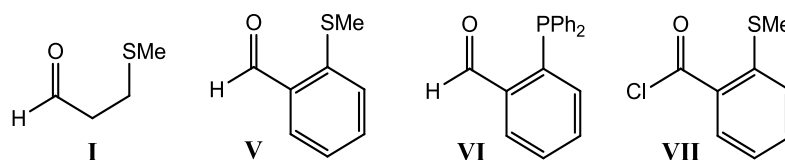


Figure 2.20: Aldehydes and acyl-chlorides added to complexes **15** and **16**.

One equivalent of the aldehydes or acyl-chloride shown above (Figure 2.20) was added to either complex **15** or **16**. However, all resulted in mixtures by NMR spectroscopy which could not be interpreted to give any reliable information regarding the complexes formed. The appearance of broad doublet hydride signals at δ -8.71 and -8.96 in the ^1H NMR spectrum of complex **15** with aldehyde **I** suggests the aldehyde has C-H activated to give an acyl-hydride species, although this compound decomposed within hours. The addition of aldehyde **V** to complex **15** gave rise to two broad doublet hydride signals in the ^1H NMR spectrum at δ -8.54 and -8.69. The addition of aldehyde **VI** to complex **15** gives rise to two doublet hydride signals at δ -3.81 and -4.79 in the ^1H NMR spectrum, which both show *trans* ^{31}P - ^1H coupling (143 and 133 Hz respectively), suggesting that the acyl-hydride species formed adopts a *meridinal* coordination mode with the hydride *trans* to the PPh_2 group of the benzaldehyde. ESI-MS of this complex gives rise to a signal at $[\text{M}]_2^{2+}$ m/z = 987.68 (calc. 987.72) which fits the empirical formula for $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-Xphos})(\text{H})(\kappa^1_{(\text{P})}\text{-}\sigma^1_{(\text{C})}\text{-COC}_6\text{H}_4\text{PPh}_2)]_2^{2+}$. Addition of acyl-chloride **VII** to complex **16** results in a ^1H NMR spectrum in which only the anion signals can be assigned, as the cation appears to have decomposed. However, ESI-MS of the sample results in a signal at $[\text{M}]_2^{2+}$ m/z = 884.13 (calc 884.12) which corresponds to $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-Xphos})(\text{Cl})(\kappa^1_{(\text{S})}\text{-}\sigma^1_{(\text{C})}\text{-COC}_6\text{H}_4\text{SMe})]_2^{2+}$.

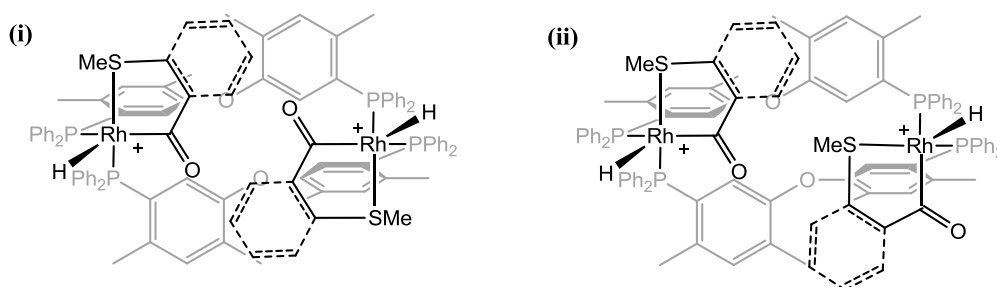
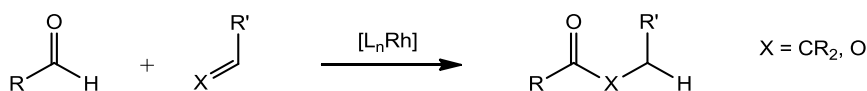


Figure 2.21: Symmetric (i) and asymmetric (ii) activation of the aldehyde. $[\text{BAR}^{\text{F}}_4]^-$ anions not shown.

On the whole, very little information could be gleaned from these experiments, other than C-H activation of the aldehyde appeared to be taking place. In each case two hydride signals were formed in differing ratios, with one signal significantly larger than the other. This suggests that the two rhodium cations of each dimer can activate an aldehyde molecule to give an environment around each rhodium centre which is identical to the other centre of the same dimer, (i, Figure 2.21) or the two centres can activate the aldehyde to give environments which are not symmetric (ii, Figure 2.21). This could explain the complex NMR spectroscopy data for complexes which, by ESI-MS, appear to be only one species.

2.4 Catalytic activity of DPEphos, POP', XANTphos and Xphos complexes

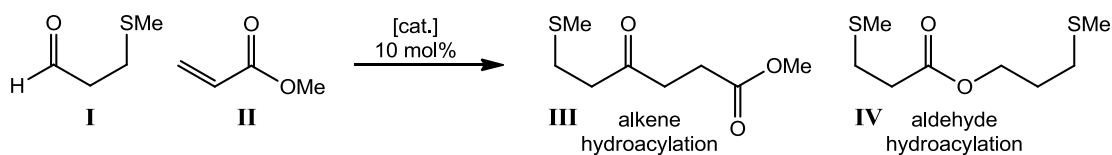
The norbornadiene precursor complexes **1** and **8** were activated by hydrogenation to give **2** and **9** *in situ*, and these complexes were tested as catalysts for the hydroacylation of methyl acrylate (**II**) by aldehyde **I**. Complex **14** and $[\text{Rh}(\text{DPEphos})(\text{NBD})][\text{BAR}^{\text{F}}_4]$ (**i-98**) were also screened under the same conditions, for comparison (Table 2.1).



Scheme 2.20: Intermolecular hydroacylation of an aldehyde and an alkene (X = CR₂) or another aldehyde (X = O).

As well as the expected product of alkene hydroacylation (**III**), the product of the coupling of two aldehydes (**IV**) was also observed. Comprising of the addition of an aldehyde across an equivalent aldehyde double bond, this coupling of two aldehydes (Tishchenko reaction)^{62, 63} can also be considered as the hydroacylation of an aldehyde (Scheme 2.20).

Table 2.1: Catalytic activity of [Rh(diphosphine)(NBD)][BAR^F₄] in the hydroacylation reaction of **I** and **II**.^a



entry	ligand	% alkene hydroacylation III	% aldehyde hydroacylation IV	total conversion of aldehyde I	time (h)	initial rate for the formation of III x10 ⁻³ (mol/L/h) ^b	initial rate for the formation of IV x10 ⁻³ (mol/L/h) ^b
1	DPEphos	93	7	100	20	96 ± 6	3 ± 1
2	POP'	6	44	50 ^c	165	10 ± 7	38 ± 12
3	XANTphos	10	20	30 ^c	145	2 ± 2	2 ± 4
4	Xphos	0	100	100	0.15	-	27749 ± 100

^aConditions: all manipulations under argon atmosphere, at room temperature, 0.043 M solution of precatalyst in d₆-acetone, hydrogenated using standard procedures, catalyst:aldehyde ratio = 1:10, substrate ratio = 1:1 aldehyde:alkene, conversion determined by ¹H NMR spectroscopy. ^bInitial rate (IR) determined by fitting first order trendline of the form $y = a(1 - \exp^{-bx})$ to the data and taking the value of the slope at $t = 0$, error in initial rate (eIR) determined by $eIR = IR \times (ea/a + eb/b)$ assuming error in trendline to be greater than error in data. ^cTotal conversion at given time.

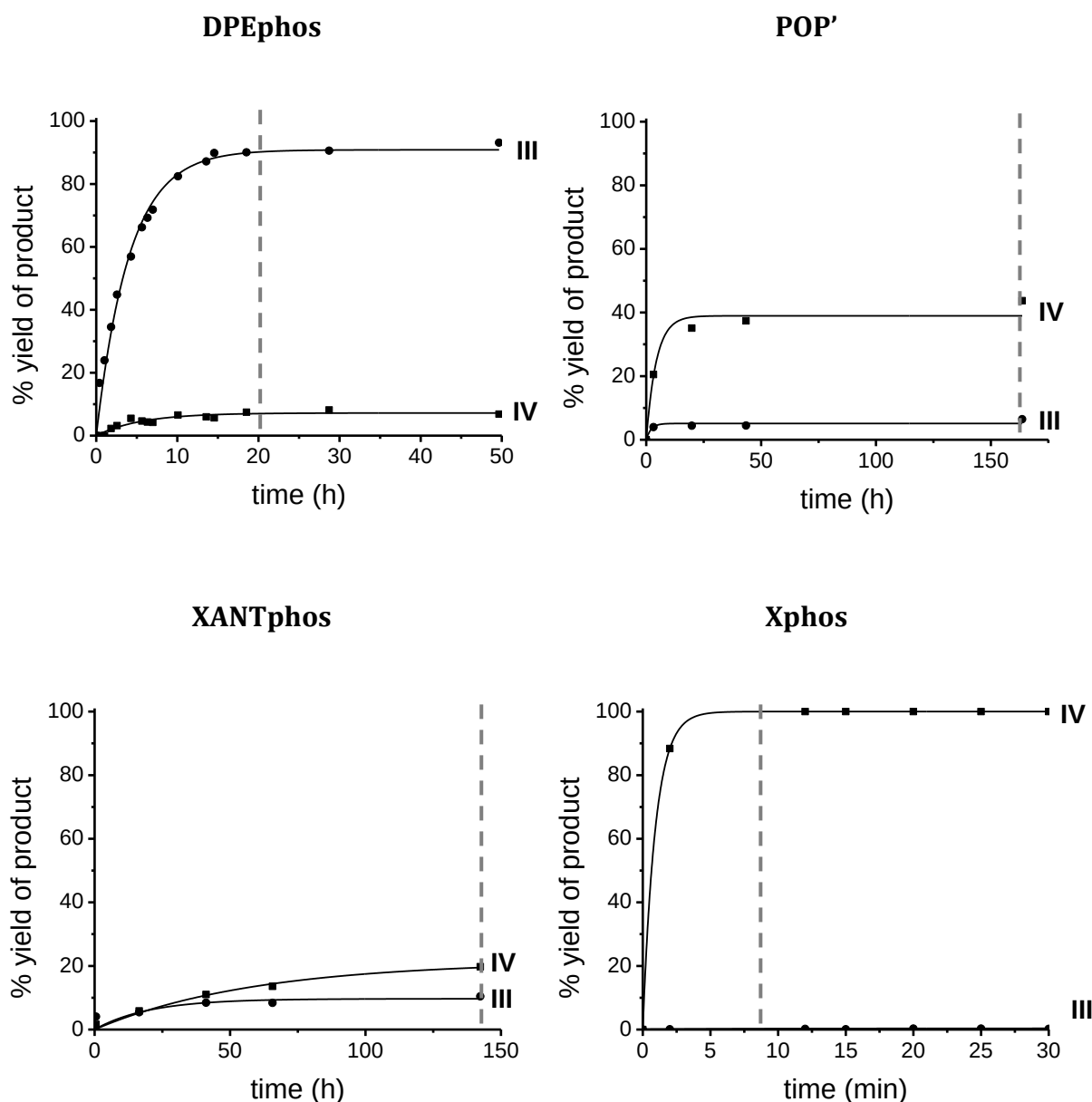


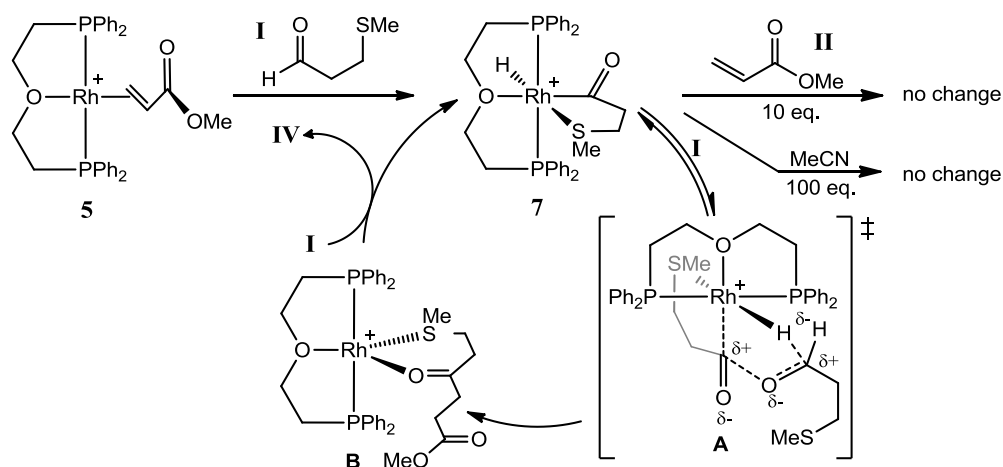
Figure 2.22: Relative yields of alkene hydroacylation (**III**, circles) and aldehyde hydroacylation (**IV**, squares) products using various catalysts. See Table 2.1 for more details. Plotted lines are first order trendlines of the form $y = a(1 - \exp^{-bx})$.

The DPEphos system (entry 1, Table 2.1) demonstrated the expected reactivity with β -S substituted pentanal (**I**) and methyl acrylate (**II**) giving predominately the product of alkene hydroacylation (**III**) although a small amount of the product of aldehyde hydroacylation (**IV**) was also observed. Previous research has shown complete selectivity for alkene hydroacylation with this substrate set, at 55 °C.^{1, 3}

At room temperature the catalyst took approximately 20 hours to turn over all of the aldehyde at 10 mol% catalyst loading. The POP' and XANTphos systems (entries 2 and 3 respectively, Table 2.1) demonstrated very poor turnover as alkene hydroacylation catalysts over an extended period of time (145-165 h). Although both systems performed slightly better as catalysts for the aldehyde hydroacylation reaction, neither reaction went to completion. The plateau observed for the yield of product (Figure 2.22) suggests both catalysts had become inactive after 60 h.

As has been observed already, both POP' and XANTphos formed unreactive rhodium(III) acyl-hydride complexes (complexes **7** and **13** respectively) which demonstrated a lack of ligand hemilabile behaviour. The lack of reactivity displayed by complex **13** as a hydroacylation catalyst is consistent with the inability of both complexes **13** and **7** to react with MeCN, methyl acrylate (**II**), or even to undergo reductive decarbonylation (Schemes 2.14 and 2.15). In both cases the ether remains tightly bound to the rhodium centre, and does not dissociate to reveal a vacant site necessary for further reactivity. However, the POP' system (**7**) does display two turnovers of aldehyde hydroacylation (~40% consumption of aldehyde), before becoming inactive, which suggests that hydroacylation may be occurring *via* an outer-sphere mechanism, such as outlined in Scheme 2.21. An aldehyde could interact with the metal-acyl-hydride complex (**7**) due to the dipolar nature of a C=O bond in comparison to a C=C bond, forming a 5-membered metallacyclic transition state (**A**), which can turnover to give the aldehyde hydroacylation product (**B**) (Scheme 2.21). Why this system only undergoes two turnovers is not clear, presumably decomposition occurs through some

mechanism, after two turnovers. Possibly *via* decarbonylation under conditions of excess aldehyde.



Scheme 2.21: A possible outer-sphere mechanism for the aldehyde hydroacylation reaction. $[\text{BAR}^{\text{F}}_4]^-$ anion not shown.

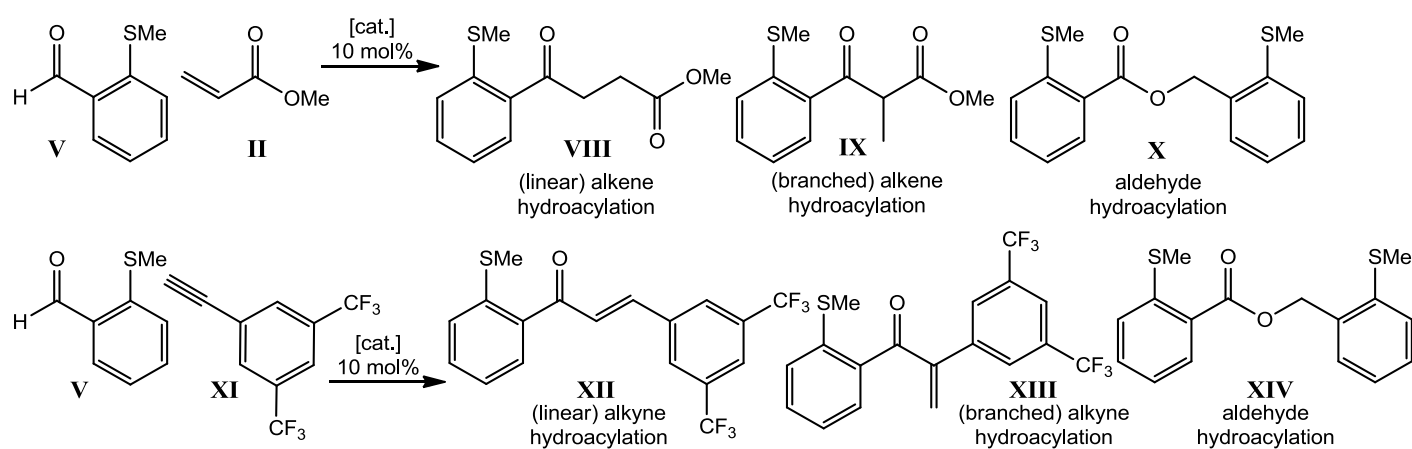
The catalyst formed with the Xphos ligand showed surprising and remarkable reactivity and selectivity (entry 4, Table 2.1). In less than 10 minutes the reaction went to completion, forming only the aldehyde hydroacylation product (**IV**). Unlike the selectivity observed with the parent ligand, DPEphos, no trace of the alkene hydroacylation product (**III**) was observed. Given the sluggish reactivity of the POP' and XANTphos complexes, only the Xphos complex was explored for further reactivity.

2.5 Further catalytic activity studies of Xphos complexes

Aromatic aldehydes are significantly more difficult to couple in the Tishchenko reaction;⁶² furthermore, results (to be discussed in the next chapter) indicated alkyne **XI** improves catalytic selectivity towards the branched alkyne

hydroacylation reaction. Therefore, to evaluate the ability of the Xphos system as a catalyst for aldehyde hydroacylation of these more challenging substrates, the aromatic analogue of aldehyde **I** (**V**) and alkyne **XI** were also explored, in the combinations: aldehyde **V** with alkene **II**; and aldehyde **V** with alkyne **XI** (Table 2.2).

Table 2.2: Catalytic activity of **14**, **15** and $[\text{Rh}(\text{PPh}_3)_2(\text{NBD})]^+$ (**18**).^a



entry	catalyst	aldehyde	alkene/ alkyne	% linear product (III , VIII or XII)	% branched product (IX or XIII)	% aldehyde product (IV , X or XIV)	time (h)	initial rate for the formation of aldehyde hydroacylation product $\times 10^{-2}$ (mol/L/h) ^c
1	14	I	II	0	0	100	0.15	277 ± 1
2	14	V	II	10	0	90	1	33.0 ± 0.9
3 ^b	15	V	II	3	0	97	1.3	30 ± 8
4	14	V	XI	8	8	78	1.5	22 ± 2
5	PPh₃	V	II	13	0	87	2.5	10 ± 2

^aConditions: all manipulations under argon atmosphere, at room temperature, 0.043 M solution (per rhodium) of precatalyst in d_6 -acetone, hydrogenated using standard procedures, catalyst:aldehyde ratio = 1:10, substrate ratio = 1:1 aldehyde:alkene, conversion determined by ^1H NMR spectroscopy. ^b $\text{C}_6\text{H}_5\text{F}$ used as solvent. ^cInitial rate (IR) determined by fitting first order trendline of the form $y = a(1 - \exp^{-bx})$ to the data and taking the value of the slope at $t = 0$, error in initial rate (eIR) determined by $\text{eIR} = \text{IR} \times (\text{ea}/a + \text{eb}/b)$ assuming error in trendline to be greater than error in data.

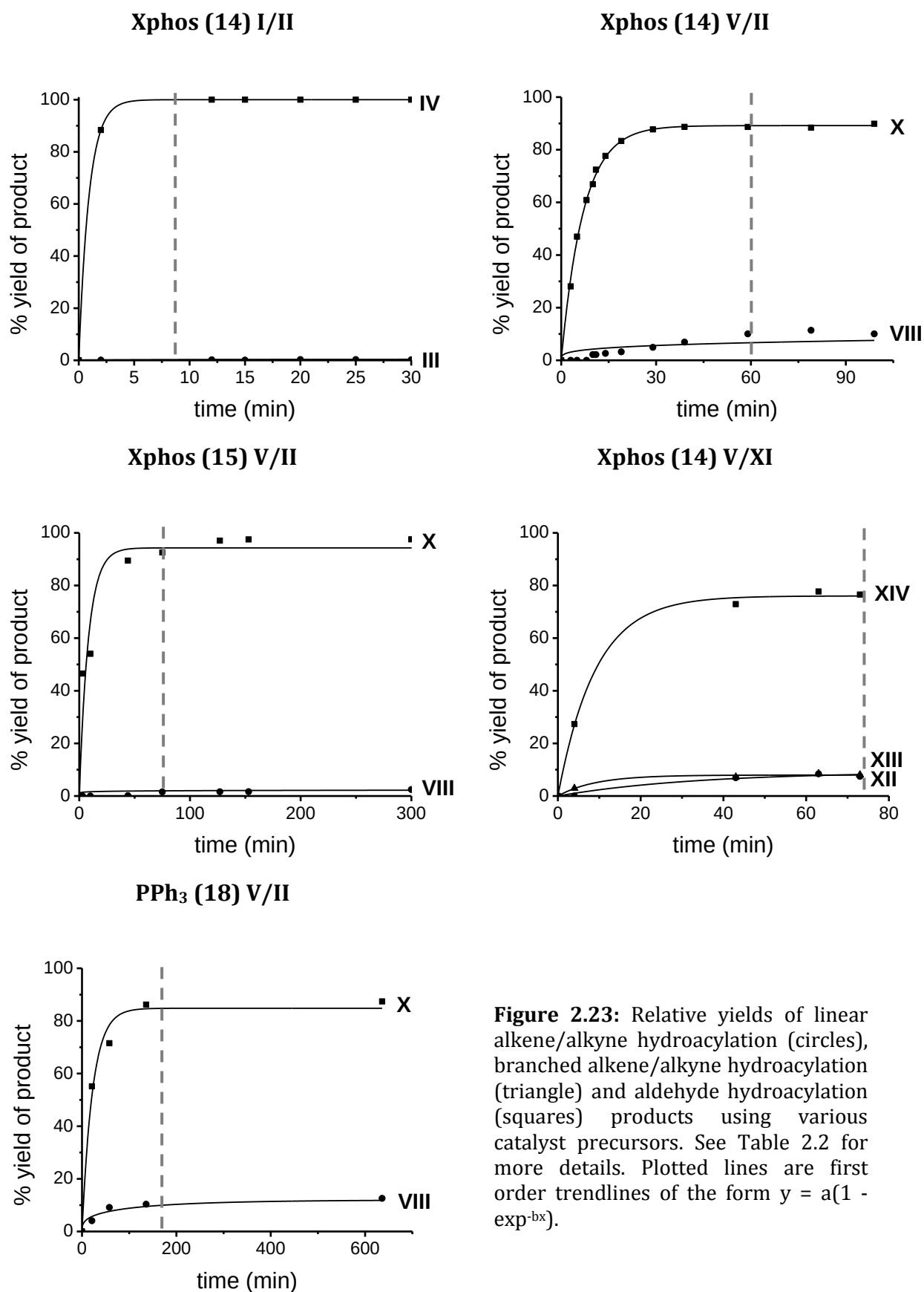


Figure 2.23: Relative yields of linear alkene/alkyne hydroacylation (circles), branched alkene/alkyne hydroacylation (triangle) and aldehyde hydroacylation (squares) products using various catalyst precursors. See Table 2.2 for more details. Plotted lines are first order trendlines of the form $y = a(1 - \exp^{-bx})$.

Under the same conditions as those used previously, complex **14** was activated by hydrogenation in d_6 -acetone and the conversion of substrates to products was monitored by ^1H NMR spectroscopy. For comparison, complex **15** was also tested as a catalyst for the hydroacylation reaction in $\text{C}_6\text{H}_5\text{F}$ solvent, as this active precatalyst species has been reliably characterised. The results are presented along with the previous result for the combination of aldehyde **I** and alkene **II** with this catalyst system, for comparison.

Table 2.2 demonstrates that the catalyst formed with Xphos shows a clear selectivity for the aldehyde hydroacylation reaction, even when confronted with an aromatic aldehyde. The catalysis of aldehyde **I** is the fastest, going to completion within 10 minutes and forming only the product of aldehyde hydroacylation (**IV**) (entry 1, Table 2.2). There is not a substantial difference in reaction rates between the catalyst formed in d_6 -acetone and the catalyst formed in $\text{C}_6\text{H}_5\text{F}$ for the catalysis of aldehyde **V** and alkene **II** (entries 2 and 3, Table 2.2), which suggests the catalyst formed is the same: $[\text{Rh}(\kappa^2_{\text{PP}}\text{-Xphos})]_2[\text{BAr}^{\text{F}}_4]_2$. Both catalyse the aldehyde hydroacylation reaction, although the product of alkene hydroacylation is also observed. Switching from alkene **II** to alkyne **XI** sees quite a dramatic change in selectivity as the branched product of alkyne hydroacylation (**XIII**) can now be observed, as well as the linear product of alkyne hydroacylation (**XII**). However, the product of aldehyde hydroacylation is still favoured over all, with 80% of the aldehyde being coupled to give the ester **XIV** (Figure 2.23).

To investigate the presence of the rhodium dimer during catalysis, complex **14** was prepared under the same catalytic conditions as those used in monitoring by ^1H NMR spectroscopy (0.043 M solution - per rhodium - of precatalyst in d_6 -acetone, hydrogenated using standard procedures (catalyst:aldehyde ratio = 1:10, substrate ratio = 1:1 aldehyde **V**:alkene **II**), and ESI-MS was taken of the sample (diluted in $\text{C}_6\text{H}_5\text{F}$) before catalysis began, at the start of catalysis, and after 40 mins. Before catalysis began there were signals corresponding to $[\text{Rh}(\kappa^2_{\text{PP}}\text{-Xphos})]_2^{2+}$ and $[\text{Rh}(\kappa^2_{\text{PP}}\text{-Xphos})(\eta^6\text{-C}_6\text{H}_5\text{F})]_2^{2+}$ at $[\text{M}]_2^{2+}$ m/z = 697.14 (calc. 697.13) and 793.18 (calc. 793.17) respectively. At the start of catalysis a signal at $[\text{M}]_2^{2+}$ m/z = 849.68 was observed, which matches the isotopic distribution of $[\text{Rh}(\kappa^2_{\text{PP}}\text{-Xphos})(\text{H})(\kappa^1_{\text{(S)}}\text{-}\sigma^1_{\text{(C)}}\text{-COC}_6\text{H}_4\text{SMe})]_2^{2+}$ (calc. 849.66), as reported earlier in this chapter. After 40 mins a signal is observed at $[\text{M}]_2^{2+}$ m/z = 925.71, which correlates to $[\text{Rh}(\kappa^2_{\text{PP}}\text{-Xphos})(\text{H})(\kappa^1_{\text{(S)}}\text{-}\sigma^1_{\text{(C)}}\text{-COC}_6\text{H}_4\text{SMe})]_2(\text{HCOC}_6\text{H}_4\text{SMe})^{2+}$ (calc. 925.72) i.e. $[\text{Rh}(\text{Xphos})]_2^{2+}$ dimer with three aldehyde molecules coordinated, or one molecule of the product of aldehyde hydroacylation and one aldehyde molecule. A further signal was observed at $[\text{M}]_2^{2+}$ m/z = 849.69 for $[\text{Rh}(\kappa^2_{\text{PP}}\text{-Xphos})(\text{H})(\kappa^1_{\text{(S)}}\text{-}\sigma^1_{\text{(C)}}\text{-COC}_6\text{H}_4\text{SMe})]_2^{2+}$, which could be two aldehyde molecules coordinated or one molecule of the product of aldehyde hydroacylation.

As it was not possible to isolate or conclusively characterise any of the reactive intermediates for the Xphos catalysts, a different approach was necessary to determine what aspect of the Xphos complex might be causing the switch in reactivity from catalysing the alkene hydroacylation reaction (in the case of DPEphos) to catalysing the aldehyde hydroacylation reaction. It was thought that

the different reactivity of the Xphos catalyst to the DPEphos catalyst could be due to a cooperative effect of the two rhodium centres being held in close proximity by the bridging ligands. However, inspection of the Rh1-Rh2 distance (7.253 Å) of the solid state structure of $[\text{Rh}(\kappa^2\text{(PP)}\text{-Xphos})(\text{NBD})]_2[\text{closo-CB}_{11}\text{H}_{12}]_2$ suggests the reactivity has a different cause. As a general rule of thumb, cooperative effects require a metal-metal distance of $\leq 3.5\text{-}6$ Å.⁶⁴⁻⁶⁶

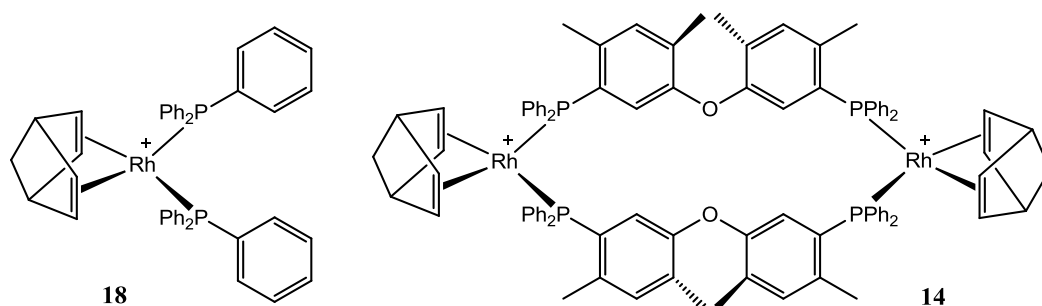
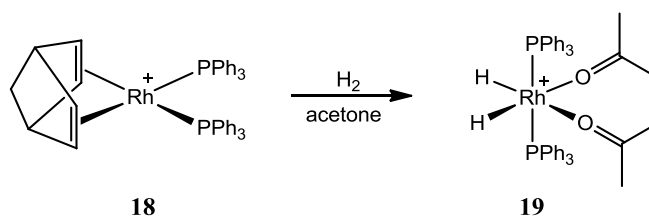


Figure 2.24: $[\text{Rh}(\text{PPh}_3)_2(\text{NBD})]^+$ (**18**) as an analogue of half of $[\text{Rh}(\kappa^2\text{(PP)}\text{-Xphos})(\text{NBD})]_2^{2+}$ (**14**). $[\text{BAR}^{\text{F}}_4]^-$ anions not shown.

To probe the possibility of cooperative effects being the cause of the switch in reactivity, the complex $[\text{Rh}(\text{PPh}_3)_2(\text{NBD})][\text{BAR}^{\text{F}}_4]$ (**18**) was prepared, as an analogue of half of $[\text{Rh}(\kappa^2\text{(PP)}\text{-Xphos})(\text{NBD})]_2[\text{BAR}^{\text{F}}_4]_2$ (**14**) i.e. without the bridging ether of the ligand (Figure 2.24). For complex **14** to be showing a cooperative effect, the catalyst ought to demonstrate a faster turnover rate than an equivalent molar concentration (per rhodium) of complex **18**. Complex **18** was activated by hydrogenation in acetone, to form the known complex $[\text{Rh}(\text{PPh}_3)_2(\text{H})_2(\text{acetone})_2][\text{BAR}^{\text{F}}_4]$ (**19**) *in situ* (Scheme 2.22).⁶⁷



Scheme 2.22: Activation of complex **18** by hydrogenation. $[\text{BAr}^{\text{F}}_4]^-$ anions not shown.

This complex was then tested as a catalyst for the hydroacylation reaction of aldehyde **V** and alkene **II** (entry 5, Table 2.2). The catalyst formed with PPh_3 demonstrates a similar reactivity (albeit a little slower) and selectivity to that displayed by the Xphos catalyst formed from **14**. This indicates that the change in reactivity is not due to any cooperativity effects, but perhaps instead by the ability of the coordinated phosphine ligands in both complexes to move independently of each other, and achieve a *trans* coordination mode which does not block a vacant site on the metal centre with a coordinating ether group, or diphosphine backbone.

2.6 Conclusion

The XANTphos, POP' and Xphos ligands were complexed to rhodium and studied, and the results compared to the DPEphos system.¹ XANTphos and POP' showed similar results to each other, but were significantly different from DPEphos; particularly in the formation of the bis-hydride complexes **2**, **3**, **9** and **10**, and the coordinated alkene complexes **5**, **6** and **12**. Both systems displayed an inability to de-coordinate the oxygen donor in the metal-acyl-hydride complexes **7** and **13**, and so favoured aldehyde hydroacylation over alkene hydroacylation, presumably

proceeding *via* an outer-sphere mechanism. Neither displayed the reversible coordination of the oxygen donor characteristic of hemilabile behaviour, and necessary for the catalysis of the alkene hydroacylation reaction.

Xphos also displayed different catalytic reactivity to DPEphos, being selective for the aldehyde hydroacylation reaction, even with challenging substrates. This was attributed to the complexes Xphos formed with rhodium, in which two ligands bridge two rhodium centres separated by 7.3 Å, which are significantly different to the complexes formed with DPEphos, POP' and XANTphos. PPh₃ was briefly investigated as a complex which is analogous to half of [Rh($\kappa^2_{(PP)}$ -Xphos)]₂²⁺, and displayed similar catalytic activity and selectivity, suggesting the effect is not due to bimetallic cooperativity effects.

A further possible reason for preferential selectivity for the aldehyde hydroacylation reaction vs. the alkene hydroacylation reaction is discussed in the next chapter. In this it is noted that wider bite angle, chelating ligands promote faster turnover, and selectivity for aldehyde hydroacylation. The PPh₃ and Xphos ligands are the final extension of this, being *trans* orientated. The hemilabile capability of DPEphos allows it to adopt a smaller bite angle (P-Rh-P *cis* bond angle is 96.23(3)° in [Rh($\kappa^2_{(PP)}$ -DPEphos)(acetone)₂]⁺ and 100.37(3)° in [Rh($\kappa^2_{(PP)}$ -DPEphos)(CO)(SMeEt)]⁺),¹ consistent with selectivity for alkene hydroacylation.

2.7 References

1. G. L. Moxham, H. Randell-Sly, S. K. Brayshaw, A. S. Weller and M. C. Willis, *Chemistry - A European Journal*, 2008, **14**, 8383-8397.
2. P. Braunstein and F. Naud, *Angewandte Chemie International Edition*, 2001, **40**, 680-699.
3. G. L. Moxham, H. Randell-Sly, E. , S. Brayshaw, K., R. L. Woodward, A. S. Weller and M. Willis, C., *Angewandte Chemie International Edition*, 2006, **45**, 7618-7622.
4. W. E. Buschmann, J. S. Miller, K. Bowman-James and C. N. Miller, in *Inorganic Syntheses*, ed. C. Dimitri, 2002, vol. 33, p. 83.
5. C. A. Reed, *Accounts of Chemical Research*, 2009, **43**, 121-128.
6. A. B. Chaplin and A. S. Weller, *European Journal of Inorganic Chemistry*, **2010**, 5124-5128.
7. W. Reilly, MChem, *Hydroacylation: New catalysts for combined C-H activation and C-C bond formation*, University of Oxford, 2011.
8. P. C. J. Kamer, P. W. N. M. van Leeuwen and J. N. H. Reek, *Accounts of Chemical Research*, 2001, **34**, 895-904.
9. R. Dallanegra, A. B. Chaplin and A. S. Weller, *Organometallics*, 2012, **31**, 2720-2728.
10. G. L. Williams, C. M. Parks, C. R. Smith, H. Adams, A. Haynes, A. J. H. M. Meijer, G. J. Sunley and S. Gaemers, *Organometallics*, 2011, **30**, 6166-6179.
11. A. J. Pontiggia, A. B. Chaplin and A. S. Weller, *Journal of Organometallic Chemistry*, **696**, 2870-2876.
12. T. Ohshima, Y. Miyamoto, J. Ipposhi, Y. Nakahara, M. Utsunomiya and K. Mashima, *Journal of the American Chemical Society*, 2009, **131**, 14317-14328.
13. D. H. M. W. Thewissen, K. Timmer, J. G. Noltes, J. W. Marsman and R. M. Laine, *Inorganica Chimica Acta*, 1985, **97**, 143-150.
14. J. M. Brown, S. J. Cook and A. G. Kent, *Tetrahedron*, 1986, **42**, 5097-5104.
15. J. M. Brown, P. A. Chaloner, A. G. Kent, B. A. Murrer, P. N. Nicholson, D. Parker and P. J. Sidebottom, *Journal of Organometallic Chemistry*, 1981, **216**, 263-276.
16. R. W. K. Paul S. Pregosin, *³¹P and ¹³C NMR of transition metal phosphine complexes*, Springer-Verlag, Berlin ; New York, 1979
17. R. Dallanegra, DPhil., *Cationic Rhodium Complexes with Chelating Phosphine and Phosphine Alkene Ligands. Application in Dehydrogenation and Dehydrocoupling Reactions.*, University of Oxford, 2011.
18. R. J. Pawley, *Role of Hemi-Labile Ligands in Rhodium Catalysed Hydroacylation of Alkenes*, University of Bath, 2007.
19. M. J. Ingleson, S. K. Brayshaw, M. F. Mahon, G. D. Ruggiero and A. S. Weller, *Inorganic Chemistry*, 2005, **44**, 3162-3171.
20. , P. Budzelaar, Cherwell Scientific Publishing, Oxford, 4.0 edn., 1997.
21. R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, 4th edn., John Wiley & Sons, Inc., New Jersey, 2005.
22. A. C. Cooper, E. Clot, J. C. Huffman, W. E. Streib, F. Maseras, O. Eisenstein and K. G. Caulton, *Journal of the American Chemical Society*, 1998, **121**, 97-106.
23. M. Grellier, L. Vendier and S. Sabo-Etienne, *Angewandte Chemie International Edition*, 2007, **46**, 2613-2615.
24. L. Helm and A. E. Merbach, *Chemical Reviews*, 2005, **105**, 1923-1960.
25. C. H. Langford and H. B. Gray, *Ligand Substitution Processes*; , W. A. Benjamin, Inc., New York, 1965.
26. N. W. Alcock, J. M. Brown and J. C. Jeffery, *Journal of the Chemical Society, Dalton Transactions*, 1976, 583-588.
27. A. J. Sandee, L. A. van der Veen, J. N. H. Reek, P. C. J. Kamer, M. Lutz, A. L. Spek and P. W. N. M. van Leeuwen, *Angewandte Chemie International Edition*, 1999, **38**, 3231-3235.
28. C. Bianchini, A. Meli, M. Peruzzini, F. Vizza and A. Albinati, *Organometallics*, 2002, **9**, 2283-2291.
29. B. Deb and D. K. Dutta, *Journal of Molecular Catalysis A: Chemical*, **326**, 21-28.
30. R. Cramer, *Journal of the American Chemical Society*, 1964, **86**, 217-222.
31. T. Kaneshima, Y. Yumoto, K. Kawakami and T. Tanaka, *Inorganica Chimica Acta*, 1976, **18**, 29-34.

32. L. A. Friedman, S. H. Meiere, B. C. Brooks and W. D. Harman, *Organometallics*, 2001, **20**, 1699-1702.
33. S. D. Pike, *Exploring New Hydroacylation Catalysts Based on Rhodium Phosphine Systems*, University of Oxford, 2010.
34. S. D. Pike, R. J. Pawley, A. B. Chaplin, A. L. Thompson, J. A. Hooper, M. C. Willis and A. S. Weller, *European Journal of Inorganic Chemistry*, **2011**, 5558-5565.
35. D. Kwon and M. D. Curtis, *Organometallics*, 1990, **9**, 1-5.
36. R. Sustmann, B. Patzke and R. Boese, *Journal of Organometallic Chemistry*, 1994, **470**, 191-197.
37. R. Bender, C. Okio, R. Welter and P. Braunstein, *Dalton Transactions*, 2009, **25**, 4901-4907.
38. A. J. Edwards, S. Elipse, M. A. Esteruelas, F. J. Lahoz, L. A. Oro and C. Valero, *Organometallics*, 1997, **16**, 3828-3836.
39. E. Hauptman, S. Sabo-Etienne, P. S. White, M. Brookhart, J. M. Garner, P. J. Fagan and J. C. Calabrese, *Journal of the American Chemical Society*, 1994, **116**, 8038-8060.
40. J. Chatt and L. A. Duncanson, *Journal of the Chemical Society (Resumed)*, 1953, **0**, 2939-2947.
41. T. A. Albright, R. Hoffmann, J. C. Thibeault and D. L. Thorn, *Journal of the American Chemical Society*, 1979, **101**, 3801-3812.
42. M. Rubio, A. Suárez, D. del Río, A. Galindo, E. Álvarez and A. Pizzano *Organometallics*, 2008, **28**, 547-560.
43. E. Calimano and T. D. Tilley, *Dalton Transactions*, **39**.
44. J. R. Dilworth, C. A. M. von Beckh W and S. I. Pascu, *Dalton Transactions*, 2005, 2151-2161.
45. X. Shan and J. H. Espenson, *Organometallics*, 2003, **22**, 1250-1254.
46. E. W. Abel, S. K. Bhargava and K. G. Orrell, in *Progress in Inorganic Chemistry*, John Wiley & Sons, Inc., 2007, pp. 1-118.
47. E. W. Abel, M. Booth and K. G. Orrell, *Journal of the Chemical Society, Dalton Transactions*, 1980, **9**, 1582-1592.
48. E. W. Abel, R. Corben, I. Moss, K. G. Orrell, N. R. Richardson and V. Sik, *Journal of Organometallic Chemistry*, 1988, **344**, 343-350.
49. E. W. Abel, G. W. Farrow and K. G. Orrell, *Journal of the Chemical Society, Dalton Transactions*, 1976, **13**, 1160-1163.
50. E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell and V. Sik, *Journal of the Chemical Society, Dalton Transactions*, 1980, **7**, 1175-1181.
51. Crystal obtained in collaboration with Gemma Moxham (Weller group).
52. A. T. Luedtke and K. I. Goldberg, *Inorganic Chemistry*, 2007, **46**, 8496-8498.
53. J. E. Marcone and K. G. Moloy, *Journal of the American Chemical Society*, 1998, **120**, 8527-8528.
54. E. Zuidema, P. W. N. M. van Leeuwen and C. Bo, *Organometallics*, 2005, **24**, 3703-3710.
55. A. B. Chaplin and A. S. Weller, *European Journal of Inorganic Chemistry*, 2010, **2010**, 5124-5128.
56. A. Woolf, A. B. Chaplin, J. E. McGrady, M. A. M. Alibadi, N. Rees, S. Draper, F. Murphy and A. S. Weller, *European Journal of Inorganic Chemistry*, 2011, **2011**, 1614-1625.
57. T. M. Douglas, A. B. Chaplin and A. S. Weller, *Organometallics*, 2008, **27**, 2918-2921.
58. Tilmann J. Geldbach and Paul S. Pregosin, *European Journal of Inorganic Chemistry*, 2002, **2002**, 1907-1918.
59. P. S. Pregosin, *Coordination Chemistry Reviews*, 2008, **252**, 2156-2170.
60. A. R. O'Connor, W. Kaminsky, D. M. Heinekey and K. I. Goldberg, *Organometallics*, 2011, **30**, 2105-2116.
61. A. Rifat, N. J. Patmore, M. F. Mahon and A. S. Weller, *Organometallics*, 2002, **21**, 2856-2865.
62. T. Andrea, E. Barnea and M. S. Eisen, *Journal of the American Chemical Society*, 2008, **130**, 2454-2455.
63. T. Seki, T. Nakajo and M. Onaka, *Chemistry Letters*, 2006, **35**, 824-829.
64. E. K. van den Beuken and B. L. Feringa, *Tetrahedron*, 1998, **54**, 12985-13011.
65. B. J. Holliday, P. A. Ulmann, C. A. Mirkin, C. L. Stern, L. N. Zakharov and A. L. Rheingold, *Organometallics*, 2004, **23**, 1671-1679.
66. R. K. Das, B. Saha, S. M. W. Rahaman and J. K. Bera, *Chemistry – A European Journal*, 2010, **16**, 14459-14468.
67. J. R. Shapley, R. R. Schrock and J. A. Osborn, *Journal of the American Chemical Society*, 1969, **91**, 2816-2817.

3 DIPHENYLPHOSPHINOALKANE LIGANDS

3.1 Introduction

The potentially hemi-labile ligand systems identified and studied in the first chapter gave poor results as catalysts for the alkene hydroacylation of aldehyde **I** and alkene **II**, and demonstrated a lack of ligand hemilability. Instead they either coordinated irreversibly through the oxygen donor blocking the vacant site necessary for further reactivity, or preferentially catalysed the aldehyde hydroacylation reaction over the alkene hydroacylation reaction. Given these results, the reactivity of ligands which have similar electronic and steric properties to POP', DPEphos and XANTphos, but which should not block the vacant site on the metal, were next explored. Research into catalysis using chelating diphenylphosphinoalkane ligands has been extensive, and shows interesting reactivity which can be controlled by systematically varying the bite angle of the diphosphine ligand.¹⁻⁶ In this chapter, the common bidentate phosphine ligands of the type $\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2$ (where $n = 2-5$) are initially reported, followed by *ortho*-substituted analogues of the dpp2 ligand, dpp2-*o*-R (where R = Me, *i*Pr) (Figure 3.1).

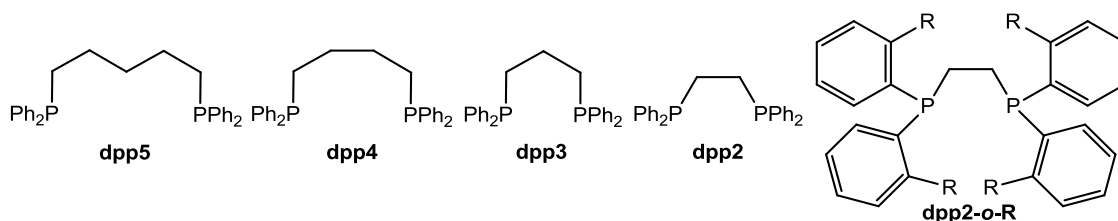
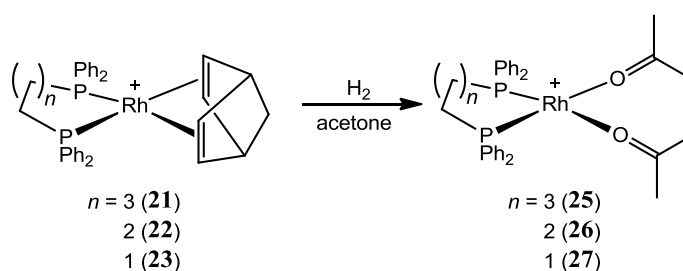


Figure 3.1: Ligands studied in this chapter, (R = Me, *i*Pr).

3.2 Complexes incorporating dpp2-5

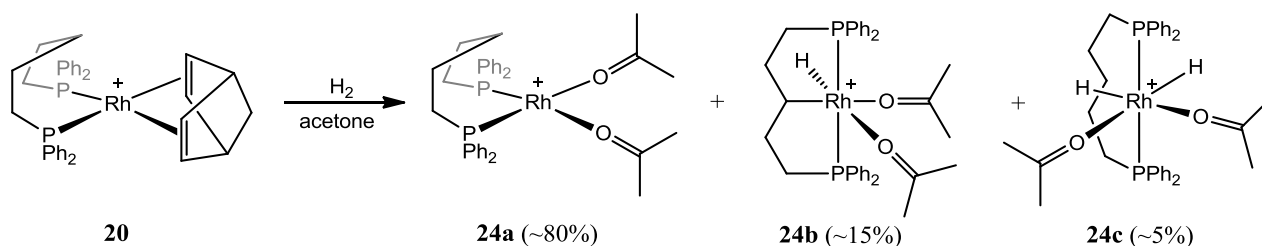
The precursor complexes: $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-dpp5})(\text{NBD})][\text{BAr}^{\text{F}}_4]$ (**20**),⁷ $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-dpp4})(\text{NBD})][\text{BAr}^{\text{F}}_4]$ (**21**),⁸ $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-dpp3})(\text{NBD})][\text{BAr}^{\text{F}}_4]$ (**22**)⁸ and $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-dpp2})(\text{NBD})][\text{BAr}^{\text{F}}_4]$ (**23**),⁸ have all been previously reported as alternative salts (ClO_4^- and BF_4^-) and complexes **20-22** were prepared according to the method outlined in Scheme 2.2 (p.71). ESI-MS, ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR data for these norbornadiene precursors were consistent with the formation of rhodium(I) pseudo-square-planar complexes as reported in the literature. Complex **23** was prepared according to a revised procedure to avoid the formation of the contaminant $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-dpp2})_2][\text{BAr}^{\text{F}}_4]$, and this new method has been reported in the experimental section of this thesis.



Scheme 3.1: Activation of rhodium(I)norbornadiene precursors (**21-23**), by hydrogenation. $[\text{BAr}^{\text{F}}_4]^-$ anions not shown.

Activation of the precursors (**20-23**) was achieved by addition of hydrogen (4 atm) in acetone solution. For the complexes **21-23**, addition of H_2 afforded the previously reported bis-acetone adducts: $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-dpp4})(\text{acetone})_2][\text{BAr}^{\text{F}}_4]$ (**25**),⁸ $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-dpp3})(\text{acetone})_2][\text{BAr}^{\text{F}}_4]$ (**26**)⁸ and $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-dpp2})(\text{acetone})_2][\text{BAr}^{\text{F}}_4]$ (**27**)⁸ as shown by NMR spectroscopy and ESI-MS (Scheme 3.1). The bis-acetone adduct formed with dpp5 has not previously been reported, and addition of H_2 to

the norbornadiene complex **20** forms a mixture of complexes: the rhodium(I)bis-acetone complex $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-dpp5})(\text{acetone})_2][\text{BAR}^{\text{F}}_4]$ (**24a**) and two rhodium(III) complexes which are tentatively characterised as the C-H activated complex $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-}\sigma^1_{\text{(C)}}\text{-PPh}_2\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2\text{PPh}_2)(\text{H})(\text{acetone})_2][\text{BAR}^{\text{F}}_4]$ (**24b**) and the dihydride bis-acetone complex $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-dpp5})(\text{H})_2(\text{acetone})_2][\text{BAR}^{\text{F}}_4]$ (**24c**) on the basis of NMR experiments (Scheme 3.2).



Scheme 3.2: Activation of complex **20** by hydrogenation. $[\text{BAR}^{\text{F}}_4]$ -anions not shown.

A similar mixture of complexes was observed by Brown *et al.* on addition of hydrogen (1 atm) to the $[\text{BF}_4]^-$ salt of complex **20** in methanol solution, leading to the formation of the methanol analogues of **24**: $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-dpp5})(\text{MeOH})_2][\text{BF}_4]$, $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-}\sigma^1_{\text{(C)}}\text{-PPh}_2\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2\text{PPh}_2)(\text{H})(\text{MeOH})_2][\text{BF}_4]$ and $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-dpp5})(\text{H})_2(\text{MeOH})_2][\text{BF}_4]$.⁷ These complexes were reported to be in equilibrium with each other, and display similar spectroscopic properties to complexes **24a-c** with two hydrides observed in the ^1H NMR spectrum at δ -22.5 [$J(\text{RhH}) = 32$, $J(\text{PH}) = 11$] and -22.9 [$J(\text{RhH}) = 27$, $J(\text{PH}) = 18$]. Two hydride signals are observed in the ^1H NMR spectrum of **24a-c**: a doublet of triplets at δ -21.68 [$J(\text{RhH}) = 27$, $J(\text{PH}) = 16$] which collapses into a doublet upon ^{31}P decoupling, and has been assigned as **24b**; and another doublet of triplets at δ -22.30 [$J(\text{RhH}) = 35$, $J(\text{PH}) = 11$] which collapses into a broad doublet upon ^{31}P decoupling, which has been assigned as

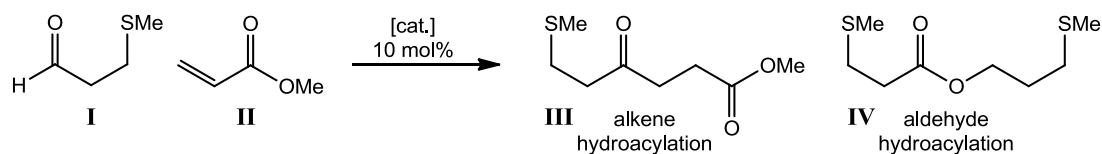
24c. The integral of these signals relative to the aromatic region (32H) is 0.20H (**24b**) and 0.14H (**24c**). The signals for the three complexes **24a-c** overlap in the alkyl region of the spectrum, preventing assignment of individual proton environments. Three environments are observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, at δ 55.3 [$J(\text{RhP}) = 133$], 37.3 [$J(\text{RhP}) = 201$] and 35.8 [$J(\text{RhP}) = 115$] in a 0.8:10:2 ratio. $^1\text{H}\{^{31}\text{P}\}$ selective decoupling NMR experiments assign these signals as **24c**, **24a** and **24b** respectively. ESI-MS of **24** diluted in acetone, shows a minor signal at $[\text{M}]^+ m/z = 659.16$ (calc. 659.17) and two major signals at $[\text{M} - \text{acetone}]^+ m/z = 601.13$ (calc. 601.13) and $[\text{M} - (\text{acetone})_2]^+ m/z = 543.08$ (calc. 543.09). The empirical formula for both **24a** and **24b** is the same, with $m/z = 659.17$, while the signal for the minor component **24c** would be masked by the isotope pattern for **24a/b**. No significant change in chemical shift is observed on cooling a d_6 -acetone solution of the mixture, although the ratios do change slightly in favour of **24b**, suggesting an equilibrium between the three complexes. Dubois *et al.* have also previously observed the formation of dihydride species on hydrogenation of rhodium(I) diphosphines, and attribute the varying ability of the complexes to oxidatively add hydrogen, to a combination of diphosphine electron-donation ability, and the size of the phosphine bite angle, with larger bite angle ligands favouring dihydride formation.^{9, 10} This correlates with the observation of the formation of a dihydride complex with the larger bite angle ligand, dpp5 (**24c**).

Stoichiometric reactions relevant to hydroacylation were undertaken to explore potential intermediates often observed in hydroacylation catalysis, in particular the metal-acyl-hydride intermediate. 1 equivalent of aldehyde **I** was added to

complexes **24-27** in d_6 -acetone solution in an attempt to isolate the C-H activated equivalents of the metal-acyl-hydride complexes **7** and **13**. The species formed could not readily be identified or characterised, with multiple species observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, which turned into broad uncharacterisable decomposition products over time. Bosnich *et al.* reported similar results on addition of 4-pentenal to their rhodium catalyst formed with the ligand dpp2.¹¹ ESI-MS of complexes **24a-c** with 1 eq. of aldehyde **I**, showed a relatively clean spectrum with a signal at $[\text{M}]^+ m/z = 751.15$ (calc. 751.15) which corresponds to the empirical formula for $[\text{Rh}(\kappa^2_{\text{PP}}\text{-dpp5})(\text{H})(\kappa^1_{\text{S}}\text{-}\sigma^1_{\text{C}}\text{-COC}_2\text{H}_4\text{SMe})]^+$. However, attempts to isolate or further characterise this species were unsuccessful. It is important to note however, that complexes **24b/c** were not observed by ESI-MS or NMR spectroscopy under these conditions, suggesting that they react with aldehyde **I** to give the same product as **24a**, which would be consistent with an equilibrium between the three complexes.

3.3 Catalytic activity of dpp2-5 complexes with aldehyde **I** and alkene **II**

The norbornadiene complexes **20-23** were tested as catalysts for the hydroacylation of methyl acrylate (**II**) by aldehyde **I** at 10 mol% loading, after activation by hydrogenation in d_6 -acetone solution to give complexes **24-27** *in situ*. The results for these reactions are reported in Table 3.1, and the relative yields and product distributions for each reaction, have been plotted in Figure 3.2.

Table 3.1: Catalytic activity of [Rh(diphosphine)NBD][BAR^F₄] in the hydroacylation reaction of **I** and **II**.^a

entry	ligand	temp. (°C)	% alkene hydroacylation III	% aldehyde hydroacylation IV	total conversion of aldehyde I	time (h)	initial rate for the formation of III x10 ⁻³ (mol/L/h) ^c	initial rate for the formation of IV x10 ⁻³ (mol/L/h) ^c
1	dpp2	22	91	8	99 ^d	60	30 ± 2	1.0 ± 3
2	dpp3	22	38	62	100	40	21 ± 1	25 ± 0.3
3	dpp4	22	50	50	100	8	134 ± 10	136 ± 9
4	dpp5	22	13	87	100	6	14 ± 7	130 ± 2
5	dpp5	40	17	83	100	0.5	^e	^e
6	dpp5	55	19	81	100	0.1	^e	^e
7 ^b	dpp5	18	30	46	76 ^d	15	76 ± 8	140 ± 20

^aConditions: all manipulations under argon atmosphere, 0.043 M solution of precatalyst in d₆-acetone, hydrogenated using standard procedures, catalyst:aldehyde ratio = 1:10, substrate ratio = 1:1 aldehyde:alkene, conversion determined by ¹H NMR spectroscopy. ^bSubstrate ratio 1:5 aldehyde:alkene. ^cInitial rate (IR) determined by fitting first order trendline to data of the form $y = a(1 - \exp^{-bx})$ and taking the value of the slope at $t = 0$; error in initial rate (eIR) determined by $eIR = IR \times (ea/a + eb/b)$ assuming error in trendline to be greater than error in data. ^dTotal conversion at given time. ^eReaction almost complete before a reliable first data point can be taken to determine initial rate.

The dpp2 system promotes the complete conversion of aldehyde over the course of 60 hours, but forms an approximate ratio of 9:1 of the alkene hydroacylation product (**III**) to aldehyde hydroacylation product (**IV**) (Table 3.1, entry 1). Previously reported studies using this ligand and substrate set have shown the catalyst to be completely selective for **III** at 55 °C, over 2 hours using an excess of alkene **II**.³ The longer time taken for complete conversion observed here is

consistent with the reaction taking place at lower temperature. Repeating the reaction at 55 °C gave the expected result, with complete conversion of **I** to **III** in 2 hours.

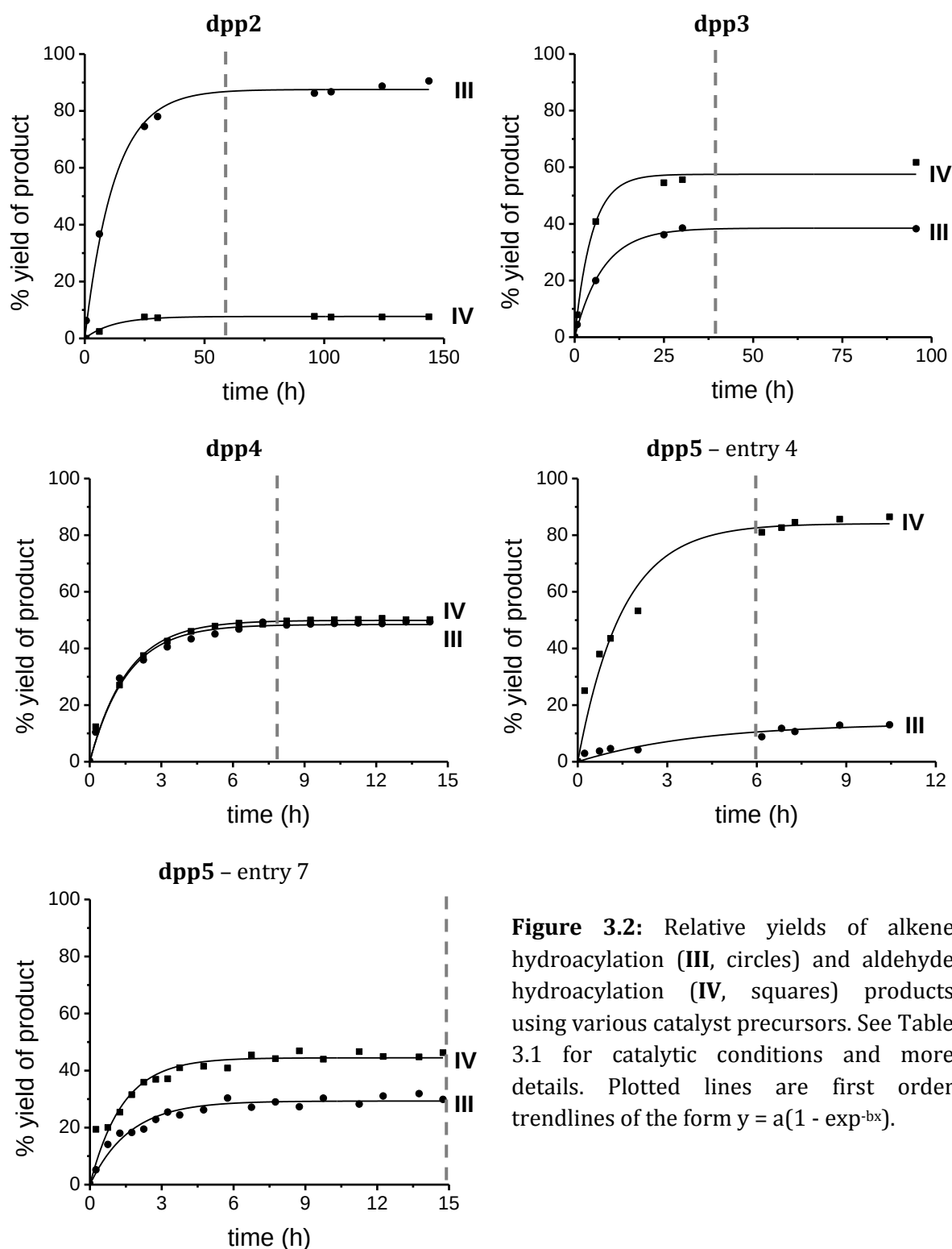


Figure 3.2: Relative yields of alkene hydroacylation (**III**, circles) and aldehyde hydroacylation (**IV**, squares) products using various catalyst precursors. See Table 3.1 for catalytic conditions and more details. Plotted lines are first order trendlines of the form $y = a(1 - \exp^{-bx})$.

Use of the larger bite angle ligand (dpp5) instead of dpp2, resulted in an unexpected switch in product selectivity, to give a 1:9 ratio of **III** to **IV** (entry 4). The reaction was repeated at 40 °C and 55 °C, resulting in a gradual change in the product distribution, from 13% **III** (at 22 °C) to 17% **III** at 40 °C, and 19% **III** at 55 °C (entries 4-6). Using a 5-fold excess of **II** with the dpp5 catalyst resulted in a large increase in selectivity for **III** (entry 7). However, a drop in reaction rate was observed, so that complete conversion of the aldehyde had not been achieved after 15 hours. Bosnich has also reported substrate inhibition in intermolecular hydroacylation,¹¹ which presumably arises in this system from the competition for coordination at the vacant site, prior to C-H activation of the aldehyde. Complexes **26** and **25** (Table 3.1, entries 2 and 3 respectively) showed no particular selectivity for either hydroacylation product.

These results show that as the ligand backbone increases in length, there is a gradual switch in product selectivity, from alkene hydroacylation to aldehyde hydroacylation. Alongside the change in selectivity, there is an observable increase in reaction rate from complex **27** (60 hours), **26** (40 hours), **25** (8 hours) to **24** (6 hours). Only one factor is being varied in these reactions: the ligand backbone chain length, which allows these results to be interpreted with respect to certain physical properties of the ligands, to understand the influence of these ligands. Different ways of measuring the steric influence of chelating phosphine ligands include: natural bite angle (β_n), flexibility range (Figure 1.11, p.12), accessible molecular surface and pocket angle; these have been assembled for the ligands

dpp2-5 (where available), which provides relevant data for this investigation (Table 3.2).

Table 3.2: Steric parameters for ligands dpp2-5.

ligand	natural bite angle β_n ($^\circ$) ^a	flexibility (range) ($^\circ$) ^a	accessible molecular surface ($\text{\AA}^2$) ^b	pocket angle $\theta_{\parallel}$ ($^\circ$) ^d	pocket angle $\theta_{\perp}$ ($^\circ$) ^d
dpp2	83.7	75.8-88.9 (13.1)	7.578	132	129
dpp3	90.7	83.3-98.4 (15.1)	5.704	108	146
dpp4	97.1	88.9-106.4 (17.5)	4.654	93	102
dpp5	98.9	90.5-107.9 (17.5)	4.66 ^c	^e	^e

^aNatural bite angle values and flexibility ranges are taken from ref 12 ^bAMS values taken from ref 13. ^cAMS value for dpp5 have not been determined, however, value for both dpp4 and dpp6 are in the range 4.65-4.66¹³ and dpp5 would be expected to fall in this range. ^dPocket angles, parallel and perpendicular, from ref 14. ^eNo data available for dpp5, however, values would be expected to be similar to dpp4.

There is a trend of increasing natural bite angle from dpp2-dpp5 as the number of atoms in the backbone increases; this is matched by a decrease in the accessible molecular surface (AMS) from dpp2 to dpp4 and a decrease in the pocket angle from dpp2 to dpp4. This indicates – as would be expected – that as the number of atoms in the ligand backbone is increased, the ligand has a larger impact on the coordination sphere about the metal. The steric parameters for dpp5 are largely unknown, but some data for dpp6 has been reported¹³ and this closely resembles that of dpp4. Presumably dpp5 will fall within the dpp4-6 range and therefore display similar steric properties. An analysis of the ligand steric properties in the rhodium(I) norbornadiene complexes is demonstrated in Figure 3.3(a). The two extremes of the rhodium(I) norbornadiene diphosphine series are shown, with the

ligands dpp2 (complex **23**) and dpp5 (complex **20**) displayed as space-filling diagrams overlaid on ball-and-stick diagrams of the crystal structures of $[\text{Rh}(\text{diphosphine})(\text{NBD})]^+$.^{15, 16} It can clearly be seen from these diagrams that the larger bite angle ligand (dpp5, complex **20**) crowds the coordination sphere about the rhodium in this pseudo-square-planar rhodium(I) complex, whereas the smaller bite angle ligand (dpp2, complex **23**) has a much more accessible metal centre.

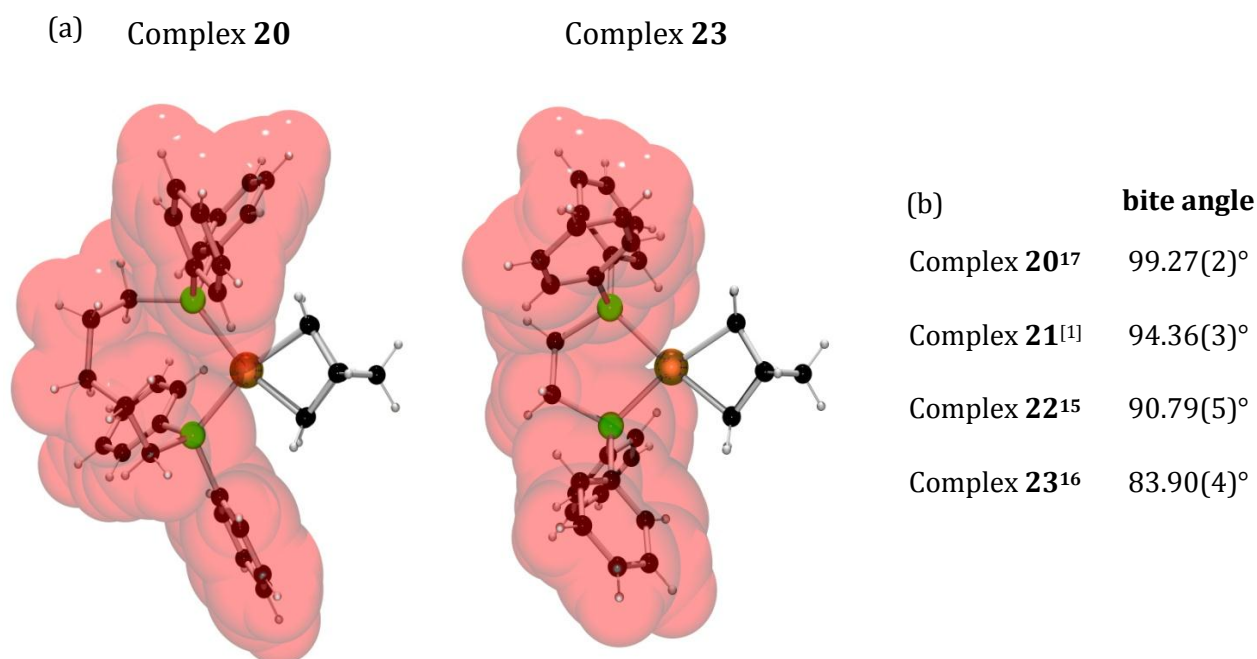
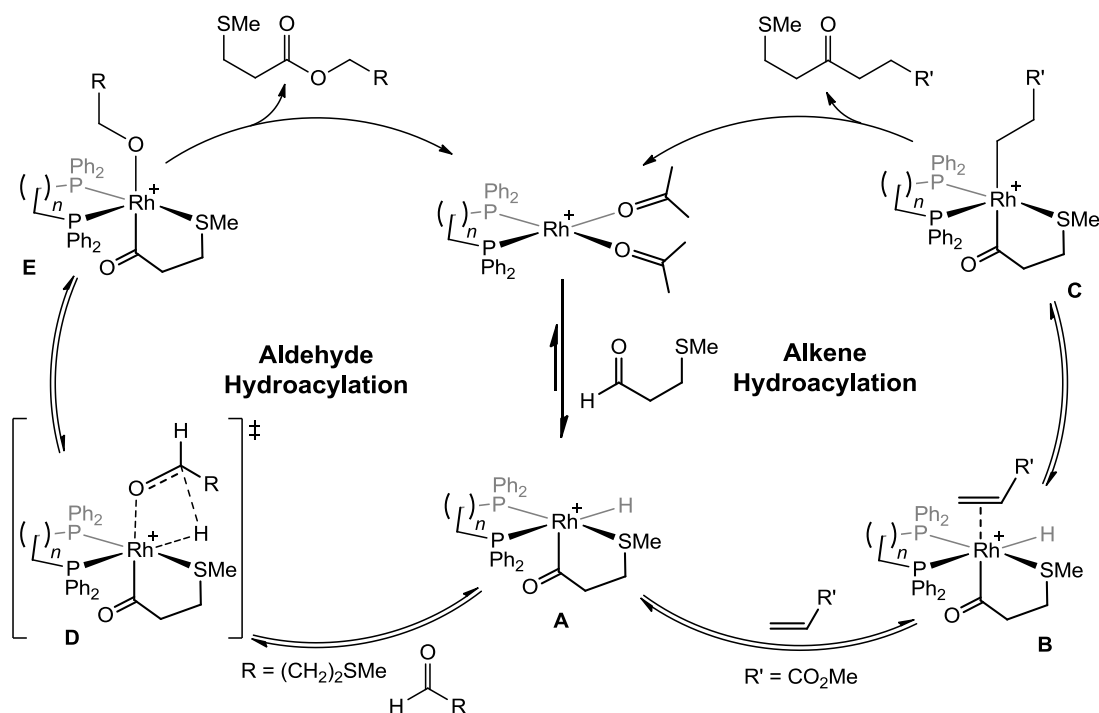


Figure 3.3: (a) Ligand space-filling diagrams of **20** and **23** showing more crowded coordination sphere of the larger bite angle ligand. (b) Diphosphine bite angles (P-Rh-P) of rhodium(I)norbornadiene complexes calculated from X-ray data. Data for complexes **22** and **23** were generated using the coordinates from the CCDC database (IBOZOP and QOPJOU, respectively). Anions omitted for clarity.

By taking these steric factors into consideration it is possible to see how the different ligands might impact each step of a probable hydroacylation catalytic cycle. Addition of aldehyde **I** to precatalysts **24-27** would give a rhodium(III)acyl-

^[1] Unpublished result, see appendix for details

hydride species (**A**, Scheme 3.3), such as is observed for complexes **7**, **13**, **i-100a** and **i-100b**, and has been calculated by Morehead and Sargent for Bosnich's intramolecular hydroacylation reaction of 4-pentanal by the $\{\text{Rh}(\text{dpp2})\}^+$ fragment.^{11, 18, 19}



Scheme 3.3: Suggested reaction pathways for aldehyde and alkene hydroacylation. $[\text{BAR}^{\text{F}}_4]^-$ anions not shown.

At this point either an alkene may coordinate to the acyl-hydride species (**A**), to give **B** which may then undergo alkene hydroacylation; or the aldehyde may coordinate to **A**, to give **D** which may then undergo aldehyde hydroacylation (Scheme 3.3). Coordination of the alkene is *via* an η^2 coordination mode, whereas the aldehyde may coordinate in both η^1 and η^2 modes. The smaller diposphine ligands which reveal a more open metal site (larger accessible molecular surface, larger pocket angle and smaller bite angle, e.g. **dpp2**) would promote η^2 -alkene coordination (**B**), and – more importantly – allow for the necessary coplanar

orientation of the alkene and hydride which is required for insertion. While the aldehyde may also coordinate, it appears the alkene is preferred given the proportion of alkene hydroacylation product to aldehyde hydroacylation product for the catalyst **27** (Table 3.1, entry 4). For the larger ligands which conceal more of the metal site (small accessible molecular surface, small pocket angle and large bite angle, e.g. dpp5) alkene coordination may be disfavoured by the bulk of the ligand, preventing the required orientation for insertion.¹⁴ In contrast, the ability of the aldehyde to adopt the sterically less demanding η^1 -coordination mode means that the aldehyde can access the metal centre in the catalysts with the larger ligands. Furthermore, the flexibility of the η^1 -coordination mode may facilitate the insertion of the hydride (**D**), as has been suggested to occur in carbonyl hydrogenation by late-transition-metal hydrides.²⁰ DFT calculations for the related process: ketone hydroacylation, have been carried out by Dong *et al.* and show that a carbonyl η^1 -intermediate is formed prior to hydride insertion, supporting the proposal of the formation of complex **D**.⁴

Further support for this argument of ligand-sterics affecting selectivity is provided by structures of the previously reported complexes $\text{Rh(I)}_2(\text{dpp2})(\text{COMe})$ ²¹ and $\text{Rh(I)}_2(\text{dpp4})(\text{COMe})$.²² Both have an acyl group *trans* to the vacant site and so are reasonable models for intermediate **A**; the space-filling diagrams of the two structures show that the metal surface is less accessible to incoming ligands in the dpp4 complex when compared to the dpp2 complex (Figure 3.4).

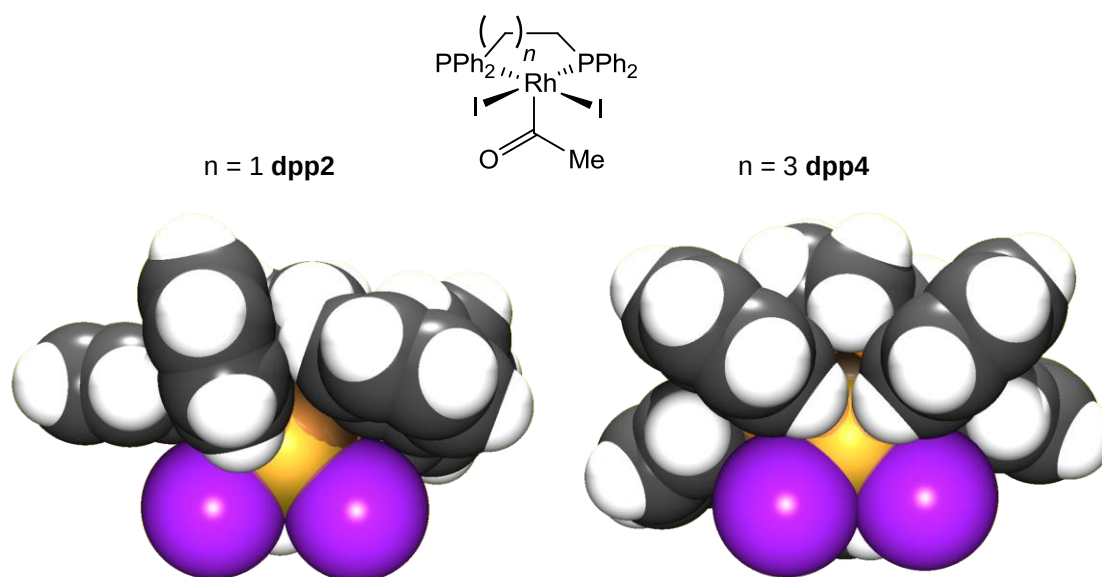


Figure 3.4: Space-filling diagrams (van der Waals radii) of the complexes $\text{Rh}(\text{I})_2(\text{dpp2})(\text{COMe})$ ²¹ and $\text{Rh}(\text{I})_2(\text{dpp4})(\text{COMe})$,²² showing the effect that changing the ligand backbone has on the accessible molecular surface of the metal centre (coloured copper). Data was generated using the coordinates from the CCDC database (OGUXUJ and HISZOZ, respectively).

Changing the reaction conditions by varying the temperature (Table 3.1, entries 5 and 6, increased temperature favours **B**) or increasing the alkene concentration (Table 3.1, entry 7, increased alkene concentration favours **B**) has an effect on the ratio of products, suggesting that there is an equilibrium between **D**, **A** and **B**. An alternative explanation for the selectivity of the different ligand-complexes is that large bite angle ligands usually increase the rate of reductive elimination²³⁻²⁶ and so hydride insertion may become the turnover limiting step, favouring aldehyde hydroacylation due to the smaller steric requirements, whereas for small bite angle ligands reductive elimination may be turnover limiting, favouring alkene hydroacylation.

3.4 Catalytic activity of dpp2-5 complexes with aldehyde V and alkene II

The norbornadiene precursor complexes **20-23** were also tested as catalysts for the hydroacylation of methyl acrylate (**II**) by aromatic aldehyde **V** at 10 mol% loading, after activation by hydrogenation in d_6 -acetone solution to give complexes **24-27** *in situ*. The results are reported in Table 3.3, and the relative yields and product distributions for each reaction have been plotted in Figure 3.5.

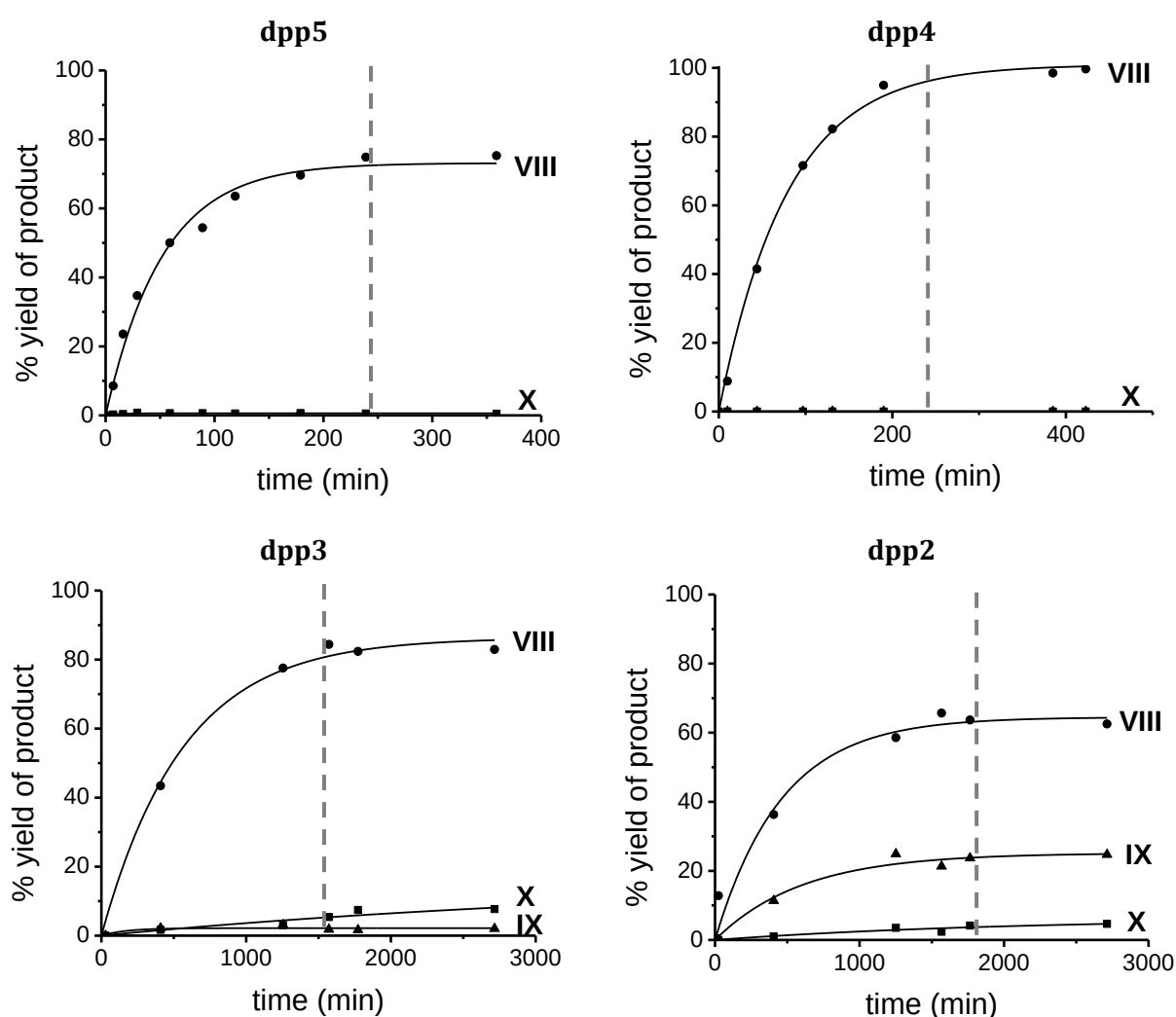
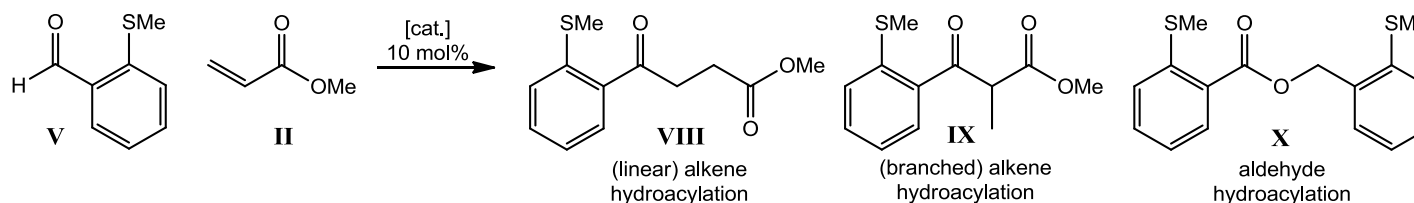


Figure 3.5: Relative yields of linear alkene hydroacylation (**VIII**, circles), branched alkene hydroacylation (**IX**, triangles) and aldehyde hydroacylation (**X**, squares) products using various catalyst precursors. See Table 3.3 for catalytic conditions and more details. Plotted lines are first order trendlines of the form $y = a(1 - \exp^{-bx})$.

Table 3.3: Catalytic activity of [Rh(diphosphine)NBD][BAR^F₄] in the hydroacylation reaction of **V** and **II**.^a

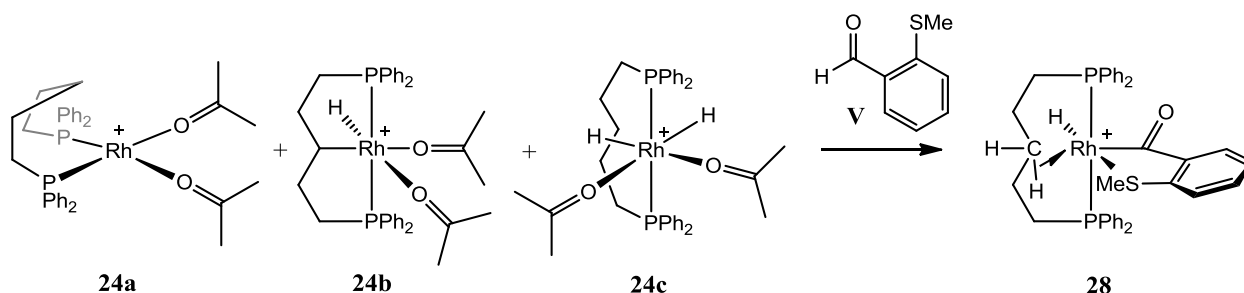
entry	ligand	% linear alkene hydroacylation VIII	% branched alkene hydroacylation IX	% aldehyde hydroacylation X	total conversion of aldehyde V	time (h)	initial rate for the formation of VIII x10 ⁻⁵ (mol/L/h) ^c	initial rate for the formation of IX x10 ⁻⁵ (mol/L/h) ^c	initial rate for the formation of X x10 ⁻⁵ (mol/L/h) ^c
1	dpp2	63	25	5	93 ^b	30	36 ± 10	11 ± 3	0.8 ± 0.9
2	dpp3	83	2	8	93 ^b	26	40 ± 5	3 ± 4	1 ± 2
3	dpp4	99	0	1	100	4	330 ± 20	-	-
4	dpp5	82	0	1	83 ^b	4	360 ± 41	-	-

^aConditions: all manipulations under argon atmosphere, 0.043 M solution of precatalyst in d₆-acetone, hydrogenated using standard procedures, catalyst:aldehyde ratio = 1:10, substrate ratio = 1:1 aldehyde:alkene, conversion determined by ¹H NMR spectroscopy. ^bTotal conversion at given time. ^cInitial rate (IR) determined by fitting first order trendline to data of the form $y = a(1 - \exp^{-bx})$ and taking the value of the slope at $t = 0$; error in initial rate (eIR) determined by $eIR = IR \times (ea/a + eb/b)$ assuming error in trendline to be greater than error in data.

The dpp4 and dpp5 systems both showed complete selectivity for the linear hydroacylation product **VIII** (Table 3.3, entries 3 and 4), although the reaction with dpp4 goes to completion while dpp5 achieves only 83% conversion over the same time frame. Interestingly, the branched product of alkene hydroacylation (**IX**) is observed with dpp3 (entry 2), and represents over 25% of the total aldehyde consumption by dpp2 (entry 1). As was observed for the hydroacylation of alkene **II** by aldehyde **I**, the larger bite angle ligands demonstrate faster rates of reaction than the smaller bite angle ligands; this is attributed to the same cause, i.e. larger bite angle ligands are known to increase the rate of reductive elimination.²³⁻²⁶ That all four catalysts favour the linear alkene hydroacylation product (**VIII**) over the aldehyde hydroacylation product (**X**) is to be expected: the majority of catalysts for aldehyde hydroacylation (the Tishchenko reaction) show sluggish activity towards the coupling of aromatic aldehydes.²⁷⁻³⁰ However, it is the appearance of the branched alkene hydroacylation product (**IX**) which is of particular interest. Linear selectivity is the most common reaction pathway, although some branched-selective hydroacylation systems requiring specific substrates are known.³¹⁻³⁶ Branched selectivity occurs at the hydride insertion step and thus smaller bite angle ligands might encourage this, or at least reductive elimination of the product through having a more open metal centre which allows the necessary orientation of the ligands for reductive elimination, to be achieved.^{37, 38}

To gain an understanding of the complexes involved in the catalytic cycle, the reaction was emulated under stoichiometric conditions. In contrast to the decomposition which was observed on addition of 1 equivalent of aldehyde **I** to

any of the activated complexes **24-27**, quantitative formation of single complexes was observed on addition of 1 equivalent of aldehyde **V**. Aldehyde **V** has been previously shown to undergo considerably slower decarbonylation than aldehyde **I**.³ The complex formed with dpp2 will be discussed later in this chapter.



Scheme 3.4: Formation of complex **28**. [BAR^F₄]⁻ anions not shown.

Addition of 1 equivalent of aldehyde **V** to complexes **24a-c** lead to the formation of a new complex [Rh(κ^2 (PP)- η^1 (CH)-dpp5)(H)(κ^1 (S)- σ^1 (C)-COC₆H₄SMe)][BAR^F₄] (**28**) (Scheme 3.4). Complex **28** was characterised by NMR spectroscopy and ESI-MS. The observation of only one species (**28**) by ³¹P{¹H} NMR spectroscopy – at δ 37.32 [br d, J (RhP) = 128] – is consistent with the presence of an equilibrium between **24a**, **b** and **c**.

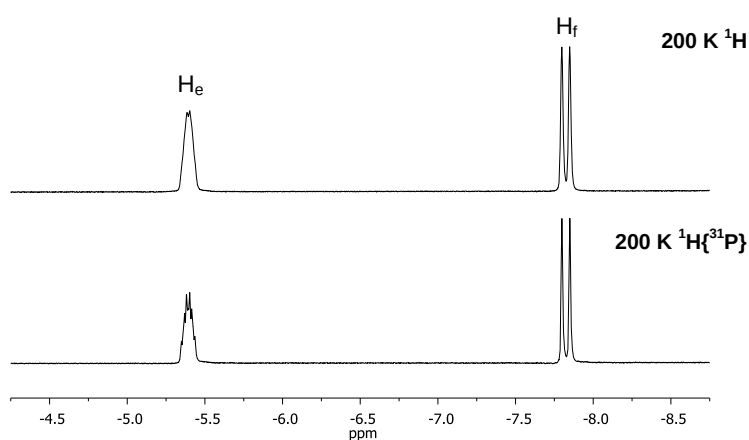


Figure 3.6: ¹H and ¹H{³¹P} NMR spectra of complex **28** at 200 K, hydride region only.

A hydride signal, integral 1H, is observed at δ -8.00 [$J(\text{RhH}) = 25$] in the ^1H NMR spectrum (Figures 3.6 and 3.7c, H_f). This is similar to the hydride signal observed in **i-100a** at δ -8.26 [$J(\text{RhH}) = 25$].³ Another high-field signal, integral 1H, is observed at δ -5.05 which shows some fine coupling upon ^{31}P decoupling (Figures 3.6 and 3.7, H_e). This signal has been assigned as one of the protons of the central ligand backbone CH_2 group, which has formed an agostic interaction to the metal centre. This signal correlates to a broad signal, integral 1H, at δ 3.11 in the COSY NMR spectrum, the second proton of this CH_2 group (Figure 3.7c, H_d and H_e). These two signals both correlate to one carbon signal at δ 45.93 in the ^1H - ^{13}C HSQC NMR spectrum, indicating the two protons are on the same carbon (Figure 3.7a, C^3).

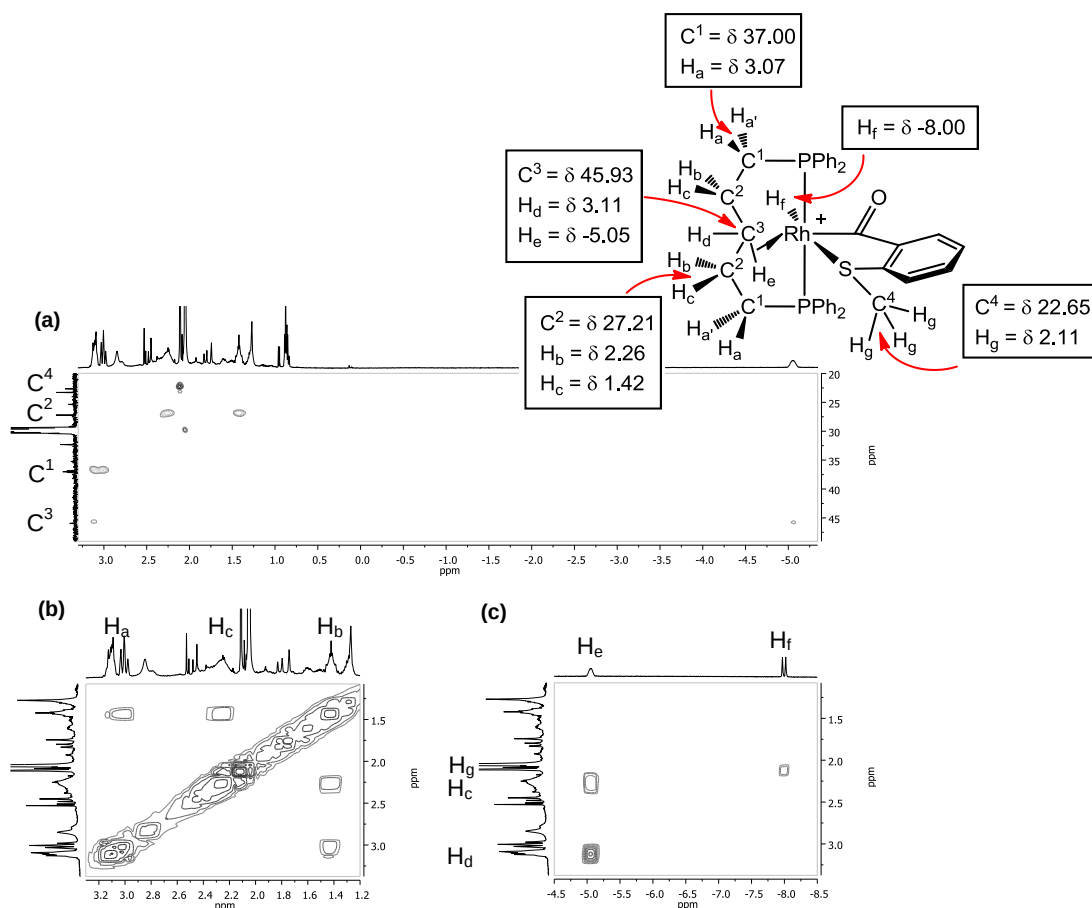


Figure 3.7: (inset) Selected ^1H and ^{13}C NMR chemical shifts of complex **28**, (a) ^1H - ^{13}C HSQC and (b and c) COSY NMR spectra of complex **31** at 295 K (selected regions).

Two sets of integral 2H signals are observed at δ 2.26 and 1.42, which correlate to each other in the COSY NMR spectrum (Figure 3.7b, H_b and H_c); a further correlation is observed between these two signals and a signal at δ 27.21 in the ¹H-¹³C HSQC NMR spectrum (Figure 3.7a, C²) indicating the two sets of proton signals are on the same carbon, i.e. the four protons equate to two CH₂ groups with inequivalent protons. The final alkyl protons of the ligand backbone are located as an integral 4H multiplet at δ 3.07 (Figure 3.7b, H_a). Agostic interactions usually give rise to shortened M-H distances and a small M---H-C angle in the solid state, which in this case has not been isolated; or by an upfield shift in the ¹H NMR spectrum, compared to the chemical shift of the uncoordinated group:^{39, 40} the signal at δ -5.05 is shifted significantly upfield from the signal at δ 3.11. Agostic interactions can be considered as precursors to complete oxidative addition of the bond in question.^{39, 41-45} Therefore, this agostic interaction between the ligand backbone and the metal fits with the ability of dpp5 to C-H activate to form complex **24c**. Another correlation is observed between the hydride signal at δ -8.00 and a signal at δ 209.3 in ¹H-¹³C HMBC NMR spectrum, which has been assigned as the acyl carbon,⁴⁶ shifted downfield on C-H activation of the aldehyde and therefore implying that this has occurred. ESI-MS of complex **28** diluted in C₆H₅F, confirms the empirical formula of the parent cation, with a signal observed at [M]⁺ *m/z* = 695.18 (calc. 695.12) which shows the correct isotope pattern. Cooling a solution of **28** in d₆-acetone to 200 K resolves the doublet observed in the 295 K ³¹P{¹H} NMR spectrum, into two doublet of doublets which show an ABX coupling pattern at δ 42.39 [dd, *J*(PP) = 292, *J*(RhP) = 130] and 32.04 [dd, *J*(PP) = 292, *J*(RhP) = 133]. The large ³¹P-³¹P coupling indicates *trans* phosphines which have been made inequivalent by the SMe group being frozen out so that it is

canted to one side, as observed for the related POP' (**7**), XANTphos (**13**) and DPEphos³ complexes. A corresponding mechanism is proposed to that already given for complexes **7** and **13**, which makes the phosphines equivalent at room temperature on the NMR time scale i.e. inversion of the SMe group, probably *via* an sp²-hybridised intermediate (Scheme 2.13, p.95).

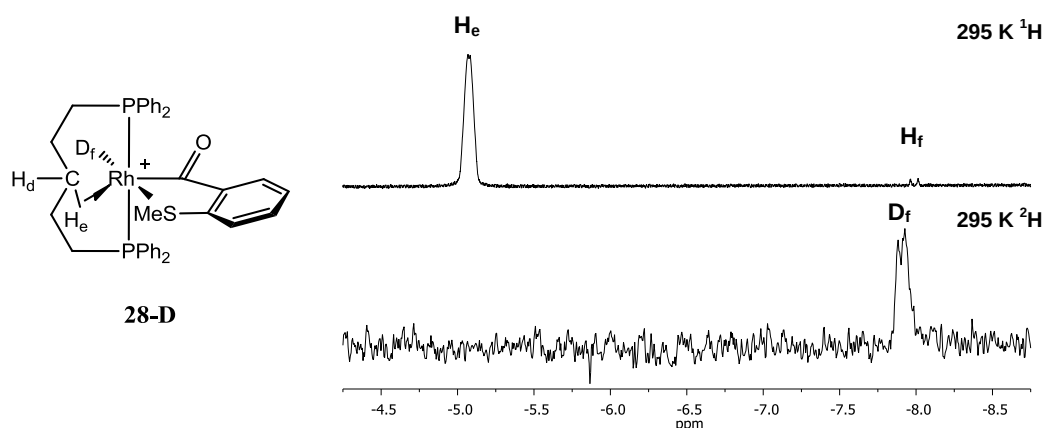
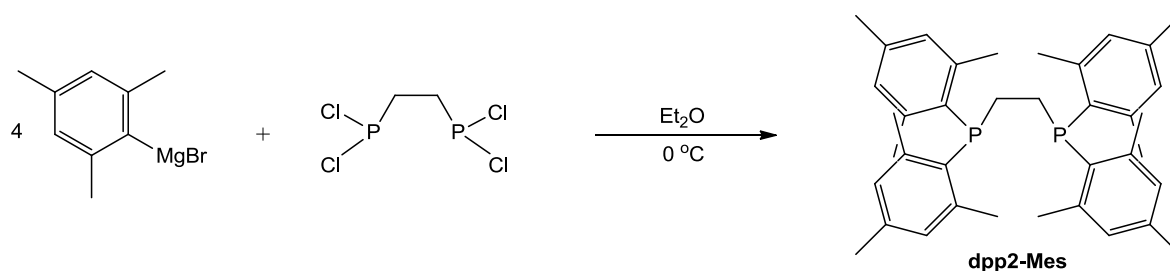


Figure 3.8: Complex **28-D**, [BAR^F₄]⁻ anion not shown. ¹H and ²H NMR spectra (hydride region only).

Addition of deuterated aldehyde **V** to complex **24** results in the formation of the deuterated complex [Rh(κ²(PP)-η¹(C-H)-dpp5)(D)(κ¹(S)-σ¹(C)-COC₆H₄SMe)][BAR^F₄] (**28-D**) (Figure 3.8). The ¹H NMR spectra of **28-D** and **28** are the same except for the almost complete absence of the signal at δ -8.00 (H_f) in the ¹H NMR spectrum and the appearance of a signal at δ -7.91 (D_f) in the ²H NMR spectrum indicating this signal is due to the oxidative addition of the aldehyde C-H bond (Figure 3.8). No scrambling of the deuterium is observed, and the small signal at δ -8.00 (H_f) in the ¹H NMR spectrum is due to residual protio aldehyde **V**, indicating no exchange is occurring between H_e and H_f.

3.5 Exploring sterically-bulky analogues of dpp2

The effect of ligand sterics on reactivity was next explored, by increasing the steric bulk of the small bite angle ligand, dpp2. The dpp2 system was chosen as it gave the greatest range of regioisomers in the reaction of aldehyde **V** and alkene **II** (Table 3.3, entry 1) therefore allowing any changes in selectivity to be more effectively observed. In addition, instead of the more linear selective methyl acrylate alkene (**II**), the more challenging terminal alkynes were explored as substrates. These have the added advantage of forming alkene products which are of greater value for onward reactivity.⁴⁷



Scheme 3.5: Preparation of dpp2-Mes.

Initially, the bulky mesityl-analogue of dpp2 (**dpp2-Mes**) was prepared according to the method outlined in Scheme 3.5. Characterisation of dpp2-Mes was achieved by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, with a singlet at δ -19.15 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The norbornadiene precursor $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-dpp2-Mes})(\text{NBD})][\text{BAr}^{\text{F}}_4]$ (**29**) was prepared according to Scheme 2.2 (p.71). Characterisation by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy confirmed a rhodium(I) norbornadiene complex, with a signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 36.80 [d, $J(\text{RhP}) = 154$]. The solid state structure demonstrates a pseudo-square-planar coordination of the ligands about the rhodium centre with unremarkable bond lengths and angles (Figure 3.9). The ligand has also been displayed as a space-filling diagram overlaid on a ball-and-

stick diagram of the crystal structures of $[\text{Rh}(\kappa^2_{\text{PP}}\text{-dpp2-Mes})(\text{NBD})]^+$, and it can clearly be seen how much more crowded the coordination sphere of the metal is by this bulky ligand, in comparison to the structures shown in Figure 3.3 (p.132).

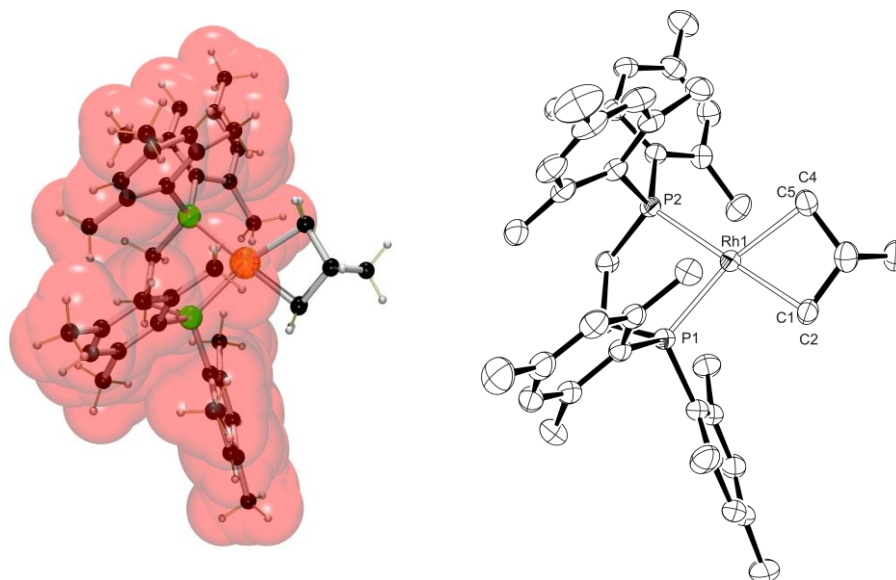
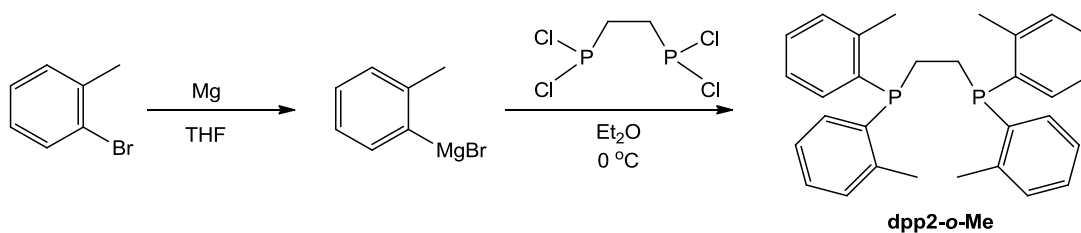


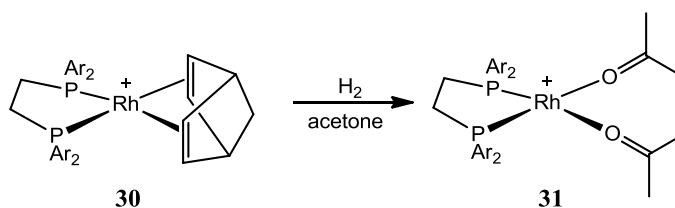
Figure 3.9: (left) Ligand space-filling diagram of **29**. (right) Molecular structure of the cationic portion of $[\text{Rh}(\kappa^2_{\text{PP}}\text{-dpp2-Mes})(\text{NBD})][\text{BARF}_4]$ (**29**). Displacement ellipsoids are drawn at the 50% probability level. The anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] Rh1-P1, 2.2898(7); Rh1-P2, 2.3617(7); Rh1-C1, 2.181(3); Rh1-C2, 2.158(3); Rh1-C4, 2.259(3); Rh1-C5, 2.256(3); C1-C2, 1.389(4); C4-C5, 1.362(4). Selected bond angles [°]: P1-Rh1-P2, 84.68(3).

To activate the precursor, a solution of **29** in d_6 -acetone was placed under 4 atmospheres of hydrogen. Despite stirring under hydrogen for several days, no change was observed by NMR spectroscopy: the norbornadiene ligand remains resolutely bound to the metal centre. One explanation for this could be that the coordination sphere about the metal is too crowded to allow for the access of hydrogen. Therefore a similar ligand to dpp2-Mes, with less steric bulk (dpp2-*o*-Me) was synthesised according to the method outlined in Scheme 3.6. This ligand is known, and ^1H , $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy confirmed its formation.⁴⁸



Scheme 3.6: Preparation of dpp2-*o*-Me.

The norbornadiene precursor $[\text{Rh}(\kappa^2(\text{PP})\text{-dpp2-}o\text{-Me})(\text{NBD})][\text{BAR}^{\text{F}}_4]$ (**30**) was synthesised following the method outlined in Scheme 2.2 (p.71). Characterisation by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, elemental analysis and ESI-MS confirms the formulation of a rhodium(I) norbornadiene complex of the correct empirical formula. A signal is observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 54.73 [$J(\text{RhP}) = 160$], and in the ESI-MS at $[\text{M}]^+ m/z = 649.18$ (calc. 649.17).



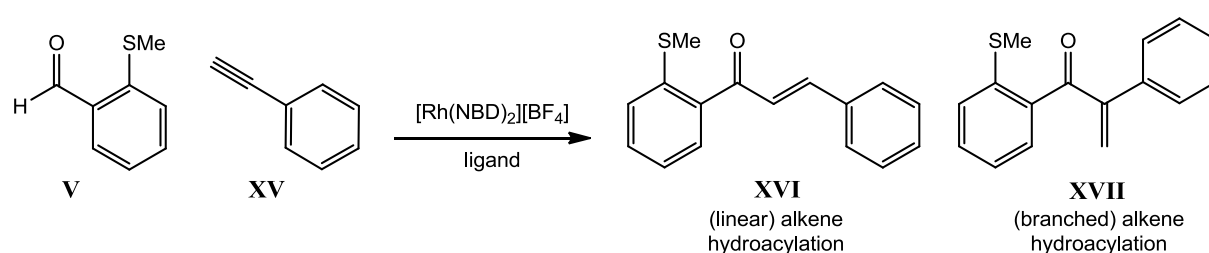
Scheme 3.7: Activation of complex **30** by hydrogenation (Ar = C₆H₄Me).
[BAR^F₄][−] anions not shown.

Activation of the precursor was achieved by hydrogenation (4 atm) of a solution of **30** in acetone to give the bis-acetone complex $[\text{Rh}(\kappa^2(\text{PP})\text{-dpp2-}o\text{-Me})(\text{acetone})_2][\text{BAR}^{\text{F}}_4]$ (**31**) (Scheme 3.7). Complex **31** is characterised by a signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 78.99 [d, $J(\text{RhP}) = 208$], an apparent doublet in the ^1H NMR spectrum at δ 2.64 [$J(\text{PH}) = 17$] due to the ethyl backbone, and a singlet at δ 2.35 due to the *ortho*-CH₃. Signals in the ESI-MS at $[\text{M}-(\text{acetone})_2]^+ m/z = 557.05$ (calc. 557.10) and $[\text{M}-(\text{acetone})]^+ m/z = 615.08$ (calc. 615.14) confirm the empirical formula.

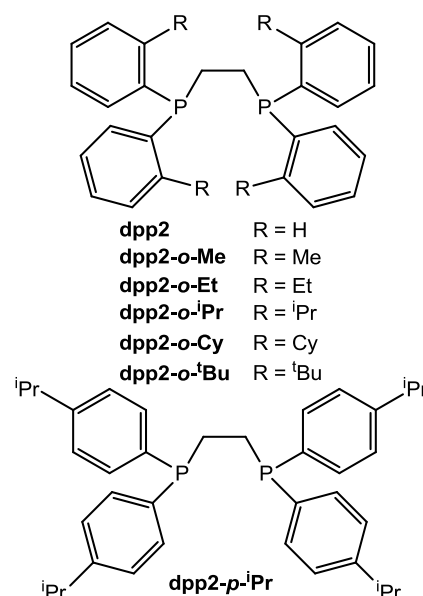
3.6 Branched selectivity of sterically-bulky analogues of dpp2

Further scoping of increasingly bulky *ortho*-substituted analogues of dpp2 was carried out in collaboration with Carlos González-Rodríguez (Willis group), and is presented here to contextualise the decision to investigate bulky *ortho*-substituted ligands (Table 3.4). The catalysts were initially formed *in situ* by addition of the ligand to a solution of $[\text{Rh}(\text{NBD})_2][\text{BF}_4]$ in acetone, and screened for their activity in the hydroacylation of phenyl acetylene (**XV**) by aldehyde **V**.

Table 3.4: Ligand effects on the Rh-catalysed hydroacylation of **V** and **XV**.^a

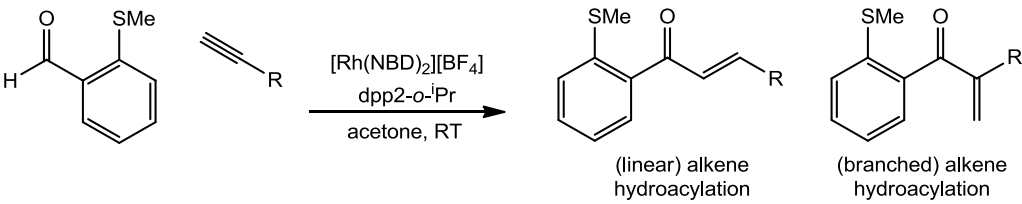


entry	ligand	ratio of linear:branched alkene hydroacylation XVI:XVII	total conversion of aldehyde V (%) ^b
1	dpp2	10:1	100
2	dpp2-<i>o</i>-Me	2.5:1	100
3	dpp2-<i>o</i>-Et	1:1	100
4	dpp2-<i>o</i>-<i>i</i>Pr	1:3	100 ^c
5	dpp2-<i>o</i>-Cy	1:2.5	100
6	dpp2-<i>o</i>-<i>t</i>Bu	3:1	45
7 ^b	dpp2-<i>p</i>-<i>i</i>Pr	7:1	100



^aConditions: aldehyde (0.3 mmol), alkyne (0.45 mmol), $[\text{Rh}(\text{NBD})_2][\text{BF}_4]$ (10 mol%), ligand (10 mol%), acetone (2 mL), 50 °C, 12 h. ^bDetermined by ¹H NMR analysis of the crude reaction mixture. ^c79% yield of isolated product.

As can be seen in Table 3.4, the ligand has a significant effect on the product selectivity. Increasing the steric bulk of the ligand *ortho*-substituent results in an increase in the relative amount of the branched product (**XVII**) from 10:1 linear:branched for the catalyst formed with dpp2 (Table 3.4, entry 1) to 1:3 linear:branched with dpp2-*o*-iPr (Table 3.4, entry 4). A further increase in the steric bulk from dpp2-*o*-iPr to dpp2-*o*-Cy does not result in an increased ratio of branched product (Table 3.4, entry 5), and using the even more bulky dpp2-*o*-tBu ligand resulted in the formation of considerably less active catalyst (Table 3.4, entry 6) suggesting that there is a 'ceiling' to the effect of steric bulk on product selectivity before the bulk begins to affect general catalytic activity. To help establish that the observed effect is due to the steric rather than the electronic properties of the ligand, the *para*-substituted isopropyl ligand (dpp2-*p*-iPr) was synthesised and screened for its catalytic properties with [Rh(NBD)₂][BF₄] (Table 3.4, entry 7). Moving the steric bulk from the *ortho* position to the *para* position resulted in a switch back to linear selectivity, in line with what was observed for the parent dpp2 ligand. Interestingly, the dpp2-*p*-iPr ligand is slightly more branched selective than the dpp2 ligand. Having established that a ligand controlled selectivity switch exists, Carlos González-Rodríguez next explored the generality of the process. Using the dpp2-*o*-iPr ligand under the same conditions as before, the catalyst was screened for the hydroacylation of a range of alkynes with aldehyde **V** (Table 3.5). Catalysis of the butyl- and 3-thienyl- substituted alkynes resulted in a similar product distribution to that seen with phenyl acetylene, with the branched isomer as the major product but with relatively modest selectivities (Table 3.5, entries 1 and 2).

Table 3.5: Scope of the branched-selective hydroacylation reaction of aldehyde **V** and a range of substituted alkynes.^a


entry	R	Yield (%) ^b	ratio of linear:branched alkyne hydroacylation product ^c
1	Bu	81	1:2.5
2	3-thienyl	79	1:2.5
3	4-CF₃-C₆H₄	90	1:8
4	3,5-CF₃-C₆H₃	92	1:>20
5	4-NO₂-C₆H₄	65	1:8
6	4-CO₂Me-C₆H₄	82	1:4
7 ^d	CO₂Me	63	1:>20
8 ^d	CO₂Et	82	1:>20
9 ^d	COPh	53	1:>20
10 ^d	(CF₂)₅CF₃	76	1:11

^aConditions: aldehyde **V** (0.3 mmol), alkyne (0.45 mmol), [Rh(NBD)₂][BF₄] (10 mol%), ligand (dpp2-*o*-iPr) (10 mol%), acetone (2 mL), RT, 2-48 h. ^bYields of isolated products. ^cDetermined by ¹H NMR analysis of the crude reaction mixture. ^dReactions performed at 50 °C.

Catalysis of the electron-deficient aryl-alkynes resulted in significantly greater branched-selectivity (Table 3.5, entries 3-6), while catalysis of non-aromatic alkynes also resulted in high selectivities of the branched product (Table 3.5, entries 7-9). In comparison, the same coupling reactions with the parent ligand, dpp2, resulted in the linear isomers as the major product, but with reduced selectivity (e.g. the combination of aldehyde **V** with the 4-CF₃-C₆H₄ substituted alkyne resulted in 4.5:1 linear:branched, while **V** with the 3,5-(CF₃)₂-C₆H₃ substituted alkyne resulted in 2:1 linear:branched), which suggests that the electronic nature of the substrates employed also has an effect on the product selectivity. However, there is undoubtedly a significant ligand effect on the

product selectivity: the dpp2 and dpp2-*o*-iPr systems result in different product selectivities for the same substrate sets.

Pringle *et al.* noted a steric effect on increasing the bulk of the *ortho*-substituents on ligands of the type $(C_6H_4R)_2PCH_2P(C_6H_4R)_2$ (where R = H, Me, *i*Pr, CF₃), with the bulkiest substituent (CF₃) forming the most active $[NiL_2Cl_2]$ catalyst for the branched polymerisation of ethylene.⁴⁹⁻⁵¹ Interestingly, in that system, the dpp2 and dpp3 analogues $[(C_6H_4R)_2P(CH_2)_nP(C_6H_4R)_2]$ (where R = H, Me, *i*Pr; n = 2, 3) were found to be inactive. To probe the factors behind the switch in selectivity in this system, stoichiometric reactions were carried out, and the structures of the active catalysts formed with dpp2 and dpp2-*o*-iPr were studied.

3.7 Mechanistic studies of complexes incorporating dpp2 and dpp2-*o*-iPr

The rhodium(I) norbornadiene precursor complex $[Rh(\kappa^2_{(PP)}\text{-dpp2-}o\text{-iPr})(NBD)][BAR^F_4]$ (**32**) was prepared according to the method outlined in Scheme 2.2 (p.71). Characterisation by NMR spectroscopy, X-ray crystallography and ESI-MS confirmed the structure of a rhodium(I) pseudo-square-planar complex. One species is observed in the $^{31}P\{^1H\}$ NMR spectrum at δ 50.92 [$J(RhP) = 157$] indicating a rhodium(I) oxidation state c.f. complex **23** δ 55.9 [d, $J(RhP) = 157$]. Three proton environments are observed for the ligand *i*Pr groups in the ^1H NMR spectrum, with 4:12:12H integral ratios at δ 3.09, 1.14 and 1.05, which show septet multiplicity [in the case of the $CH(CH_3)_2$ protons] and doublet multiplicity [in the case of the protons of the diastereotopic methyl groups, $CH(CH_3)_2$]

respectively. The spectroscopic data is otherwise unremarkable from that of complex **23**. ESI-MS confirms the empirical formula with a signal at $m/z = 761.29$ (calc. 761.29). Crystals suitable for X-ray diffraction were obtained by diffusion of pentane into a solution of **32** in CH_2Cl_2 at 4 °C (Figure 3.10). The solid-state structure of **32** is similar to the solid-state structures of **23**¹⁶ and **29**, and is consistent with the solution NMR data. The P1-Rh-P2 bond angle of 84.15(3)° falls within the range of these two structures [83.90(4)-84.68(3)°]. The H of the *i*Pr groups lies within the plane of the phenyl rings, eclipsing the P-C bond, as has been observed in all solid-state structures bearing this *ortho*-*i*Pr substituent.⁴⁹⁻⁵²

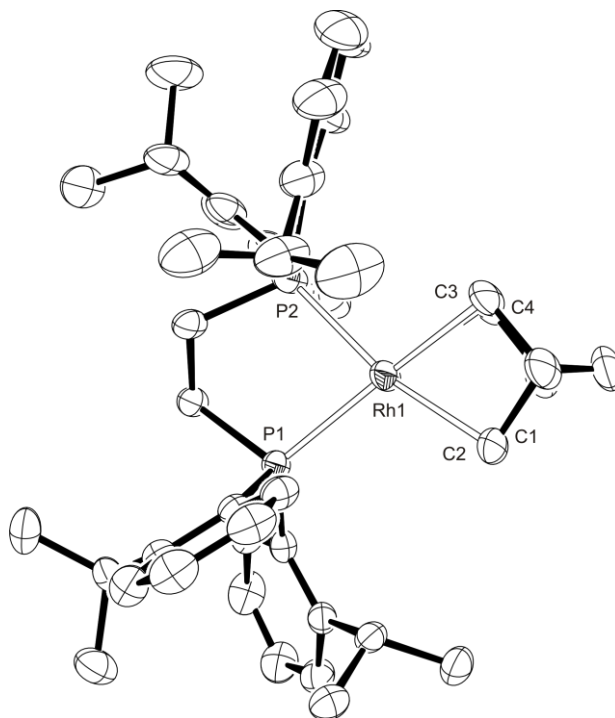
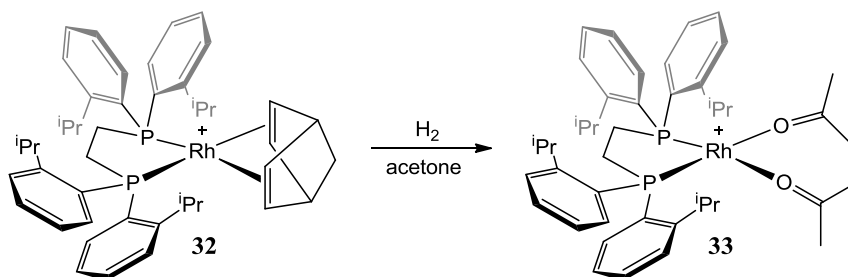


Figure 3.10: Molecular structure of the cationic portion of $[\text{Rh}(\kappa^2_{\text{PP}}\text{-dpp2-}o\text{-iPr})(\text{NBD})][\text{BAR}^{\text{F}}_4]$ (**32**). Displacement ellipsoids are drawn at the 50% probability level. The anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] Rh1-P1, 2.3401(8); Rh1-P2, 2.2757(9); Rh1-C1 2.235(3); Rh1-C2 2.219(4); Rh1-C3 2.192(4); Rh1-C4 2.177(4); C1-C2, 1.355(6); C3-C4, 1.372(7). Selected bond angles [°]: P1-Rh1-P2, 84.15(3).

The active precatalyst complex $[\text{Rh}(\kappa^2_{\text{PP}}\text{-dpp2-}o\text{-iPr})(\text{acetone})_2][\text{BAR}^{\text{F}}_4]$ (**33**) was accessed by addition of hydrogen (4 atm) to a solution of **32** in acetone (Scheme

3.8). Characterisation by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy indicates a rhodium(I) oxidation state with a signal at δ 79.24 [$J(\text{RhP}) = 205$]. The ligand methylene backbone signal in the ^1H NMR spectrum is an apparent doublet of doublets at δ 2.63 [$J(\text{PH}) = 17$, $J(\text{HH}) = 1.0$], and the isopropyl groups are observed as three signals in a 4:12:12H integral ratio at δ 3.70, 1.18 and 1.12, showing septet and doublet multiplicity for the $\text{CH}(\text{CH}_3)_2$ and $\text{CH}(\text{CH}_3)_2$ protons respectively.



Scheme 3.8: Formation of complex **33**. $[\text{BAr}^{\text{F}}_4]^-$ anions not shown.

ESI-MS of **33** in acetone gives rise to a signal for the parent cation, as well as signals which indicate loss of one or both acetone ligands, at $[\text{M}]^+ m/z = 785.32$ (calc. 785.31); $[\text{M-acetone}]^+ m/z = 727.28$ (calc. 727.27) and $[\text{M-(acetone)}_2]^+ m/z = 669.23$ (calc. 669.23). Crystals suitable for X-ray diffraction were obtained by diffusion of pentane into a solution of complex **33** in acetone at 4 $^\circ\text{C}$ (Figure 3.11). The solid-state structure confirms a pseudo-square-planar rhodium centre coordinated with two acetone ligands, similar to that seen with $[\text{Rh}(\kappa^2_{\text{PP}}\text{-DPEphos})(\text{acetone})_2][\text{BAr}^{\text{F}}_4]$ (**i-99**).² The phenyl groups are orientated such that the bulky isopropyl groups point away from the metal centre while also minimising steric interactions with each other, with what appears to be C_2 symmetry about an axis in the P1-P2-Rh1-O1-O2 plane. The ability of the ligand to adopt a variety of conformations can be measured by the wide range of dihedral angles of the arenes with respect to the Rh-P bond, for example, Rh1-P2-C36-C37,

-1.8(3)°; Rh1-P1-C18-C19, 92.9(3)° (phenyl rings for which the dihedral angle has been calculated are highlighted in red in Figure 3.11).

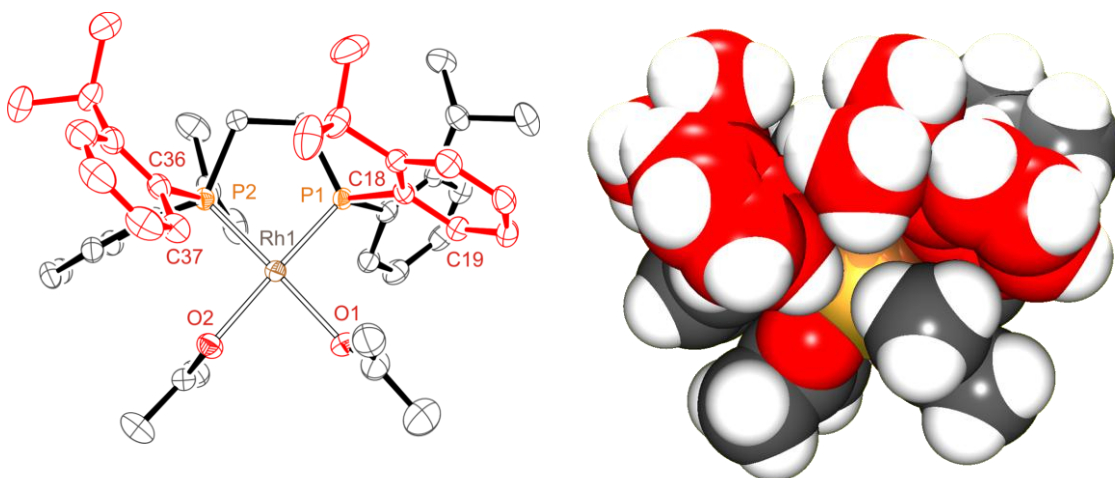
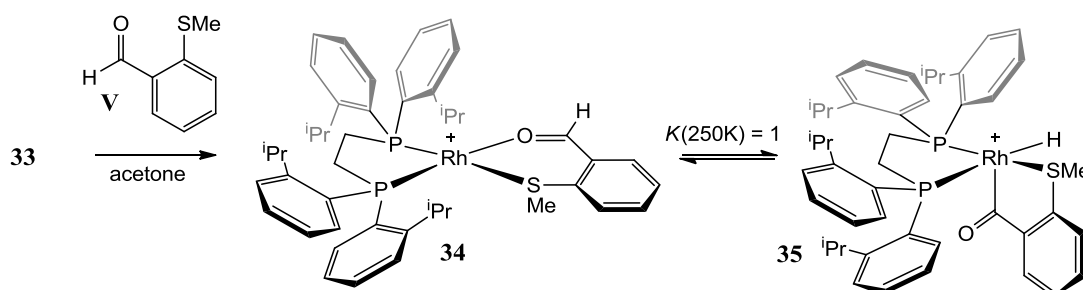


Figure 3.11: Molecular structure of the cationic portion of $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-dpp2-}o\text{-iPr})(\text{acetone})_2][\text{BARF}_4]$ (**33**). Displacement ellipsoids are drawn at the 50% probability level (left) and van der Waals radii (right). The anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Rh1-P1, 2.1749(9); Rh1-P2, 2.1778(9); Rh1-O1, 2.154(3); Rh1-O2, 2.173(2). Selected bond angles [°]: P1-Rh1-P2, 87.34(3); (dihedral) Rh1-P2-C36-C37, -1.8(3); Rh1-P1-C18-C19, 92.9(3).

Addition of ~1 equivalent of aldehyde **V** to complex **33** results in an equilibrium mixture of the substrate bound rhodium(I) complex $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-dpp2-}o\text{-iPr})\{\kappa^2_{(\text{OS})}\text{-(OHC)C}_6\text{H}_4\text{SCH}_3\}][\text{BARF}_4]$ (**34**) and the C-H activated rhodium(III) complex $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-dpp2-}o\text{-iPr})(\text{H})(\kappa^1_{(\text{S})}\text{-}\sigma^1_{(\text{C})}\text{-COC}_6\text{H}_4\text{SCH}_3)][\text{BARF}_4]$ (**35**) (Scheme 3.9). Complexes **34** and **35** are in exchange with each other in solution at room temperature, as shown by the broad signals in both the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. However, progressive cooling to 200 K resolves separate sharp signals in the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. The ratio of **34**:**35** is 3:1 at 200 K, which changes to 1:1 at 250 K, confirming an equilibrium process. The formation of the acetone complex (**33**) in equilibrium with **34** and **35** cannot be discounted. However, it must be low relative concentration, and is not observed. ESI-MS of the mixture in

acetone gives rise to two signals at $[M]^+$ $m/z = 821.30$ (calc. 821.26) and $[M-HCO_6H_4SCH_3]^+$ $m/z = 669.26$ (calc. 669.23), which cannot be assigned specifically to either complex as both have the same empirical formula.



Scheme 3.9: Addition of 1 equivalent of aldehyde **V** to complex **33**. $[\text{BAR}^{\text{F}_4}]^-$ anions not shown.

Complex **34** is formed as an interconverting mixture of two substrate-bound isomers: **34** and **34'**, which are trapped out at 200 K in the ratio 1:0.37 as identified by broad doublet signals at δ 10.25 and 10.18 in the ^1H NMR spectrum for the bound aldehyde, both of which show $J(\text{RhH})$ coupling of 6.1 Hz. These signals are both shifted to higher frequency than the singlet signal observed at δ 10.10 for free aldehyde. These isomers may be due to restricted rotation of the bulky arene groups and/or restricted inversion at the SMe at low temperature, so that only one isomer of **34** is observed in the room temperature ^1H NMR spectrum, at δ 10.20. Inequivalent phosphine environments which show coupling to a rhodium(I) centre are observed in the 200 K $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 78.90 [dd, $J(\text{RhP}) = 189$, $J(\text{PP}) = 32$] and 44.96 [br d, $J(\text{RhP}) = 172$] for complex **34**, and δ 84.36 [dd, $J(\text{RhP}) = 187$, $J(\text{PP}) = 20$] and 55.98 [dd, $J(\text{RhP}) = 168$, $J(\text{PP}) = 20$] for complex **34'**. Separate correlations are observed between these signals and either the aldehyde or SMe resonances in a ^{31}P - ^1H HMBC experiment (Figure 3.12).

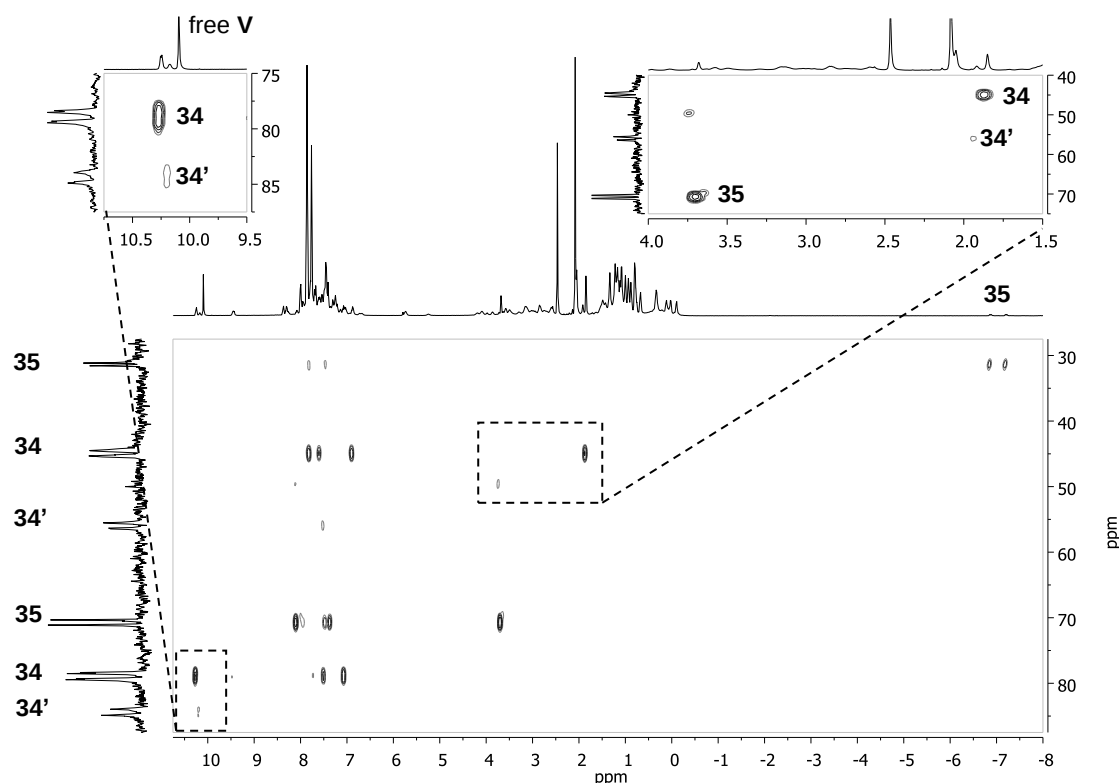
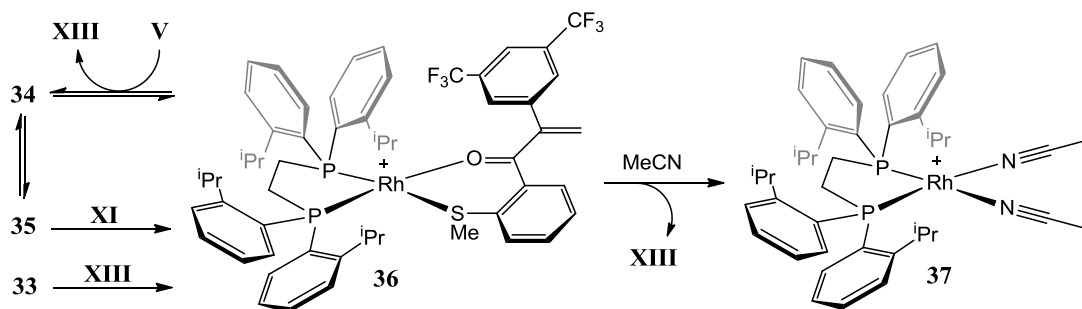


Figure 3.12: 200 K ^{31}P - ^1H HMBC spectrum of complexes **34**, **34'** and **35** showing correlations between phosphines and aldehyde/hydride or SME resonances.

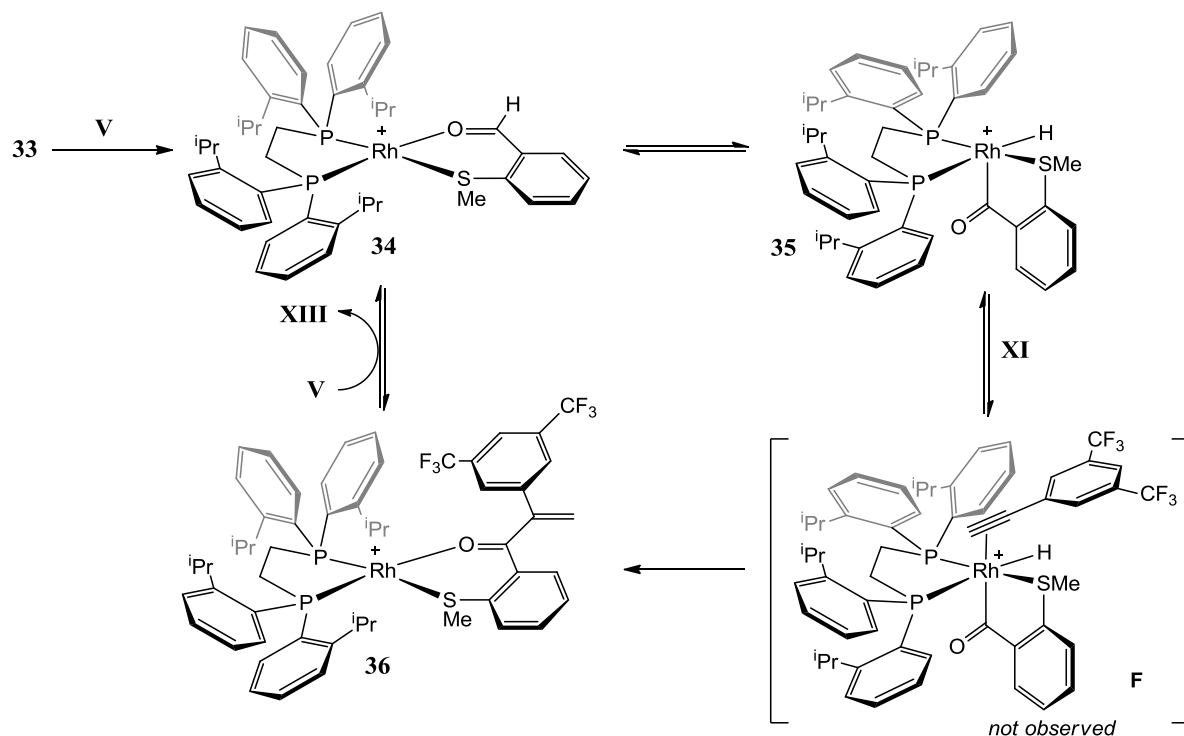
The rhodium(III) product of oxidative-addition, complex **35**, is characterised at 200 K by a signal in the hydride region of the ^1H NMR spectrum at δ -7.04 [dd, $J(\text{PH}) = 169$, $J(\text{RhH}) = 16$] which shows *trans* coupling to a phosphine; a broad singlet at δ 3.68 assigned as the SME environment which shows a strong correlation in the ^{31}P - ^1H HMBC spectrum; and inequivalent phosphine environments in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 70.72 [d, $J(\text{RhP}) = 160$] and 31.37 [d, $J(\text{RhP}) = 87$]. The reduced ^{103}Rh - ^{31}P coupling constant (87 Hz) is consistent with a phosphine which is opposite a high *trans* influence ligand such as a hydride.⁵³ This places the acyl group *trans* to a vacant site, or weakly bound acetone ligand. Similar structures have been reported with the DPEphos ligand,³ and calculated for the intramolecular hydroacylation of 4-pentenals.¹⁹



Scheme 3.10: Formation of complex **36** from addition of 1 equivalent of alkyne **XI** to **34/35**, or addition of branched product **XIII** to complex **33**. Liberation of product **XIII** from complex **36** by addition of MeCN. $[\text{Bar}^{\text{F}_4}]^-$ anions not shown.

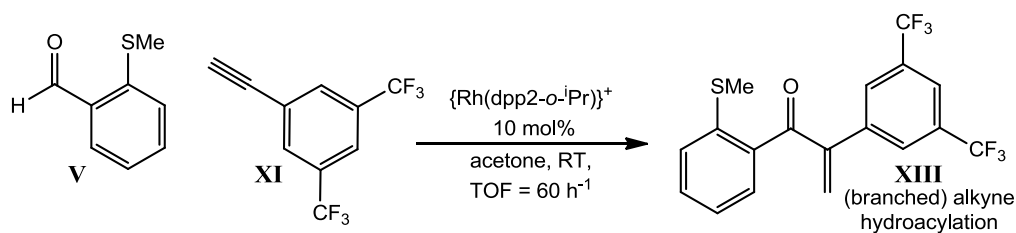
Addition of ~1 equivalent of alkyne **XI** to the mixture of **34** and **35** formed *in situ*, leads to the formation of a new complex, spectroscopically characterised as the coordinated branched product of hydroacylation $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-dpp2-}o\text{-iPr})(\text{H}) \{ \kappa^2_{(\text{OS})}\text{-SCH}_3\text{C}_6\text{H}_4\text{C}(\text{O})\text{C}(\text{=CH}_2)\text{C}_6\text{H}_3(\text{CF}_3)_2 \}][\text{Bar}^{\text{F}_4}]$ (**36**) (Scheme 3.10). This turnover to give only the branched product provides further evidence for an equilibrium between complexes **34** and **35**, while also confirming their role within the catalytic cycle. Complex **36** was characterised by two integral ^1H singlet signals at δ 6.86 and 6.24 in the ^1H NMR spectrum, which are assigned as the vinylic protons, and an integral 3H signal at δ 2.26 for the SMe group. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is broad with two signals observed, one of which shows doublet of doublet multiplicity, indicating inequivalent phosphine environments and a rhodium(I) oxidation state, δ 81.01 [br dd, $J(\text{RhP}) = 198$, $J(\text{PP}) = 32$] and 51.63 (br s). ESI-MS of **36** gives rise to a signal at $[\text{M}]^+ m/z = 1059.30$ (calc. 1059.28) the same species is also accessed by addition of isolated branched product (**XIII**) to the bis-acetone complex **33** (Scheme 3.10). Addition of MeCN to complex **36** liberates branched product **XIII** alongside the formation of a species characterised as $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-dpp2-}o\text{-iPr})(\text{MeCN})_2][\text{Bar}^{\text{F}_4}]$ (**37**), which resembles the spectroscopic data observed for

33 (see experimental chapter for details). Addition of a further equivalent of aldehyde **V** to complex **36** generates a mixture of complexes **34**, **35** and **36** alongside free branched product **XIII**, demonstrating turnover.



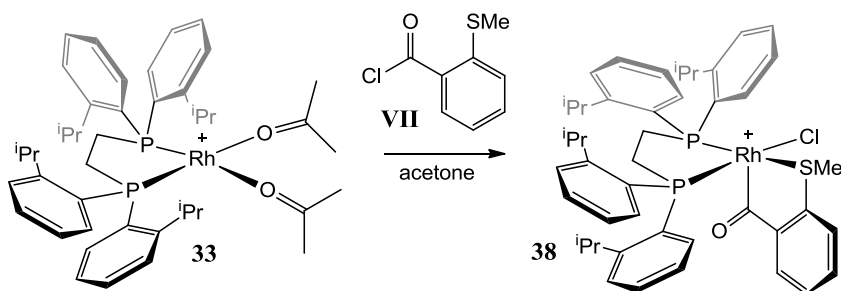
Scheme 3.11: Proposed catalytic cycle for the branched intermolecular hydroacylation of **V** and **XI** by $\{Rh(dpp2-o-iPr)\}^+$. $[BAr^F_4]^-$ anions not shown.

The hydroacylation reaction of **XI** and **V** catalysed by **33** was repeated under standard conditions, i.e. 10 mol% catalyst, room temperature, 0.43 M solution of precatalyst (**33**) in d_6 -acetone, aldehyde:alkyne ratio = 1:1 (Scheme 3.12). This resulted in complete consumption of the substrates to give 100% conversion of aldehyde **V** to branched hydroacylation product **XIII**. Catalysis was too rapid (TOF 60 h^{-1}) to be followed by ^1H NMR spectroscopy. However, at the end of catalysis complex **36** is observed. Addition of a further 10 equivalents each of aldehyde **V** and alkyne **XI** restarted catalysis. A suggested mechanism for catalysis is shown in Scheme 3.11.



Scheme 3.12: Intermolecular branched-selective alkyne hydroacylation of **V** and **XI** by $\{\text{Rh}(\text{dpp2-}o\text{-iPr})\}^+$.

Crystalline material of the mixture of complexes **34** and **35** was not obtained, so to probe the solid-state structure of these intermediates the acyl-chloride analogue of aldehyde **V**, $\text{ClCOC}_6\text{H}_4\text{SMe}$ (**VII**), was used. Cl^- is capable of stabilising a low coordinate complex through $p_\pi\text{-}d_\pi$ interactions; moreover, chlorides do not undergo migratory insertion, effectively trapping out the analogue of the metal-acyl-hydride intermediate. Acyl-iodides have been used in a similar manner to isolate $[\text{Rh}(\text{dppn})(\text{I})_2\text{COMe}]$ ($n = 2,^{21} 4^{22}$, Figure 3.4, p. 135). Addition of 1 equivalent of **VII** to **33** yields the product of oxidative addition as a single isomer: $[\text{Rh}(\kappa^2(\text{PP})\text{-dpp2-}o\text{-iPr})(\text{Cl})(\kappa^1(\text{S})\text{-}\sigma^1(\text{C})\text{-COC}_6\text{H}_4\text{SCH}_3)][\text{BAR}^{\text{F}_4}]$ (**38**) (Scheme 3.13).



Scheme 3.13: Formation of acyl-chloride complex **38**. $[\text{BAR}^{\text{F}_4}]^-$ anions not shown.

The room temperature ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complex **38** are both broad, however, cooling a solution of the complex in d_6 -acetone to 200 K results in greater resolution of the signals. Each of the aryl isopropyl groups displays separate resonances for each CH proton and CH_3 group, giving rise to 12 signals

for the 28 protons, alongside separate resonances for each of the four ligand P-CH₂ backbone protons, indicating a structure with low symmetry. In combination with a ¹H-¹H COSY NMR spectrum it is possible to assign these resonances in the 200 K ¹H NMR (see experimental chapter for details). The SMe group is observed at a similar chemical shift to that observed for the acyl-hydride complex **35**, at δ 3.32 (c.f. 3.68 ppm for **35**). The 200 K ³¹P{¹H} NMR spectrum of **38** shows two signals at δ 62.03 [d, $J(\text{RhP}) = 127$] and 59.89 [d, $J(\text{RhP}) = 149$]. The second signal has been assigned as *trans* to the SMe group on the basis of a selective ¹H{³¹P} NMR experiment. Acyl ligands are high *trans* influence groups and would be expected to have an effect on the ¹⁰³Rh-³¹P coupling constant,^{3, 54, 55} on the basis of which the first signal has been tentatively assigned as *trans* to the chloride group, as seen in the analogous acyl-hydride complex **35**. ESI-MS of **38** gives rise to a signal at [M]⁺ $m/z = 855.25$ (calc. 855.22) which shows the distinctive chloride isotope pattern.

Changing from the [BAr^F₄]⁻ anion to the [BAr^{Cl}₄]⁻ anion (Ar^{Cl} = 3,5-Cl₂C₆H₃)⁵⁶ allowed the isolation of crystalline material suitable for X-ray diffraction (Figure 3.13). The solid-state structure of **38** shows a 5-coordinate rhodium(III) pseudo-square based pyramidal structure, with the acyl group *trans* to a vacant site, and the SMe and chloride *trans* to the phosphine groups. This arrangement of ligands matches the structure of the hydride complex **35** as inferred from the low temperature solution spectroscopic data. Comparing this structure to the precursor complex **33**, suggests underlying reasons for the linear/branched selectivity switch observed in the catalytic process. The oxidative addition of an acyl-chloride results in a structure in which the phenyl groups adopt a more

restricted and directional conformation than is observed in the bis-acetone precursor **33** (Figure 3.11). The arenes are all rotated so that the isopropyl groups are directed away from the metal centre, potentially acting as steric ‘anchors’, so that the arene groups point directly into the vacant site on the metal centre, as shown by the dihedral angles: Rh1-P1-C20-C21, $-5.1(5)^\circ$ and Rh1-P2-C38-C39, $14.6(5)^\circ$.

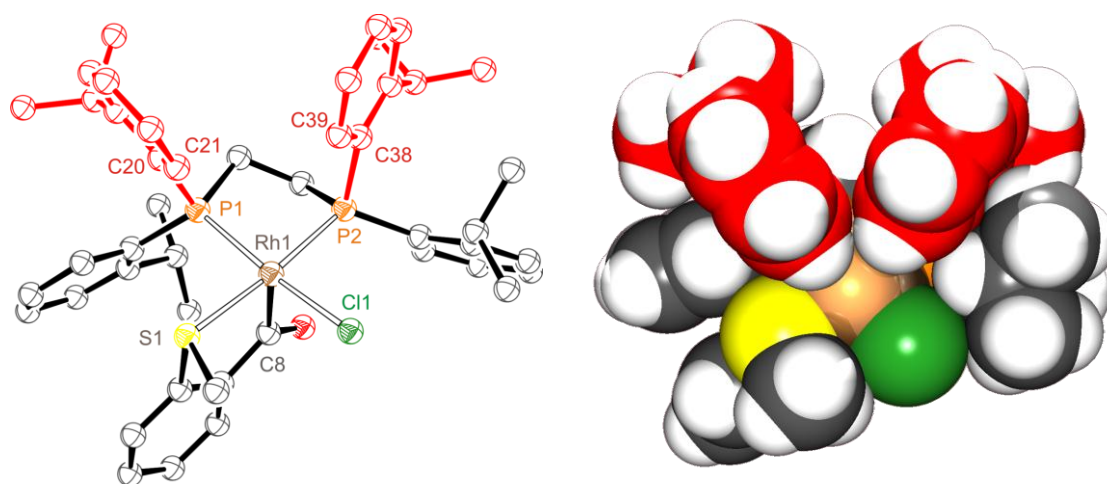
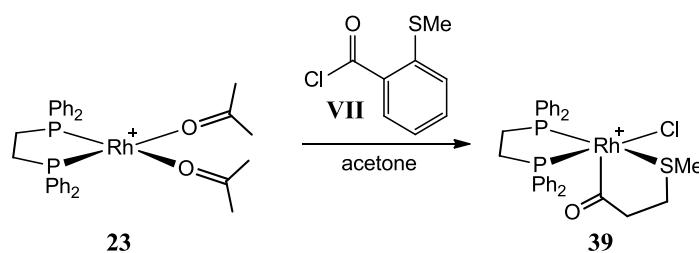


Figure 3.13: Molecular structure of the cationic portion of $[\text{Rh}(\kappa^2_{\text{(pp)}}\text{-dpp2-}o\text{-iPr})(\text{Cl})(\kappa^1_{\text{(S)}}\text{-}\sigma^1_{\text{(C)}}\text{-COC}_6\text{H}_4\text{SCH}_3)][\text{BAR}^{\text{Cl}_4}]$ (**38**). Displacement ellipsoids are drawn at the 50% probability level (left) and van der Waals radii (right). The anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Rh1-P1, 2.300(1); Rh1-P2, 2.335(1); Rh1-Cl1, 2.341(1); Rh1-S1, 2.395(1); Rh1-C8. Selected bond angles [°]: P1-Rh1-P2, 85.52(5); (dihedral) Rh1-P1-C20-C21, $-5.1(5)$; Rh1-P2-C38-C39, $14.6(5)$.

Direct structural comparison between **38** and the dpp2 analogue (**39**) would help emphasise this idea of conformational restriction, as a more flexible orientation of the phenyl groups would correlate with the lower selectivity for the branched product, observed with dpp2. Addition of 1 equivalent of acyl-chloride **VII** to the $[\text{BAR}^{\text{Cl}_4}]^-$ salt of the bis-acetone dpp2 complex (**23**) yields the product of oxidative addition: $[\text{Rh}(\kappa^2_{\text{(pp)}}\text{-dpp2})(\text{Cl})(\kappa^1_{\text{(S)}}\text{-}\sigma^1_{\text{(C)}}\text{-COC}_6\text{H}_4\text{SCH}_3)][\text{BAR}^{\text{Cl}_4}]$ (**39**) as a single isomer (Scheme 3.14).



Scheme 3.14: Formation of acyl-chloride complex **39**. $[\text{BAR}^{\text{Cl}_4}]^-$ anions not shown.

The ^1H NMR spectrum of **39** is similar to the low temperature spectrum of **38**, with a signal observed at δ 3.35 assigned to the SMe group, and the ligand backbone protons are observed as multiplet signals at δ 3.94-3.40 (integral 3H) and 3.18 (integral 1H). Two broad doublet of doublets are observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, at δ 61.26 [$J(\text{RhP}) = 143$, $J(\text{PP}) = 7.3$] and 54.21 [$J(\text{RhP}) = 135$, $J(\text{PP}) = 8.1$]; the first of which has been assigned as *trans* to the SMe group on the basis of a selective $^1\text{H}\{^{31}\text{P}\}$ NMR experiment, and the second signal has been tentatively assigned as *trans* to the chloride, as the high *trans* influence acyl group would be expected to have an effect on the ^{103}Rh - ^{31}P coupling constant. ESI-MS of complex **39** confirms the empirical formula with a signal at $[\text{M}]^+ m/z = 687.05$ (calc. 687.03) which shows the correct isotope pattern. Unfortunately crystals suitable for X-ray diffraction were not obtained. However, a ^1H - $^{13}\text{C}\{^1\text{H}\}$ HSQC experiment shows only sixteen $^1J(\text{CH})$ environments for the ligand and acyl aryl-protons, indicating free rotation of the ligand phenyl groups at 295 K (Figure 3.14). This free rotation of the ligand aryl groups would not be expected to occur for dpp2-*o*- ^iPr ,⁴⁹ and – due to the non-symmetrical nature of the ligand aryl groups – cannot be assessed by a similar ^1H - $^{13}\text{C}\{^1\text{H}\}$ HSQC experiment, as the aryl protons would always be inequivalent.

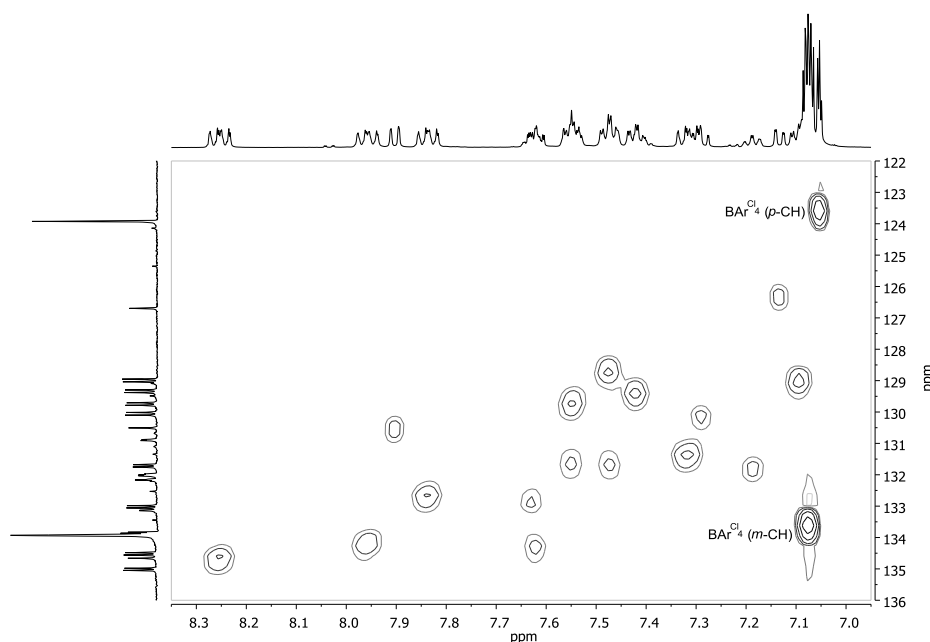
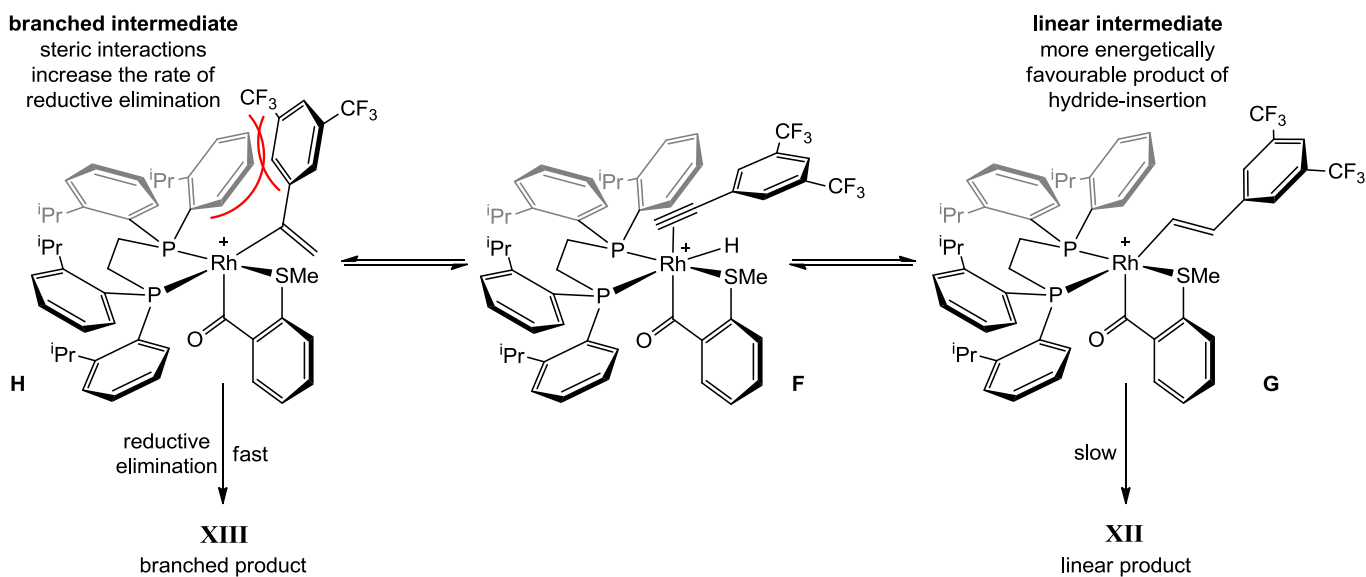


Figure 3.14: ^1H - $^{13}\text{C}\{^1\text{H}\}$ HSQC NMR spectrum of complex **39**, showing sixteen $^1\text{J}(\text{CH})$ ligand and acyl Ar-H environments.

Restricted rotation has been noted in complexes with chelate ligands closely related to dpp2-*o*-iPr;⁴⁹ while – returning to the complex $[\text{Rh}(\text{dpp2})(\text{I})_2(\text{COMe})]^{21}$ (Figure 3.4, left image) – close inspection of this related structure shows significantly rotated phenyl groups (with dihedral angles of -70.8° and -24.7°) compared to complex **38**, which suggests a less rigid conformation of the phenyl groups in the dpp2 complex. Overall these observations support the idea that the orientation of the aryl groups in complex **35**, and the increased product selectivity, is as a result of minimising the steric strain between the bulky isopropyl groups and the C-H activated aldehyde at the metal centre.



Scheme 3.15: Hypothetical hydride-inserted branched alkenyl (**G**) and linear alkenyl (**H**) intermediate species before reductive elimination has taken place. $[\text{BAr}^{\text{F}}_4]^-$ anions not shown.

The stereochemistry of the product is selected at the hydride insertion step, which ought to favour linear product selectivity, as the bulkier branched alkenyl intermediate (**H**, Scheme 3.15) would be expected to be a higher energy complex than the linear alkenyl intermediate (**G**).^{18, 19, 57-59} Therefore, the branched product selectivity displayed by the bulky dpp2-*o*-iPr ligand suggests that the final regiochemistry of the product is not determined by the hydride insertion step, perhaps due to forming *via* a lower energy transition state than the linear transition state (as observed by Goldman in the dimerization of alkynes, Figure 1.18, p.41).³⁸ The rate of irreversible reductive-elimination of the product would, however, be expected to be increased from the bulkier branched alkenyl intermediate (**H**) than the linear alkenyl intermediate (**G**), provided the transition state is accessible.^{18, 38} If hydride insertion is reversible, then the final regiochemistry of the product will be dictated by the alkenyl intermediate which undergoes the fastest reductive elimination, favouring the branched product in the

dpp2-*o*-ⁱPr system. That is, reductive elimination is usually increased in sterically hindered intermediates. Therefore, if the rate of reductive-elimination (favouring the branched product) is turnover limiting (as is usually the case),^{37, 38} then a bulkier ligand will control the final regiochemistry of the product by having a greater impact on the rate of reductive elimination from the branched alkenyl intermediate (**H**), than the linear alkenyl intermediate (**G**).

Reversible hydride insertion into alkynes is rare, but has been reported on iridium(III) PCP centres **i-44** (outlined in the introduction).³⁸ Faster reductive elimination of branched isomers, and equilibria between branched and linear intermediates, has also been reported for the [Cp*Rh(H₂C=CHSiMe₃)₂] catalytic alkene hydroacylation system, (Cp* = η⁵-C₅Me₅).⁵⁸ The {Rh(PCP)}⁺ system (PCP = PtBu₂CH₂PtBu₂) (**i-77**) used in the catalytic alkyne hydroacylation by Weller *et al.* has demonstrated reversible hydride insertion in deuterium experiments, although this system is linear selective.⁵⁴ The experimental observation that electron poor alkynes give the best branched selectivity could be related to an enhanced rate of reductive elimination which is associated with these alkynes.⁵⁸

For less bulky ligands, the effect of the ligand bulk on the rate of reductive elimination would be less marked, allowing the rate of reductive elimination from the linear alkenyl intermediate to become competitive. This can be seen in the progressive decrease in selectivity of the ligands for the branched product, as the bulk of the *ortho*-substituent decreases from ⁱPr>Et>Me>H (Table 3.4). Another

speculative explanation for the difference in rates of reductive elimination is that the alkenyl and acyl groups require a “side-on” orientation to undergo reductive elimination. If these groups are not in the correct relative orientation in the linear intermediate, this will result in a slow rate of reductive elimination, whereas a correct orientation of the alkenyl and acyl groups will result in rapid reductive elimination. Such a scenario, outlined by Goldman and Krogh-Jespersen,³⁷ could be taking place here, but computational studies would be necessary to support this.

3.8 Conclusion

The diphosphine ligands dpp2-5 were complexed to rhodium and studied as hydroacylation catalysts for the combination of aldehyde **I** with alkene **II**, and aldehyde **V** and alkene **II**. With the alkyl aldehyde (**II**) a trend in selectivity was observed, with the small bite angle ligand (dpp2) favouring alkene hydroacylation, and the large bite angle ligand (dpp5) favouring aldehyde hydroacylation. This was attributed to the steric effects of the diphosphine ligands. For the aromatic aldehyde (**V**) all ligands were selective for alkene hydroacylation, although the smaller bite angle ligands displayed less stereoisomeric selectivity, catalysing both the linear and branched reactions. The dpp5 ligand formed interesting rhodium complexes in which the C-H bond of the central atom of the ligand backbone had been activated (in **24b**) or formed an agostic interaction (in **28**). This may be due to the backbone containing the correct number of atoms to form two favourable 5 membered metallacycles.

Branched product selectivity was further explored with the bulky *ortho*-substituted dpp2-*o*-*i*Pr ligand, and the substrates aldehyde **V** and alkyne **XI**. The selectivity of the dpp2-*o*-*i*Pr system was attributed to the effect of the steric bulk, which appears to increase the rate of reductive elimination from the branched alkenyl intermediate. The catalytic metal-acyl-hydride intermediate, complex **24**, was isolated, as well as the analogous acyl-chloride complexes **33** and **39**. As a further note, Willis has recently developed a {Rh(dcpe)}⁺ catalytic system which is capable of excellent linear selectivity for the combination of aldehyde **V** and alkyne **XI**.⁶⁰ Therefore, one set of substrates can be combined to give either the linear or branched product by careful use of an appropriate catalyst. Currently only Dong has also demonstrated this ability to selectively form linear or branched products, and only for a single substrate set, by use of two different catalysts (Scheme 1.42, p.58).⁶¹

3.9 References

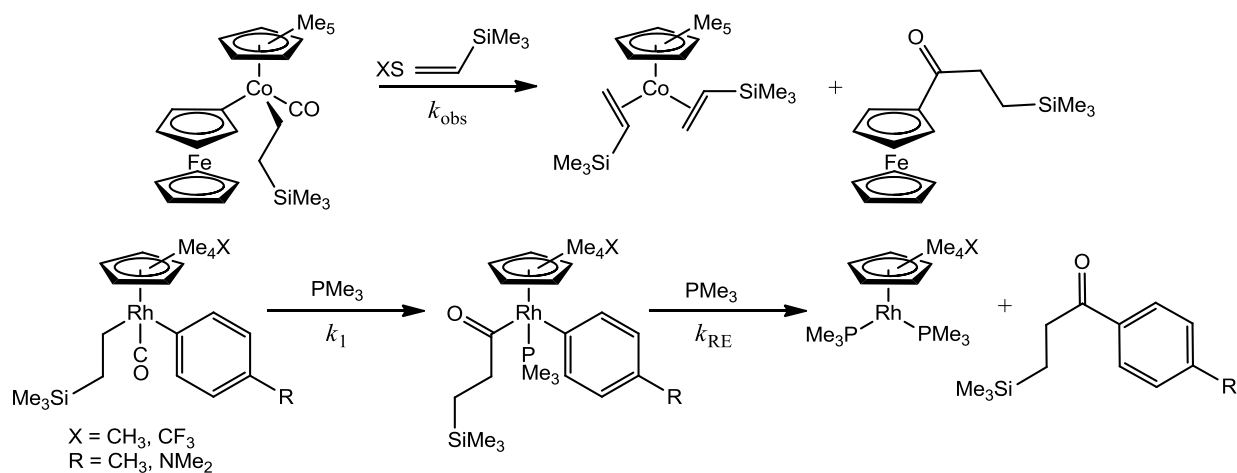
1. M. C. Willis, S. J. McNally and P. J. Beswick, *Angewandte Chemie International Edition*, 2004, **43**, 340-343.
2. G. L. Moxham, H. Randell-Sly, E. , S. Brayshaw, K., R. L. Woodward, A. S. Weller and M. Willis, C., *Angewandte Chemie International Edition*, 2006, **45**, 7618-7622.
3. G. L. Moxham, H. Randell-Sly, S. K. Brayshaw, A. S. Weller and M. C. Willis, *Chemistry - A European Journal*, 2008, **14**, 8383-8397.
4. Z. Shen, P. K. Dornan, H. A. Khan, T. K. Woo and V. M. Dong, *Journal of the American Chemical Society*, 2009, **131**, 1077-1091.
5. K. Tanaka, Y. Shibata, T. Suda, Y. Hagiwara and M. Hirano, *Organic Letters*, 2007, **9**, 1215-1218.
6. K. Tanaka and G. C. Fu, *Journal of the American Chemical Society*, 2001, **123**, 11492-11493.
7. J. M. Brown, P. A. Chaloner, A. G. Kent, B. A. Murrer, P. N. Nicholson, D. Parker and P. J. Sidebottom, *Journal of Organometallic Chemistry*, 1981, **216**, 263-276.
8. S. H. Bergens, D. P. Fairlie and B. Bosnich, *Organometallics*, 2002, **9**, 566-571.
9. D. L. DuBois, D. M. Blake, A. Miedaner, C. J. Curtis, M. R. DuBois, J. A. Franz and J. C. Linehan, *Organometallics*, 2006, **25**, 4414-4419.
10. B. R. James and D. Mahajan, *Canadian Journal of Chemistry*, 1980, **58**, 996-1004.
11. D. P. Fairlie and B. Bosnich, *Organometallics*, 1988, **7**, 946-954.
12. P. D. Achord, P. Kiprof and B. Barker, *Journal of Molecular Structure: THEOCHEM*, 2008, **849**, 103-111.
13. K. Angermund, W. Baumann, E. Dinjus, R. Fornika, H. Görls, M. Kessler, C. Krüger, W. Leitner and F. Lutz, *Chemistry – A European Journal*, 1997, **3**, 755-764.
14. Y. Koide, S. G. Bott and A. R. Barron, *Organometallics*, 1996, **15**, 2213-2226.
15. R. Kempe, A. Spannenberg, H.-J. Drexler and D. Heller, *Z.Kristallogr.-New Cryst.Struct.*, 2001, **216**, 153.
16. H.-J. Drexler, S. Zhang, A. Sun, A. Spannenberg, A. Arrieta, A. Preetz and D. Heller, *Tetrahedron: Asymmetry*, 2004, **15**, 2139-2150.
17. R. J. Pawley, *Role of Hemi-Labile Ligands in Rhodium Catalysed Hydroacylation of Alkenes*, University of Bath, 2007.
18. D. P. Fairlie and B. Bosnich, *Organometallics*, 1988, **7**, 936-945.
19. I. F. D. Hyatt, H. K. Anderson, A. T. Morehead and A. L. Sargent, *Organometallics*, 2008, **27**, 135-147.
20. S. E. Clapham, A. Hadzovic and R. H. Morris, *Coordination Chemistry Reviews*, 2004, **248**, 2201-2237.
21. L. Gonsalvi, H. Adams, G. J. Sunley, E. Ditzel and A. Haynes, *Journal of the American Chemical Society*, 2002, **124**, 13597-13612.
22. G. Lamb, M. Clarke, A. M. Z. Slawin, B. Williams and L. Key, *Dalton Transactions*, 2007, **47**.
23. J. M. Brown and P. J. Guiry, *Inorganica Chimica Acta*, 1994, **220**, 249-259.
24. J. E. Marcone and K. G. Moloy, *Journal of the American Chemical Society*, 1998, **120**, 8527-8528.
25. E. Zuidema, P. W. N. M. van Leeuwen and C. Bo, *Organometallics*, 2005, **24**, 3703-3710.
26. T. Kohara, T. Yamamoto and A. Yamamoto, *Journal of Organometallic Chemistry*, 1980, **192**, 265-274.
27. M. Sharma, T. Andrea, N. J. Brookes, B. F. Yates and M. S. Eisen, *Journal of the American Chemical Society*, 2011, **133**, 1341-1356.
28. T. Andrea, E. Barnea and M. S. Eisen, *Journal of the American Chemical Society*, 2008, **130**, 2454-2455.
29. K. Fuji, T. Morimoto, K. Tsutsumi and K. Kakiuchi, *Chemical Communications*, 2005, **26**, 3295-3297.
30. M. R. Crimmin, A. G. M. Barrett, M. S. Hill and P. A. Procopiou, *Organic Letters*, 2006, **9**, 331-333.
31. S. Omura, T. Fukuyama, J. Horiguchi, Y. Murakami and I. Ryu, *Journal of the American Chemical Society*, 2008, **130**, 14094-14095.
32. F. Shibahara, J. F. Bower and M. J. Krische, *Journal of the American Chemical Society*, 2008, **130**, 14120-14122.

33. M. Imai, M. Tanaka, K. Tanaka, Y. Yamamoto, N. Imai-Ogata, M. Shimowatari, S. Nagumo, N. Kawahara and H. Suemune, *The Journal of Organic Chemistry*, 2004, **69**, 1144-1150.
34. Y. Inui, M. Tanaka, M. Imai, K. Tanaka and H. Suemune, *Chemical and Pharmaceutical Bulletin*, 2009, **57**, 1158-1160.
35. M. M. Coulter, K. G. M. Kou, B. Galligan and V. M. Dong, *Journal of the American Chemical Society*, 2010, **132**, 16330-16333.
36. C.-H. Jun, H. Lee, J.-B. Hong and B.-I. Kwon, *Angewandte Chemie*, 2002, **114**, 2250-2251.
37. R. Ghosh, T. J. Emge, K. Krogh-Jespersen and A. S. Goldman, *Journal of the American Chemical Society*, 2008, **130**, 11317-11327.
38. R. Ghosh, X. Zhang, P. Achord, T. J. Emge, K. Krogh-Jespersen and A. S. Goldman, *Journal of the American Chemical Society*, 2007, **129**, 853-866.
39. G. J. Kubas, *Metal Dihydrogen and σ -Bond complexes*, Kluwer Academic/Plenum Publishers, New York, 2001.
40. M. Brookhart, M. Green and G. Parkin *Proceedings of the National Academy of Sciences of the United States of America*, 2007, **104**, 6908-6914.
41. A. B. Chaplin, A. I. Poblador-Bahamonde, H. A. Sparkes, J. A. K. Howard, S. A. Macgregor and A. S. Weller, *Chemical Communications*, 2009, **2**, 244-246.
42. A. B. Chaplin and A. S. Weller, *Organometallics*, **29**, 2332-2342.
43. M. Gandelman, L. J. W. Shimon and D. Milstein, *Chemistry – A European Journal*, 2003, **9**, 4295-4300.
44. B. Rybtchinski, L. Konstantinovsky, L. J. W. Shimon, A. Vigalok and D. Milstein, *Chemistry – A European Journal*, 2000, **6**, 3287-3292.
45. A. Vigalok, O. Uzan, L. J. W. Shimon, Y. Ben-David, J. M. L. Martin and D. Milstein, *Journal of the American Chemical Society*, 1998, **120**, 12539-12544.
46. S. C. van der Slot, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. A. Iggo and B. T. Heaton, *Organometallics*, 2001, **20**, 430-441.
47. C. González-Rodríguez, R. J. Pawley, A. B. Chaplin, A. L. Thompson, A. S. Weller and M. C. Willis, *Angewandte Chemie International Edition*, **50**, 5134-5138.
48. J. Chatt, W. Hussain, G. J. Leigh, H. M. Ali, C. J. Pickett and D. A. Rankin, *Journal of the Chemical Society, Dalton Transactions*, 1985, **6**, 1131-1136.
49. R. A. Baber, A. G. Orpen, P. G. Pringle, M. J. Wilkinson and R. L. Wingad, *Dalton Transactions*, 2005, **4**, 659-667.
50. J. N. L. Dennett, A. L. Gillon, K. Heslop, D. J. Hyett, J. S. Fleming, C. E. Lloyd-Jones, A. G. Orpen, P. G. Pringle, D. F. Wass, J. N. Scutt and R. H. Weatherhead, *Organometallics*, 2004, **23**, 6077-6079.
51. S. J. Dossett, A. Gillon, A. G. Orpen, J. S. Fleming, P. G. Pringle, D. F. Wass and M. D. Jones, *Chemical Communications*, 2001, **8**, 699-700.
52. S. Daly, M. F. Haddow, A. G. Orpen, G. T. A. Rolls, D. F. Wass and R. L. Wingad, *Organometallics*, 2008, **27**, 3196-3202.
53. M. C. Willis, H. E. Randell-Sly, R. L. Woodward, S. J. McNally and G. S. Currie, *The Journal of Organic Chemistry*, 2006, **71**, 5291-5297.
54. A. B. Chaplin, J. F. Hooper, A. S. Weller and M. C. Willis, *Journal of the American Chemical Society*, 2012, **134**, 4885-4897.
55. J. F. Hooper, A. B. Chaplin, C. González-Rodríguez, A. L. Thompson, A. S. Weller and M. C. Willis, *Journal of the American Chemical Society*, **134**, 2906-2909.
56. A. B. Chaplin and A. S. Weller, *European Journal of Inorganic Chemistry*, 2010, **2010**, 5124-5128.
57. Y.-T. Hong, A. Barchuk and M. J. Krische, *Angewandte Chemie*, 2006, **118**, 7039-7042.
58. A. H. Roy, C. P. Lenges and M. Brookhart, *Journal of the American Chemical Society*, 2007, **129**, 2082-2093.
59. M. C. Willis, *Chemical Reviews*, 2009, **110**, 725-748.
60. S. J. Poingdestre, J. D. Goodacre, A. S. Weller and M. C. Willis, *Chemical Communications*, 2012, **48**, 6354-6356.
61. M. M. Coulter, P. K. Dornan and V. M. Dong, *Journal of the American Chemical Society*, 2009, **131**, 6932-6933.

4.1 Introduction

The development of new and better catalysts for hydroacylation – or any catalytic reaction – can be better guided by an understanding of the properties of current catalysts. To this end, many different groups have undertaken mechanistic and computational studies on a range of systems.¹⁻⁸ Subtle changes to ligand properties, such as varying the bite angle or steric bulk of the aryl-substituents, can have a marked effect on the selectivity of the catalyst for particular products.⁹ This might be caused by a destabilisation of a reactant, or stabilisation of a desired transition state, or intermediate; or by increasing the rate of one step in the catalytic cycle over another competing step. The branched-product selectivity in the hydroacylation reaction, observed with the dpp2-*o*-ⁱPr system is thought to be due to the effect the ligand bulk has on increasing the rate of reductive elimination of the product from the branched alkenyl intermediate.⁹ For intramolecular hydroacylation reactions, branched and linear selectivities can be affected by preferential formation of a 5-membered metallacycle upon hydride insertion, such as observed by Dong.¹⁰ The variety of effects which different catalysts may have on the same system, and the potential for one step of a catalytic cycle to be favoured or disfavoured over another step; all serve to highlight how important it is to understand the mechanism by which a reaction occurs.

Examples of intermediates which directly precede the rate-limiting (and therefore, usually, product-selecting) step of the hydroacylation catalytic cycle are limited. Short-lived acyl-alkyl intermediates of the type: $[\text{Rh}(\kappa^3_{\text{POP}}\text{-DPEphos})(\kappa^1_{\text{(S)}}\text{-}\sigma^1_{\text{(C)}}\text{-COC}_6\text{H}_4\text{SMe})(\sigma^1_{\text{(C)}}\text{-CH}_2\text{CH}_2\text{COOMe})][\text{closo-CB}_{11}\text{H}_6\text{Cl}_6]$ (three geometric isomers) (**i-102**), have been reported for the hydroacylation reaction of methyl acrylate (**II**) by aldehyde **V** using the DPEphos catalytic system. However, characterisation of these intermediates was only tentative and no kinetic data was obtained.¹¹ Brookhart measured the effective rate of reductive elimination in cobalt and rhodium hydroacylation systems, from the isolated alkyl-aryl-carbonyl complexes which are the resting state in these systems.^{12, 13} However, the carbonyl must first insert into the alkyl ligand to give the acyl-alkyl intermediates which can then undergo reductive elimination. The kinetics of these reactions were probed using trapping ligands (PMe_3) or ferrocenecarbaldehyde as a substrate (Scheme 4.1)



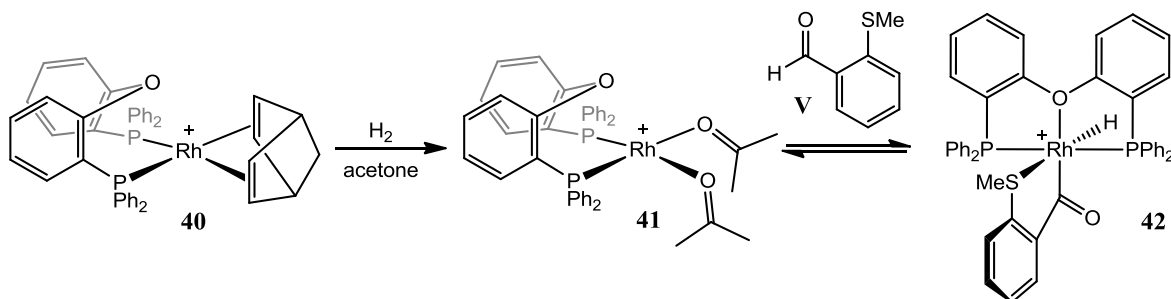
Scheme 4.1: The effective rate of reductive elimination in cobalt and rhodium hydroacylation systems, as measured by Brookhart.

There are no examples where the intermediate immediately prior to reductive elimination has been isolated for the DPEphos or related hydroacylation catalytic systems. The isolation of such an intermediate would give important structural

and mechanistic data pertinent to C-C bond formation, product selectivity and the overall reaction pathway. To date these problems have only been addressed computationally.^{5, 14-16}

4.2 Known complexes incorporating DPEphos

Given the success of the DPEphos system as a catalyst for intermolecular hydroacylation, this catalyst has served as a benchmark for every substrate combination scoped with the various catalysts throughout this thesis. Therefore, upon identifying the combination of aldehyde **V** and alkyne **XI** as favouring the formation of the branched product (**XIII**) in the previous chapter, these substrates were also screened with the DPEphos catalyst.



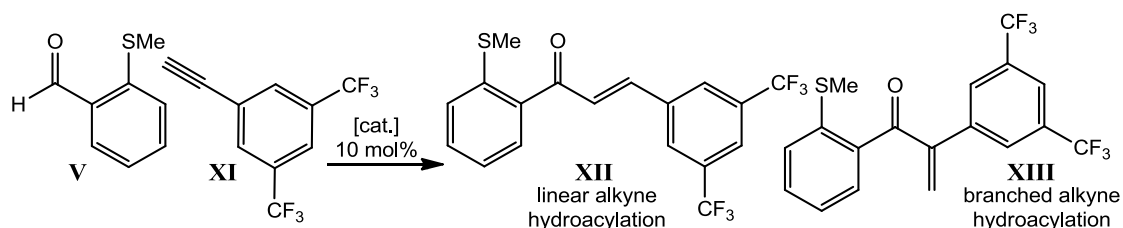
Scheme 4.2: Known complexes of DPEphos: rhodium(I) norbornadiene (**40**), rhodium(I) bis(acetone) (**41**) and rhodium(III) acylhydride (**42**). [*closo*-CB₁₁H₁₂]⁻ anions not shown.

The known rhodium(I) norbornadiene precursor complex [Rh(*cis*-κ²(PP)-DPEphos)(NBD)][*closo*-CB₁₁H₁₂] (**40**) was prepared in accordance with the method in Scheme 2.2 (p.71).¹⁷ The [*closo*-CB₁₁H₁₂]⁻¹⁸ and [*closo*-CB₁₁H₆Br₆]⁻¹⁸ anions were chosen for their property of forming less soluble salts which allow the

isolation of relatively unstable complexes as solids, and have been used interchangeably with the $[\text{BAr}^{\text{F}}_4]^-$ anion.¹⁹ Previous research has shown these anions to have no effect on catalysis.²⁰ ^1H and ^{31}P NMR spectroscopy of complex **40** confirmed its formulation. Addition of hydrogen (4 atm) to a solution of complex **40** in acetone forms the active precatalyst rhodium(I) bis(acetone) complex $[\text{Rh}(\text{cis-}\kappa^2_{\text{PP}}\text{-DPEphos})(\text{acetone})_2][\text{closo-CB}_{11}\text{H}_{12}]$ (**41**) which is also known, and the formation of which was verified by ^1H and ^{31}P NMR spectroscopy (Scheme 4.2).¹⁷ Addition of 1 equivalent of aldehyde **V** forms the previously reported acyl-hydride complex $[\text{Rh}(\text{mer-}\kappa^3_{\text{POP}}\text{-DPEphos})(\text{H})(\kappa^1_{\text{S}}\text{-}\sigma^1_{\text{C}}\text{-COC}_6\text{H}_4\text{SMe})][\text{closo-CB}_{11}\text{H}_{12}]$ (**42**), which was verified by ^1H and ^{31}P NMR spectroscopy (Scheme 4.2).^{17, 21} These complexes were all isolated in good yield.

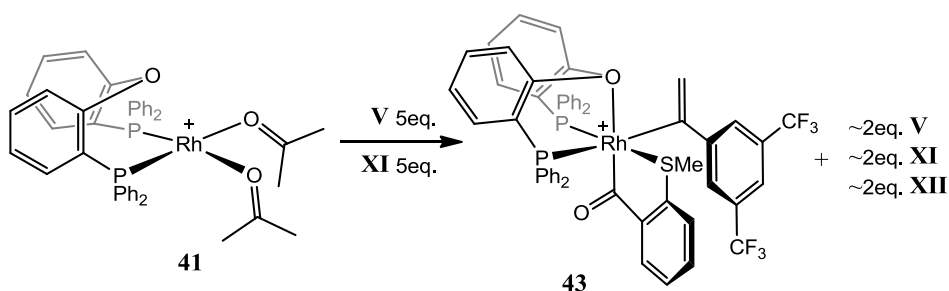
4.3 Initial results and synthesis of the branched intermediate

The rhodium(I) bis(acetone) precursor complex (**41**) was screened as a catalyst for the hydroacylation of alkyne **XI** by aldehyde **V** under the standard catalytic conditions of 10 mol% catalyst, 0.4 mL d_6 -acetone, RT, 1:1 aldehyde:alkyne (Scheme 4.3).



Scheme 4.3: Intermolecular hydroacylation of aldehyde **V** and alkyne **XI**.

Although ~2 equivalents of linear product (**XII**) were observed immediately, no change in the concentration of **XII** or any further catalytic activity were observed over the course of 24 hours. Only one organometallic species was observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (*vide infra*). Raising the temperature to 50 °C led to catalytic activity with the complete conversion of substrates **V** and **XI** to a ~2:1 mixture of linear:branched hydroacylation products (**XII** and **XIII** respectively) over a period of 24 hours, throughout which the aforementioned organometallic species was observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The catalytic results will be discussed in more detail later in this chapter; however, of immediate interest is the organometallic complex observed before and during catalysis.



Scheme 4.4: Formation of complex **43**. [*closo*-CB₁₁H₁₂]⁻ anions not shown.

In an attempt to isolate the species observed throughout catalysis, one equivalent of alkyne **XI** was added to complex **42**. However, this resulted in the – reproducible – formation of a mixture of five organometallic species as identified by ^{31}P NMR spectroscopy (NMR experiment started immediately after the addition of alkyne to complex **42**), one of which is the species observed during catalysis, complex **43** (*vide infra*). In contrast, the addition of an excess of aldehyde **V** and alkyne **XI** (5 eq.) to complex **41**, resulted in the formation of a single organometallic species alongside approx. 2 equivalents of the linear hydroacylation product (**XII**). This organometallic species was isolated in good

yield (86 %), and has been identified as the branched acyl-alkyl intermediate $[\text{Rh}(\text{fac-}\kappa^3(\text{POP})\text{-DPEphos})(\kappa^1(\text{S})\text{-}\sigma^1(\text{C})\text{-COC}_6\text{H}_4\text{SMe})\{\sigma^1(\text{C})\text{-C(=CH}_2\text{)C}_6\text{H}_3(\text{CF}_3)_2\}][\text{closo-CB}_{11}\text{H}_{12}]$ (**43**) (Scheme 4.4). None of the branched hydroacylation product (**XIII**) was observed under these conditions (295 K, 1 hour), although this is not the case when the reaction is run at higher temperature, or over a longer period of time (*vide infra*). It is proposed that under these conditions (5 eq. of **V** and **XI**) complex **42** is formed initially, and then turns over in catalysis.

Pale yellow crystals of **43** suitable for X-ray diffraction were prepared by the diffusion of hexane into a solution of the isolated complex in acetone at 4 °C (Figure 4.1). The solid-state structure of **43** shows rhodium(III) in a pseudo-octahedral environment, with the alkyne having undergone insertion into the hydride of complex **42** to give the branched alkenyl complex rather than the linear alkenyl complex. The DPEphos ligand adopts a *fac*- κ^3 coordination mode, reducing the P1-Rh1-P2 bond angle from 155.93(5)° in the solid-state structure of **42**, in which the DPEphos ligand adopts a *mer*- κ^3 coordination mode,²¹ to 95.41(2)° in **43**, and placing the oxygen donor of the ligand *trans* to the acyl ligand. The high *trans* influence of the acyl ligand can be seen in the longer Rh-O bond distance of 2.3458(17) Å, compared to the Rh-O bond length in complex **42** [2.248(3) Å]. The 1,1-alkenyl group is another high *trans* influence ligand, affecting the Rh1-P1 bond length of the phosphine *trans* to the alkenyl group, in comparison to the Rh1-P2 bond distance which is *trans* to the thio-ether group [2.4542(7) and 2.2953(7) Å respectively]. The C1-C2 1,1-alkenyl bond distance of 1.32(7) Å is similar to those found in other related 1,1-alkenyls such as (PCP)Ir(PhC=CH₂)(CCPh)(CO) [PCP =

$\kappa^3\text{-C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^t\text{Bu}_2)_2$] ^{8} [1.343(3) Å] and (PCP')Ru(PhC=CH₂)Cl [PCP' = *N,N'*-bis(diisopropylphosphino)dipyrromethane] [1.322(6) Å].²² The alkenyl group is directed along the Rh1-O1 vector as seen in the O1-Rh1-C1-C2 dihedral angle of 8.9(3)°.

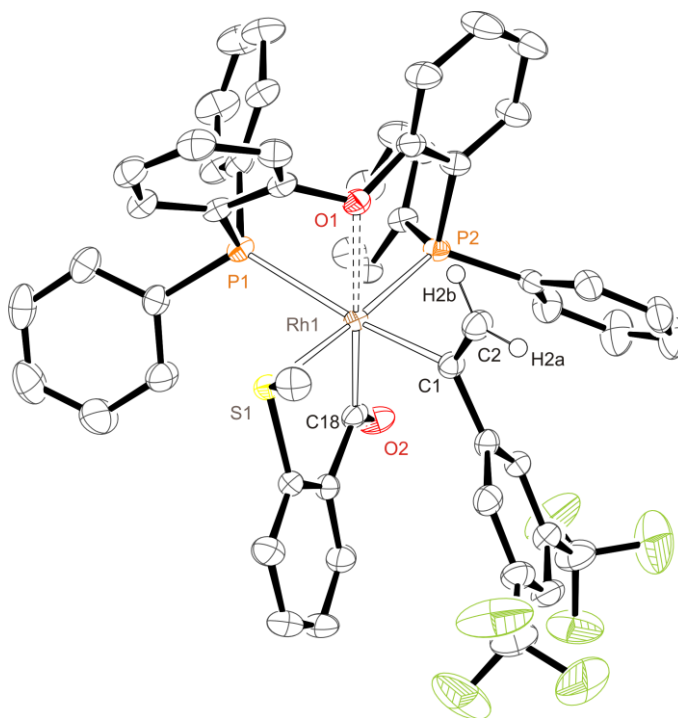


Figure 4.1: Molecular structure of the cationic portion of [Rh(*fac*- κ^3 (POP)-DPEphos)(κ^1 (S)- σ^1 (C)-COC₆H₄SMe){ σ^1 (C)-C(=CH₂)C₆H₃(CF₃)₂}] [*closo*-CB₁₁H₁₂] (**43**). Displacement ellipsoids are drawn at the 50% probability level. The anion and hydrogen atoms, apart from H2a and H2b, are omitted for clarity. Selected bond lengths [Å]: Rh1–P1, 2.4542(7); Rh1–P2, 2.2953(7); Rh1–O1, 2.3458(17); Rh1–C18, 1.977(3); Rh1–S1, 2.3757(7); Rh1–C1, 2.097(3); C1–C2, 1.327(4); C18–O2, 1.212(3). Selected bond angles [°]: C1–Rh1–P1, 162.90(7); P2–Rh1–S1, 175.17(2); O1–Rh1–C18, 179.50(9); P1–Rh1–P2, 95.41(2); (dihedral) O1–Rh1–C1–C2, 8.9(3).

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **43** is consistent with the solid-state structure, showing two doublet of doublet signals at δ 21.87 [$J(\text{RhP}) = 166.5$, $J(\text{PP}) = 27.0$] and 13.12 [$J(\text{RhP}) = 78.7$, $J(\text{PP}) = 27.0$] which indicate *cis* inequivalent phosphine environments; the smaller coupling constant places the higher field phosphine (δ 13.12) *trans* to the high *trans* influence alkenyl group, while the other phosphine

(δ 21.87) is *trans* to the low *trans* influence thioether group. A $^1\text{H}\{^{31}\text{P}\}$ NMR experiment shows a sharpening of the broad singlet signal observed for the SMe group at δ 2.59, and a correlation is observed between the phosphine signal at δ 21.87 and the SMe signal in a $^1\text{H}\text{-}^{31}\text{P}\{^1\text{H}\}$ HMBC NMR experiment, providing further evidence that these groups are *trans*. Similar correlations were observed between the *trans* hydride and SMe groups in the acyl-hydride complexes of POP' (**7**), XANTphos (**13**) and DPEphos (**42**)²¹.

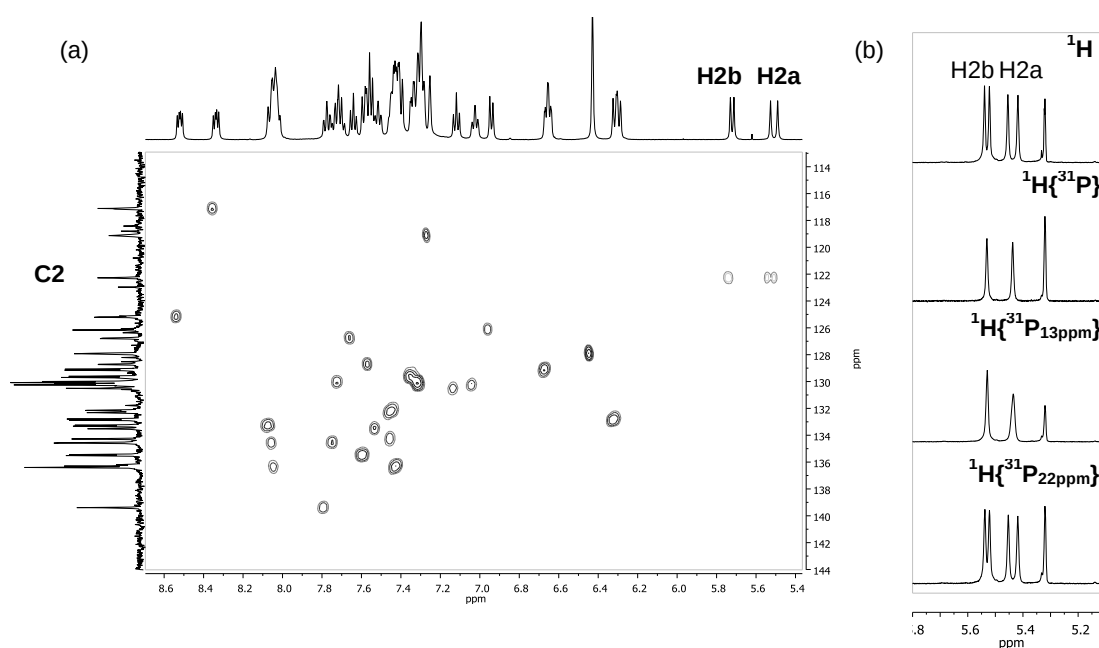


Figure 4.2: (a) $^1\text{H}\text{-}^{13}\text{C}\{^1\text{H}\}$ HSQC; and (b) ^1H , broadband, and selective $^1\text{H}\{^{31}\text{P}\}$ NMR spectra of complex **43** (aryl and alkenyl region only).

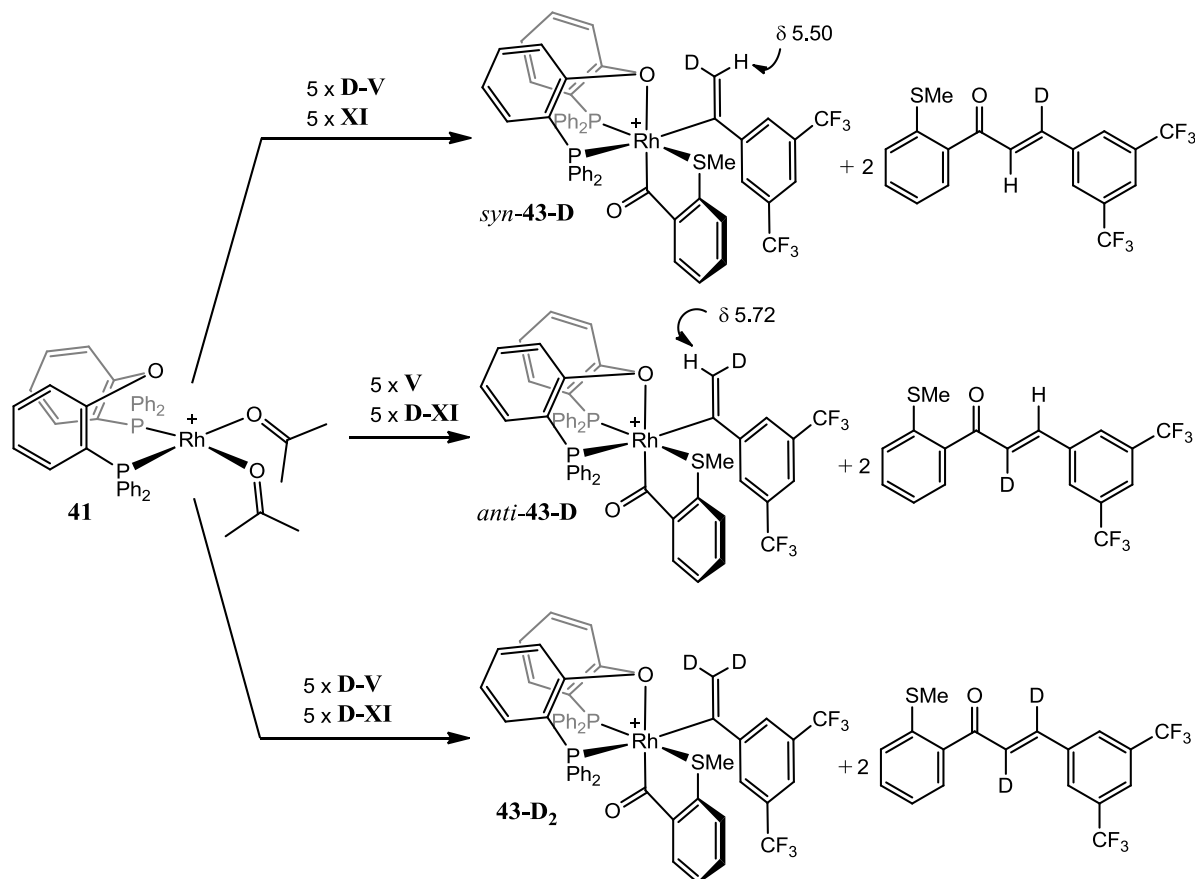
The ^1H NMR spectrum also shows two broadened doublets at δ 5.72 [$J(\text{PH}) = 8.9$] and 5.50 [$J(\text{PH}) = 18.1$] which have been assigned as the alkenyl protons (i.e. H2b and H2a in Figure 4.1). These two chemical shifts correlate to each other in a COSY NMR experiment, and to one ^{13}C signal in the $^1\text{H}\text{-}^{13}\text{C}\{^1\text{H}\}$ HSQC NMR spectrum at δ 122.2 (Figure 4.2a). The chemical shifts are in the range for those reported in the

complex (PCP)Ir(PhC=CH₂)(CCPh) (δ 4.35 and 4.39; and δ 4.79 and 6.65; for two geometric isomers).⁸ Selective ¹H{³¹P} NMR experiments demonstrate that the coupling is due to the phosphine which is observed at δ 13.12 in the ³¹P{¹H} NMR spectrum (Figure 4.2b) confirming the *trans* relationship. The signal at δ 5.50 in the ¹H NMR spectrum has been assigned as the geminal proton *anti* to P1 (i.e. H2a in Figure 4.1) on the basis of the larger *J*(PH) coupling constant, placing the signal at δ 5.72 as the proton *syn* to P1 (i.e. H2b). Different coupling constants have previously been noted in the related 1,1 alkenyl systems of Pd-diphosphines, with the largest coupling constant assigned to the proton *anti*-to the phosphine.²³ A single environment is observed in the ¹⁹F NMR spectrum at δ 62.92 (br s, fwhm = 2.6) indicating free rotation of the alkenyl arene group, although the slight broadening of the signal may be consistent with some restriction of rotation about the Rh1-C1 bond, as has been noted to occur in several 1,1-alkenyl complexes.^{5, 8, 24} The NMR spectroscopic data is consistent with a structure in solution that is the same as the solid state structure. Characterisation by ESI-MS shows a single signal at [M]⁺ *m/z* = 1031.15 (calc. 1031.12) with the predicted isotope pattern, and further confirmation of the empirical formulation of **43** is provided by elemental analysis, which found an elemental composition for C₅₅H₅₂B₁₁F₆O₂P₂RhS (1174.8291) of: C 56.31, H 4.44 (requires: C 56.23, H 4.46).

By using selectively deuterated equivalents of aldehyde **V** and alkyne **XI**, the identity of the signals at δ 5.72 and 5.50 in the ¹H NMR spectrum can be confirmed as forming from the aldehyde and alkyne protons. Addition of excess (5 eq. each) **D-V** and **D-XI** to complex **41** at 295 K formed the deuterated complex [Rh(*fac*-

$\kappa^3(\text{POP})\text{-DPEphos}(\kappa^1(\text{S})\text{-}\sigma^1(\text{C})\text{-COC}_6\text{H}_4\text{SMe})\{\sigma^1(\text{C})\text{-C(=CD}_2\text{)C}_6\text{H}_3(\text{CF}_3)_2\}[\text{CB}_{11}\text{H}_6\text{Br}_6]$

(**43-D₂**) (Scheme 4.5) which (once isolated) is confirmed by an absence of the alkenyl signals at δ 5.72 and 5.50 in the ^1H NMR spectrum (Figure 4.3a).



Scheme 4.5: Selective incorporation of deuterated equivalents of **V** and **XI** into complex **43**. [*closo*- $\text{CB}_{11}\text{H}_6\text{Br}_6$] $^-$ anions not shown.

The use of a combination of one deuterated and one protic substrate allow the individual assignment of the signal at 5.72 ppm as forming from the aldehyde proton, while the signal at 5.50 ppm forms from the alkyne. This confirms that complex **43** occurs by *syn*-insertion of the hydride into the alkyne, as would be expected,²⁴ so that addition of **D-V** and **XI** selectively forms **syn-43-D** in which the proton *syn* to P1 (i.e. H2b) is replaced with D, observed as an absence of the signal at δ 5.72 in the ^1H NMR spectrum (Figure 4.3b). Addition of **V** and **D-XI** forms *anti*-

43-D with incorporation of D into the position *anti* to P1 (i.e. H2a) (Figure 4.3c). ^2H NMR spectroscopy confirms all of these observations. Approx. two equivalents of the corresponding deuterated linear product (**XII**), formed in >99% selectivity of D-incorporation, are also observed *in situ* prior to isolation of the complexes as solids, with no scrambling of the D into other positions.

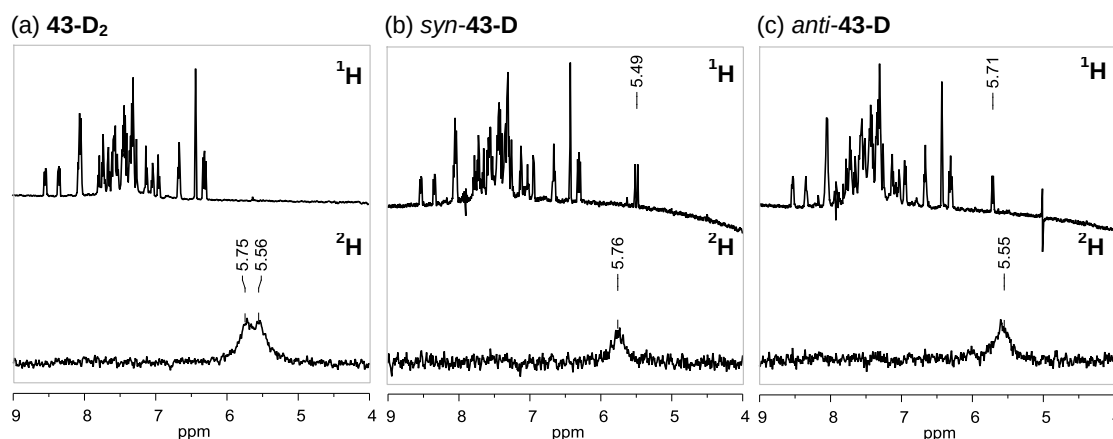
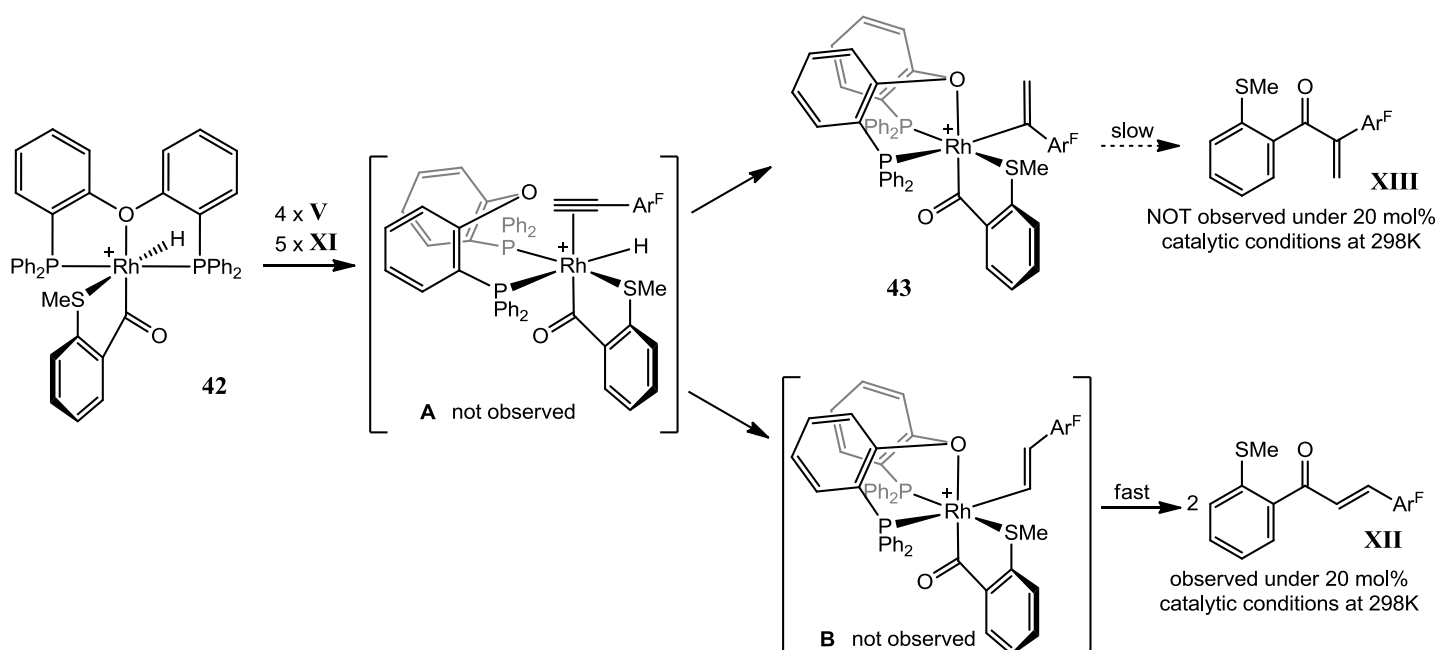


Figure 4.3: ^1H and ^2H NMR spectra of isolated complexes: (a) **43-D₂**; (b) *syn*-**43-D**; and (c) *anti*-**43-D** (aryl region only).

Only the linear product (**XII**) is observed under the catalytic conditions (20 mol%, 295 K) necessary for the isolation of the branched intermediate complex, while the only organometallic species observed is the branched intermediate (**43**). This suggests that the catalytic cycle bifurcates at the hydride insertion step to give both the linear alkenyl (**B**, Scheme 4.6) and branched alkenyl (complex **43**) intermediates, but that the barrier to reductive elimination is much greater from complex **43** than from the linear equivalent, i.e. the formation of the branched product (**XIII**) is significantly slower than the formation of linear product (**XII**) as a result of a larger barrier to C-C bond formation/reductive elimination from complex **43** than from the unobserved linear intermediate (**B**).

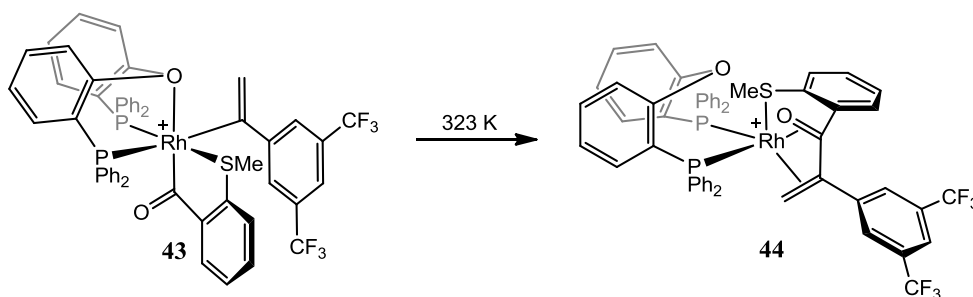


Scheme 4.6: Under catalytic conditions of 20mol% at 295 K, complex **43** and **XII** are observed. [*closo*-CB₁₁H₁₂]⁻ anions not shown.

This is consistent with the observation that under stoichiometric conditions (addition of one equivalent of alkyne **XI** to metal-acyl-hydride complex **42**) a mixture of species including complex **43**, are observed. Analysis of these species indicates that the branched and linear hydroacylation catalytic cycles partition 2:1 linear:branched at the hydride insertion step (**A**, Scheme 4.6), i.e. addition of 1 equivalent of alkyne to complex **42** forms a ~2:1 mixture of linear:branched organometallic species (*vide infra*). A related scenario has been observed by Krogh-Jespersen and Goldman, in their mechanistic studies into alkyne dimerization using {(PCP)Ir} complexes. They observe only the branched organometallic species, but reductive elimination of the linear product is faster than reductive elimination of the branched product.⁸

4.4 Reductive elimination from the branched intermediate

To establish the role of complex **43** as a genuine catalytic intermediate, the C-C bond forming reductive elimination step was studied. In d_6 -acetone solution at 295 K, complex **43** underwent reductive elimination very slowly (~5 days). However, heating the solution to 323 K for 12 hours resulted in the quantitative formation of the coordinated branched complex $[\text{Rh}(\text{cis-}\kappa^2(\text{PP})\text{-DPEphos})(\eta^2(\text{CC})\text{-}\eta^2(\text{CO})\text{-}\kappa^1(\text{S})\text{-C=CH}_2(\text{C}_6\text{H}_3(\text{CF}_3)_2)\text{C=O}(\text{C}_6\text{H}_4)\text{SMe})][\text{closo-CB}_{11}\text{H}_{12}]$ (**44**) (Scheme 4.7).



Scheme 4.7: In solution, at 323 K, complex **43** undergoes reductive elimination to form complex **44**. $[\text{closo-CB}_{11}\text{H}_{12}]^-$ anions not shown.

The solution NMR data of **44** is consistent with the formation of a rhodium(I) complex. Two doublet of doublet signals are observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 31.65 [$J(\text{RhP}) = 151.5$, $J(\text{PP}) = 38.4$] and 27.90 [$J(\text{RhP}) = 171.0$, $J(\text{RhP}) = 39.1$], indicative of *cis* inequivalent phosphines which are *trans* to weak *trans* influence ligands. A correlation was observed in the ^1H - $^{13}\text{C}\{^1\text{H}\}$ HSQC NMR spectrum between both C=CH_2 proton signals and one carbon at δ 41.2 (Figure 4.4c). The ^1H NMR spectrum shows the vinylic proton signals shifted significantly upfield to δ 3.60 and 2.24 (cf. alkene signals of free product at δ 6.60 and 5.95). The signal at 2.24 ppm also shows splitting into an apparent doublet of doublet of triplets (Figure 4.4a). A broadband $^1\text{H}\{^{31}\text{P}\}$ NMR experiment shows the collapse of

the multiplet into an apparent triplet, while selective $^1\text{H}\{^{31}\text{P}\}$ NMR experiments show the smaller doublet coupling is due to the phosphine signal observed at δ 31.65 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, and the larger doublet coupling is due to the signal at δ 27.90. The apparent triplet multiplicity is due to coupling of a similar magnitude to both the rhodium and the other vinylic proton. The sulphur methyl group is observed as a singlet at δ 1.92, which is comparable to the same group in the rhodium(III) acyl-hydride species (**42**) observed at δ 1.89 in that complex.

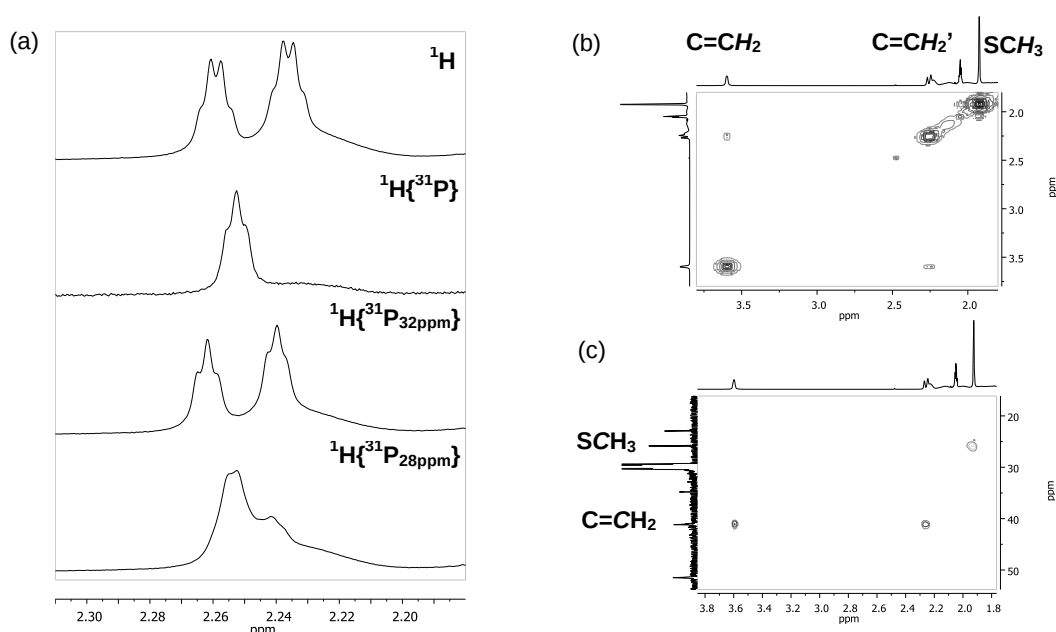
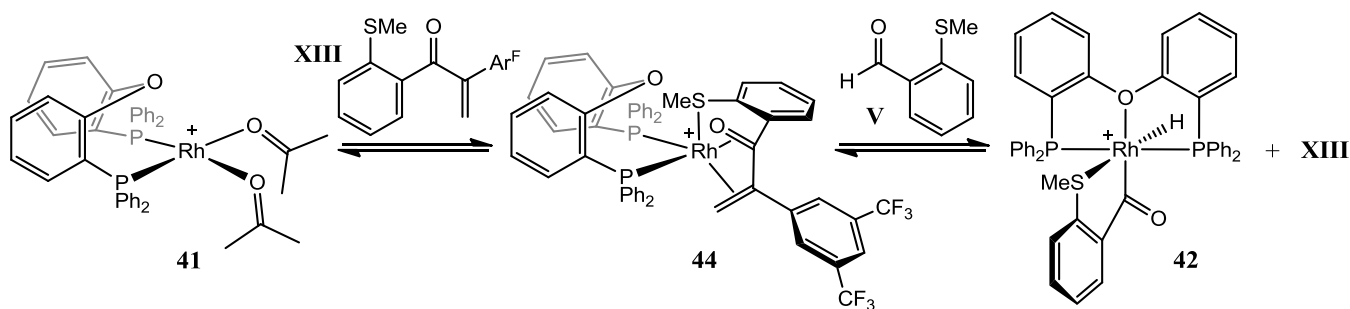


Figure 4.4: (a) ^1H , broadband and selective $^1\text{H}\{^{31}\text{P}\}$; (b) COSY; and (c) ^1H - $^{13}\text{C}\{^1\text{H}\}$ HSQC NMR spectra of complex **44** (alkyl region only).

A ^1H - ^1H COSY NMR experiment demonstrates coupling between the two signals assigned as the vinylic protons (Figure 4.4b), and selective $^1\text{H}\{^{31}\text{P}\}$ NMR experiments show no coupling between the sulphur methyl and either phosphine, indicating that the sulphur atom, if it is coordinated to the rhodium, is not *trans* to either phosphine.



Scheme 4.8: Formation of complex **44** by addition of product **XIII** to complex **41**, and regeneration of complex **42** by addition of aldehyde **V** to complex **44**. [*closo*-CB₁₁H₁₂][−] anions not shown.

Addition of aldehyde **V** to complex **44** yields the rhodium(III) acyl hydride species (**42**) and releases one equivalent of branched product (Scheme 4.8). Complex **44** may also be prepared by direct addition of isolated branched product (**XIII**) to the bis-acetone species (**41**) (Scheme 4.8). Crystals suitable for X-ray diffraction were obtained by diffusion of pentane into an acetone solution of complex **43** prepared *via* this method, at 295 K (Figure 4.5). As further evidence for the formation of complex **44** from **43**, crystals of **44** were also obtained from the slow (~5 days) diffusion of pentane into a solution of complex **43** in acetone at 295 K. The process of reductive elimination occurred more rapidly than crystallisation, and so only complex **44** was observed. Inspection of the crystal structure accounts for many of the features observed in the NMR experiments. The five-coordinate rhodium(I) complex adopts a distorted pseudo-trigonal bipyramidal geometry, with the phosphines and thioether group all mutually *cis*, and the branched product further coordinated through η^2 -alkene and η^2 -carbonyl interactions. This coordination mode has been observed previously by Lavigne in the complex [Ru(PPh₃)(η^2 (CC)- η^2 (CO)- κ^1 (P)-PPh₂C₆H₄C=OC(Ph)=CHPh)(CO)], 2-diphenylphosphanylbenzaldehyde was used to achieve chelation assisted stoichiometric hydroacylation of an

internal alkyne ($\text{PhC}\equiv\text{CPh}$).²⁵ The long Rh-O distance ($\text{Rh1-O2} = 3.395 \text{ \AA}$) is consistent with the DPEphos ligand adopting a *cis*- $\kappa^2_{(\text{PP})}$ coordination mode. The lack of coupling between the thioether and phosphines in the NMR experiments is explained by their mutually *cis* orientation, while the high field chemical shift and the observed multiplicity of the vinylic protons are due to the coordination of the *exo*-methylene group to the metal.

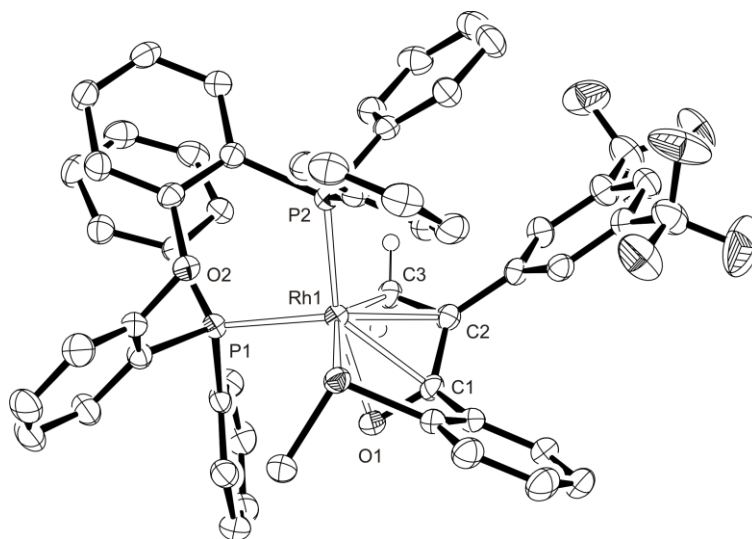


Figure 4.5. Molecular structure of the cationic portion of $[\text{Rh}(\text{cis-}\kappa^2_{(\text{PP})}\text{-DPEphos})(\eta^2_{(\text{CC})}\text{-}\eta^2_{(\text{CO})}\text{-}\kappa^1_{(\text{S})}\text{-C=CH}_2(\text{C}_6\text{H}_3(\text{CF}_3)_2)\text{C=O}(\text{C}_6\text{H}_4)\text{SMe})][\text{closo-CB}_{11}\text{H}_{12}]$ (**44**). Displacement ellipsoids are drawn at the 50% probability level. The anion and the majority of hydrogen atoms are omitted for clarity. Selected bond lengths [$\text{\AA}$]: Rh1-P1, 2.3483(13); Rh-P2, 2.2810(13); Rh1-O1, 2.139(3); Rh1-C1, 2.148(5); Rh1-C2, 2.216(5); Rh1-C3, 2.123(5); Rh1-S1, 2.4579(12); Rh1-O2, 3.395(5). Selected bond angles [$^\circ$]: P2-Rh1-O1, 166.49(10); P1-Rh1-P2, 97.87(5), S1-Rh1-P1, 106.30(4).

The conversion of **43** into **44** was followed by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, and the rate of reductive elimination was determined by monitoring the concentrations of each species (**43** and **44**) over time (Figure 4.6). No free linear product (**XII**) was observed, and the only organometallic species observed are complexes **43** and **44**, which suggests non-reversible hydride insertion into the alkyne. The rate of decay of the *geminal* complex (**43**) followed first order kinetics,

with a plot of $\ln([43]_t/[43]_0)$ vs. t giving a straight line from which the rate constant for the reaction at that temperature could be determined (Figure 4.6).

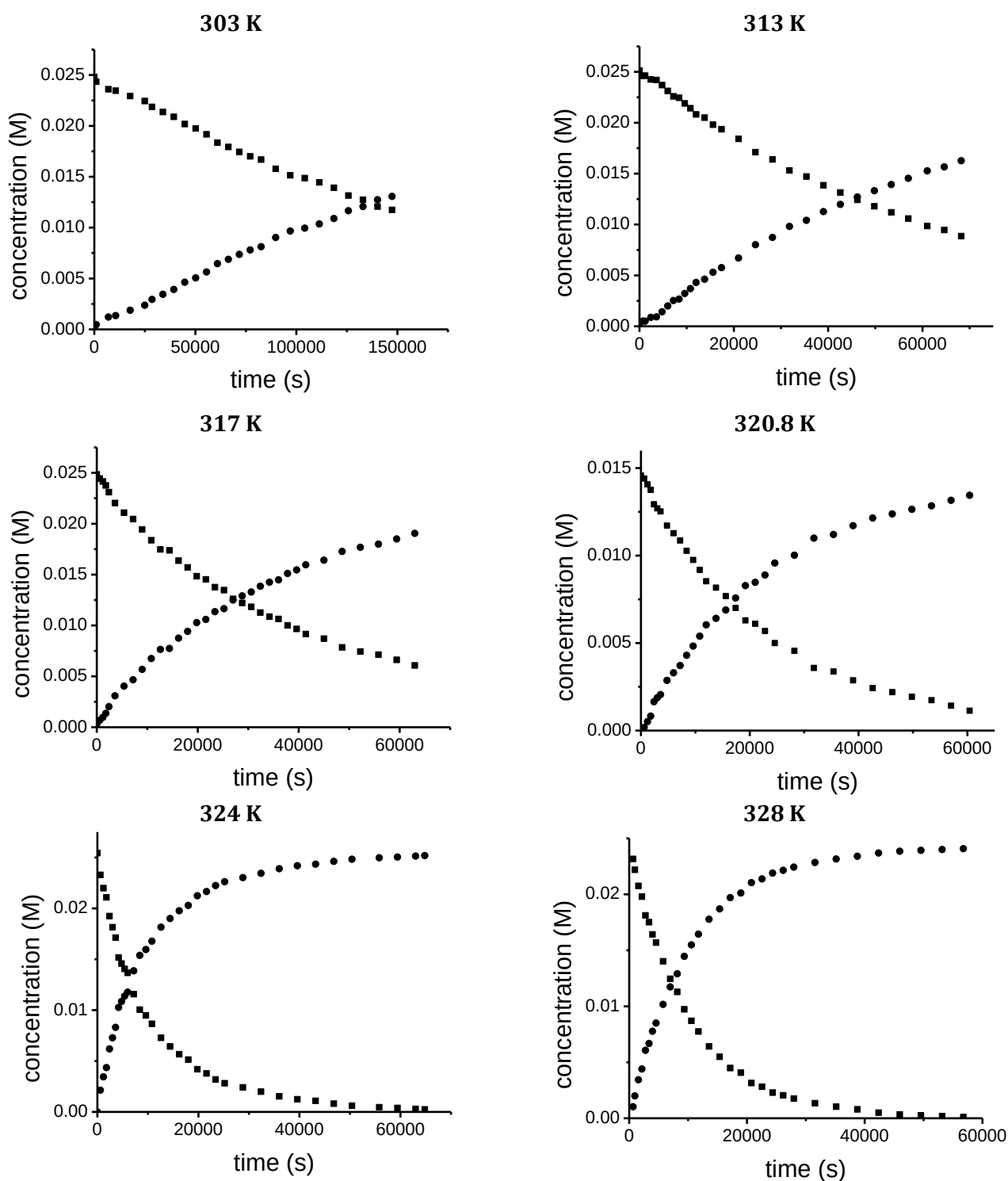


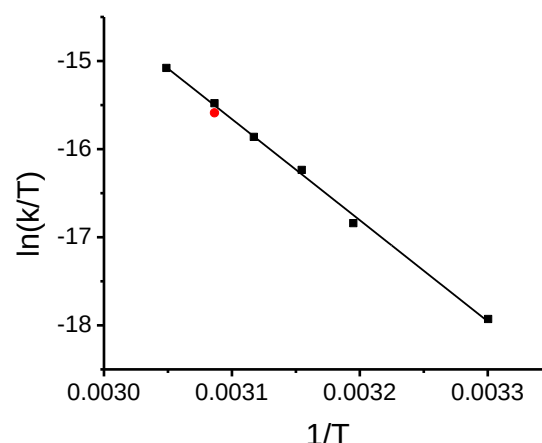
Figure 4.6: Time vs. concentration plots for the conversion of 43 to 44 at stated temperatures.

The rate of reductive elimination at 324 K ($k_{\text{obs}} = 6.1 \times 10^{-5} \text{ s}^{-1}$) (entry 2, Table 4.1) is comparable to the rate of ketone reductive elimination from $(\eta^5\text{-C}_5\text{Me}_4\text{CF}_3)\text{Rh}(\text{PMe}_3)(\sigma^1_{\text{C}}\text{-COCH}_2\text{CH}_2\text{SiMe}_3)(\text{C}_6\text{H}_4\text{Me})$ ($k_{\text{obs}} = 2.0 \times 10^{-5} \text{ s}^{-1}$),¹³ which is also similar to that determined for the related Co system (see Scheme 4.1).¹² The experiment was repeated at six different temperatures (303 to 328 K, Table 4.1 and Figure 4.6), and an Eyring plot of the different rate constants against the respective temperatures gave a straight line from which $\Delta H^\ddagger$ and $\Delta S^\ddagger$ could be determined from the gradient of the slope and the intercept (Figure 4.7).

Table 4.1: Conversion of **43** to **44** over a range of temperatures.^a Conversion of *anti*-**43-D** to **44-H/D** at 324 K.^b

entry	T (K)	$k \times 10^{-5}$
1	328	9.28(5)
2	324	6.14(4)
3 ^b	324	5.50 (3)
4 ^c	320.8	4.15(2)
5	317	2.82(1)
6	313	1.520(4)
7	303	0.496(3)

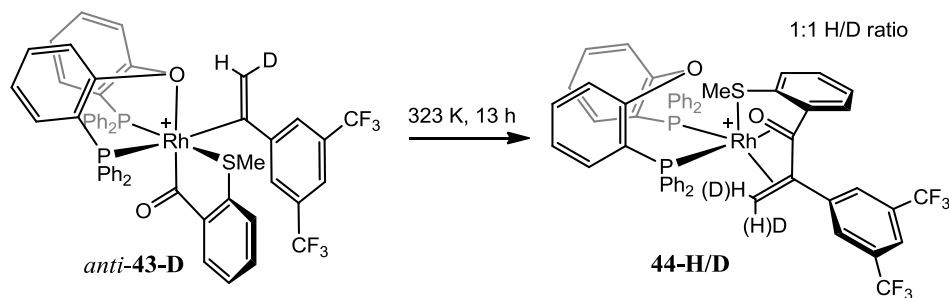
Figure 4.7: Eyring plot of conversion of **43** to **44** over a range of temperatures. Conversion of *anti*-**43-D** to **44-H/D** at 324 K (red circle).



^aConditions: all manipulations under Argon atmosphere, 0.024 M solution of complex **43** in d_6 -acetone at stated temperatures, conversion determined by ^1H NMR spectroscopy. Rates determined by fitting zero order trendlines to the integrated data. ^bComplex *anti*-**43-D** was studied to determine KIE. ^c0.015 M solution.

The values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ have been calculated as $+95.4 (\pm 2.3) \text{ kJ mol}^{-1}$ and $-32.0 (\pm 7.3) \text{ J mol}^{-1} \text{ K}^{-1}$ respectively, and a $\Delta G^\ddagger_{295}$ of $+104.9 (\pm 4.5) \text{ kJ mol}^{-1}$ derived from these values. The small, negative entropy of activation suggests a transition state for reductive elimination which is more ordered,⁷ which is consistent with an intramolecular process.

The experiment was repeated, starting from the *anti*-**43-D** complex at 324 K (entry 3, Table 4.1), which gave a first order rate constant of $k_{\text{obs}} = 5.5 \times 10^{-5} \text{ s}^{-1}$ and corresponding $k_{\text{H}}/k_{\text{D}}$ of 1.1. This negligible KIE is consistent with an irreversible hydride insertion step (*vide infra*), and the reductive elimination step being rate limiting for complex **43**.



Scheme 4.9: Heating *anti*-**43-D** at 324 K forms a 1:1 mixture of complex **44-H/D** with scrambling of D into both vinylic positions. [*closo*-CB₁₁H₆Br₆][−] anions not shown.

Another process was highlighted by the heating of the selectively deuterated *anti*-**43-D** complex: scrambling of the deuterium was observed in an approx. 1:1 ratio across both positions of the vinyl group of the branched product (Scheme 4.9). Likewise, the *anti*-**43-D** complex undergoes isomerisation to give a mixture of *anti*-**43-D** and *syn*-**43-D** (Figure 4.8). Monitoring the ¹H NMR spectra over time shows the immediate reduction in intensity of the *anti*-**43-D** signal at δ 5.72, alongside the appearance of the *syn*-**43-D** vinylic proton at δ 5.50 (Figure 4.8). The ratio of *anti*-**43-D** to *syn*-**43-D** never reaches 1:1. However, the deuterium is observed equally scrambled into both positions of the product complex **44-H/D**.

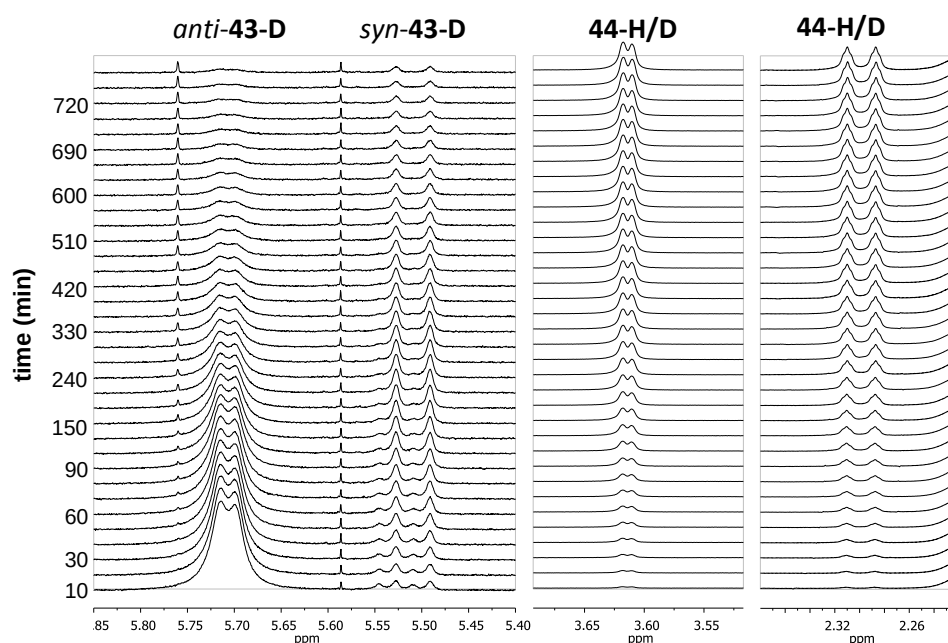
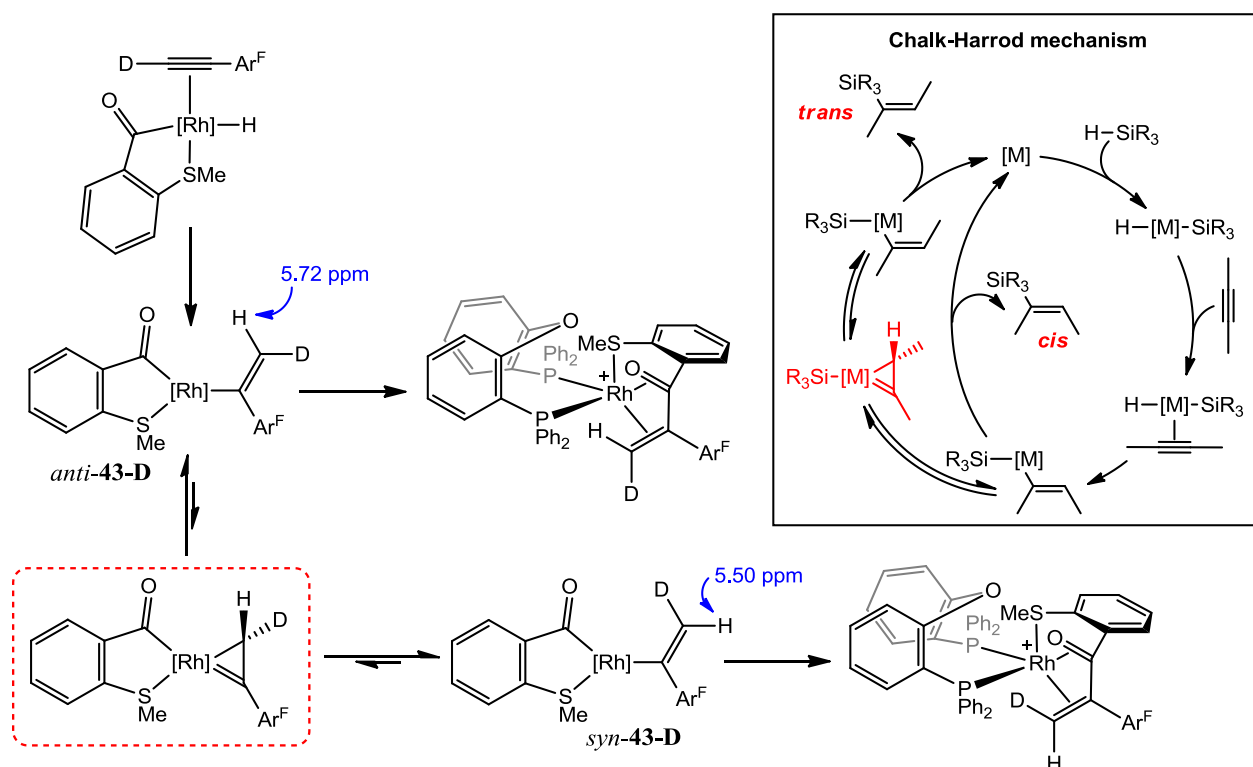


Figure 4.8: ^1H NMR spectra arrayed over time, showing scrambling of D into both vinylic signals at 5.72 and 5.50 ppm. D is observed equally in both alkene positions in the product **44-H/D**.^[1]

This behaviour is consistent with an equilibrium being established between both isomers of complex **43**. It is proposed that isomerisation may take place *via* a metallacyclopropene intermediate, such as has been discussed in the context of the apparent *trans*-addition in the hydrosilylation of alkenes (The Chalk-Harrod mechanism)^{26, 27} and in intramolecular alkyne hydroacylation^{1, 28} (Scheme 4.10). Cyclopropene intermediates have also been discussed in relation to the *trans*-hydroboration of alkynes.²⁹ The observation, in the system under investigation here, of only the *cis*-addition linear product (**XII**) would appear to indicate that either the rate of isomerisation (which would give the *trans*-addition product) is much slower than the rate of reductive elimination from the linear intermediate, or isomerisation is prevented by the steric and electronic effect of the Ar^{F} group.

^[1] The second doublet at 5.52 ppm is assigned as an impurity of protic alkyne in the deuterated alkyne sample, so that a small amount of the CH_2 -vinyl species also formed.

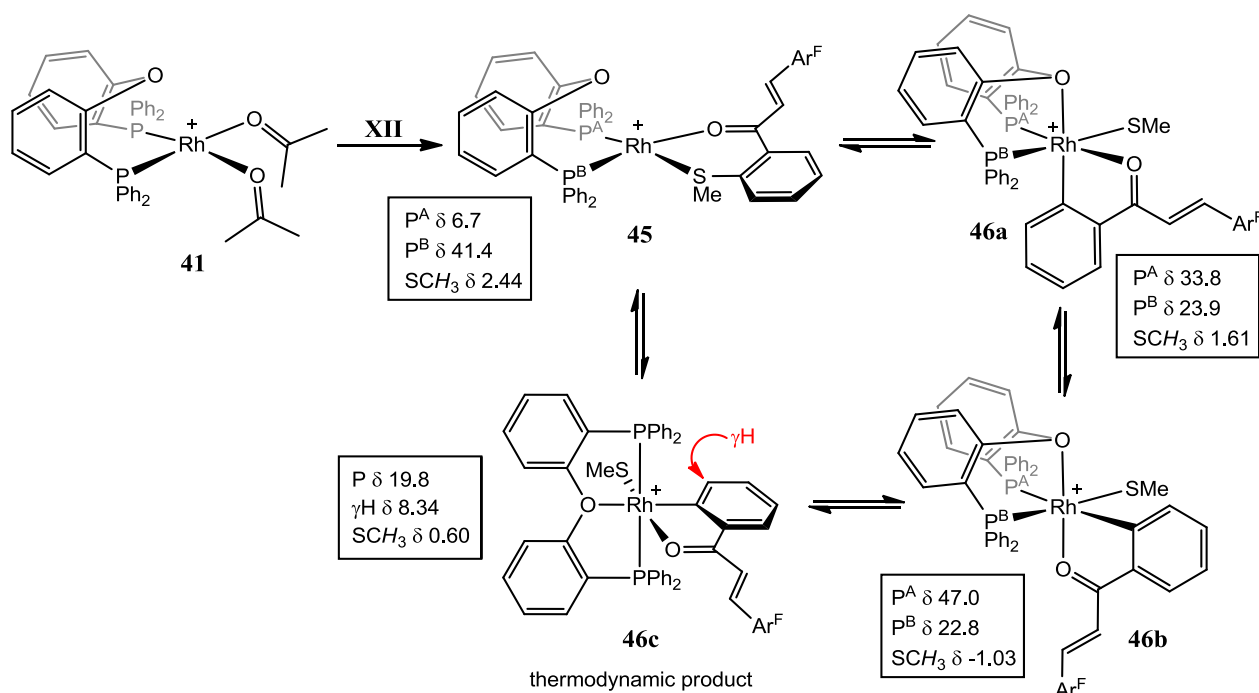


Scheme 4.10: Proposed mechanism for isomerisation of *anti*-43-D to *syn*-43-D. $[\text{CB}_{11}\text{H}_{12}]^-$ anions not shown.

4.5 Characterisation of linear complexes

In an attempt to prepare the linear analogue of complex **44**, isolated linear product (**XI**) was added to the bis-acetone species (**41**). However, this instead led to the formation of an equilibrium mixture of four species by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Only one of these four species is the coordinated product complex $[\text{Rh}(\text{cis-}\kappa^2_{(\text{PP})}\text{-DPEphos})\{\kappa^2_{(\text{OS})}\text{-C}_6\text{H}_3(\text{CF}_3)_2\text{CH=CHCO}(\text{C}_6\text{H}_4)\text{SMe}\}][\text{closo-CB}_{11}\text{H}_{12}]$ (**45**) (Scheme 4.11), which is observed as a doublet of doublets at δ 41.36 [$J(\text{RhP}) = 155.3$, $J(\text{PP}) = 38.6$] and 6.68 [$J(\text{RhP}) = 162.7$, $J(\text{PP}) = 38.6$], with a signal at δ 2.46 in the ^1H NMR spectrum, which is due to the SMe group. The related complex, $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-}^t\text{Bu}_2\text{PCH}_2\text{CH}_2\text{P}^t\text{Bu}_2)(\kappa^2_{(\text{OS})}\text{-CH}_3\text{C=OC}_6\text{H}_4\text{SCH}_3)][\text{Bar}^{\text{F}}_4]$ (**i-85**) shows

similar spectroscopic properties with signals observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 28.9 [dd, $J(\text{RhP}) = 165$, $J(\text{PP}) = 61$] and 7.5 [dd, $J(\text{RhP}) = 150$, $J(\text{PP}) = 61$], and at δ 2.44 in the ^1H NMR spectrum.³⁰ The other three complexes are the result of C-S activation occurring in complex **45**, and are isomeric forms of $[\text{Rh}(\kappa^3(\text{POP})\text{-DPEphos})(\text{SMe})(\kappa^1(\text{C})\text{-(C}_6\text{H}_4)\text{C=OCH=CH(C}_6\text{H}_3(\text{CF}_3)_2)]$ [*closo*-CB₁₁H₁₂]**(46a-c)**.



Scheme 4.11: Formation of coordinated linear product complex (**45**) and three isomers of the C-S activated complex (**46a-c**). [*closo*-CB₁₁H₁₂]⁻ anions not shown.

The C-S activated rhodium(III) complex (**46c**) with the DPEphos ligand adopting a *meridinal* configuration and the SMe *trans* to the coordinated oxygen group of the carbonyl, can be identified by a doublet signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 19.84 [$J(\text{RhP}) = 111.1$], a signal at δ 8.34 in the ^1H NMR spectrum which shows doublet of triplet multiplicity due to coupling of the γ -aryl proton to rhodium and

both phosphines [$J(\text{RhH}) = 8.5$, $J(\text{PH}) = 2.5$] and a singlet at δ 0.60 due to the SMe group, which shows a correlation to the phosphine signal in a ^1H - $^{31}\text{P}\{^1\text{H}\}$ HMBC NMR experiment (Figure 4.9). Similar spectroscopic data is observed for the related complex $[\text{Rh}(\text{mer-}\kappa^3(\text{POP})\text{-DPEphos})(\text{SMe})\{\sigma^1(\text{C})\text{-(C}_6\text{H}_4\text{)COCH}_3\}][\text{BAR}^{\text{F}}_4]$ (**i-107**), with a signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 20.0 [d , $J(\text{RhP}) = 109$], and at δ 8.35 [dt , $J(\text{RhH}) = 8.1$, $J(\text{PH}) = 1$] and δ 0.54 for the γ -aryl proton and SMe signals respectively, in the ^1H NMR spectrum.³¹

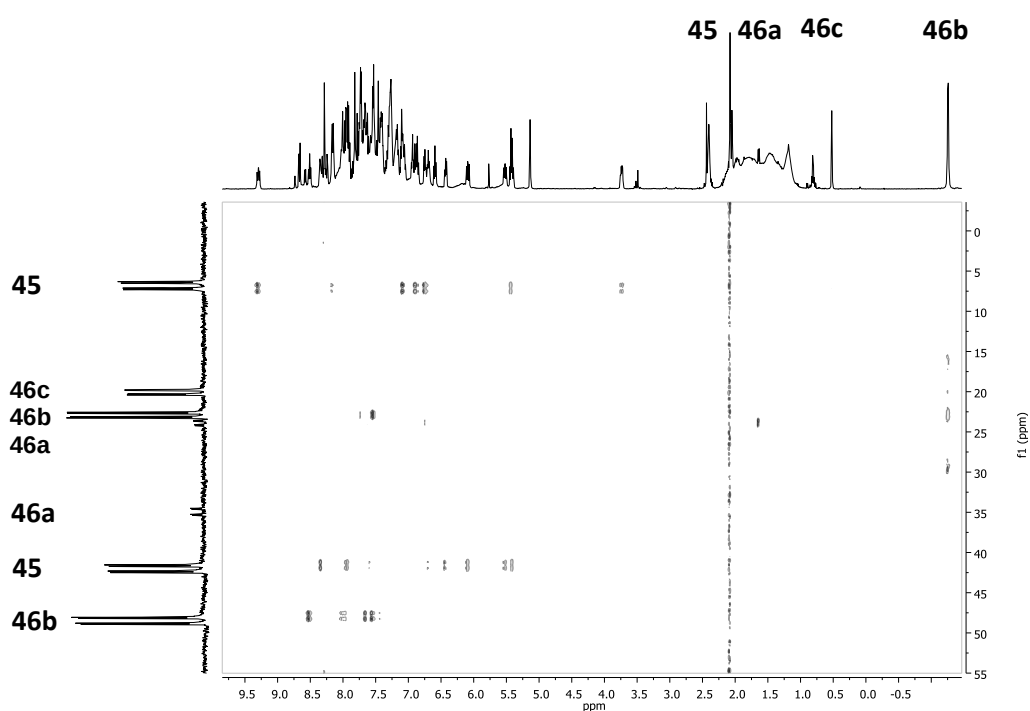


Figure 4.9: ^1H - $^{31}\text{P}\{^1\text{H}\}$ HMBC NMR spectrum (200 K) of coordinated linear product (**45**) and three isomers of C-S activated species (**46a–c**).

In the other two isomers, the DPEphos ligand has adopted a *facial* configuration, with either the SMe and carbonyl *trans* to the phosphines (**46a**), or the SMe and aryl group *trans* to the phosphines (**46b**). The spectroscopic data for these two complexes are similar; both are characterised by two doublet of doublet signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 33.86 [$J(\text{RhP}) = 151.5$, $J(\text{PP}) = 20.2$] and 23.95

[$J(\text{RhP}) = 107.6$, $J(\text{PP}) = 22.2$] for complex **46a**, with the SMe signal observed at δ 1.61 in the ^1H NMR spectrum. This is comparable to the related complex $[\text{Rh}(\text{fac-}\kappa^3(\text{POP})\text{-DPEphos})(\text{SMe})\{\sigma^1(\text{C})\text{-(C}_6\text{H}_4\text{)COCH}_3\}][\text{BAr}^{\text{F}}_4]$ (**i-109**), in which the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows δ 34.5 [dd, $J(\text{RhP}) = 151$, $J(\text{PP}) = 21$] and 25.3 [dd, $J(\text{RhP}) = 105$, $J(\text{PP}) = 21$], with the SMe signal at δ 1.51 in the ^1H NMR spectrum.³¹ The final complex, **46b**, is identified by signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 47.01 [$J(\text{RhP}) = 148.3$, $J(\text{PP}) = 28.9$] and 22.76 [$J(\text{RhP}) = 111.8$, $J(\text{PP}) = 28.5$], and the SMe at δ -1.03 in the ^1H NMR spectrum. The geometry of the final complex (**46b**) is assigned on the basis that the alternative C-S activated *facially* coordinated DPEphos isomer with the SMe group *trans* to the DPEphos ether linkage would not show the observed coupling between the sulphur and phosphorus in an ^1H - $^{31}\text{P}\{^1\text{H}\}$ HMBC experiment, which indicates they are mutually *trans*. ESI-MS of this mixture formed *in situ* results in a single signal observed at $[\text{M}]^+ m/z = 1031.16$ (calc. 1031.12) which matches the empirical formula for all four species (Figure 4.10). Over time the *meridionally* coordinated species (**46c**) is the only species observed, suggesting it is thermodynamically favoured.

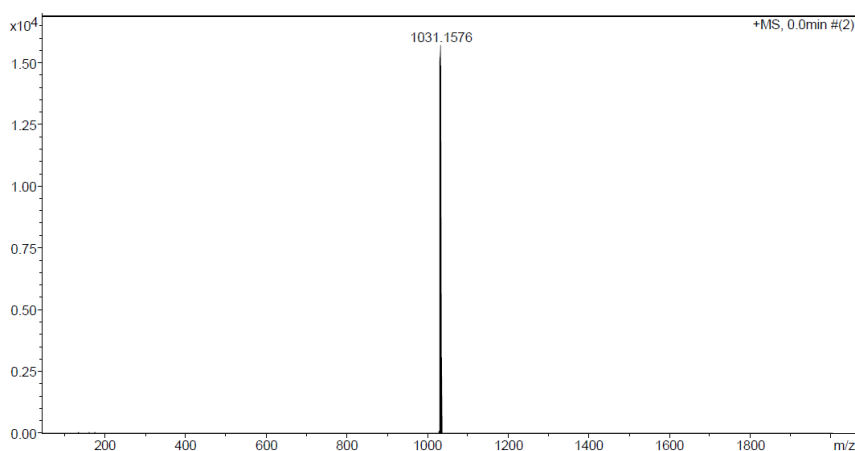
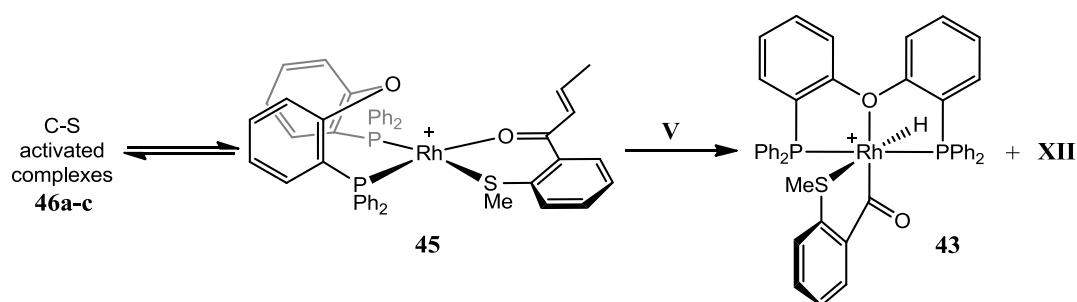


Figure 4.10: ESI-MS of complexes **45** and **46a-c**.

Addition of 1eq. of aldehyde **V** to the mixture of linear complexes (**45** and **46a – c**) slowly liberates free linear product (**XII**) and forms the acyl-hydride complex **43**. This indicates that C-S activation is reversible, and also that the rate of reductive elimination of the C-S activated products (reforming complex **45** which may then release free linear product **XII** and coordinate aldehyde **V**) is relatively slow (~ 2 hours) (Scheme 4.12).

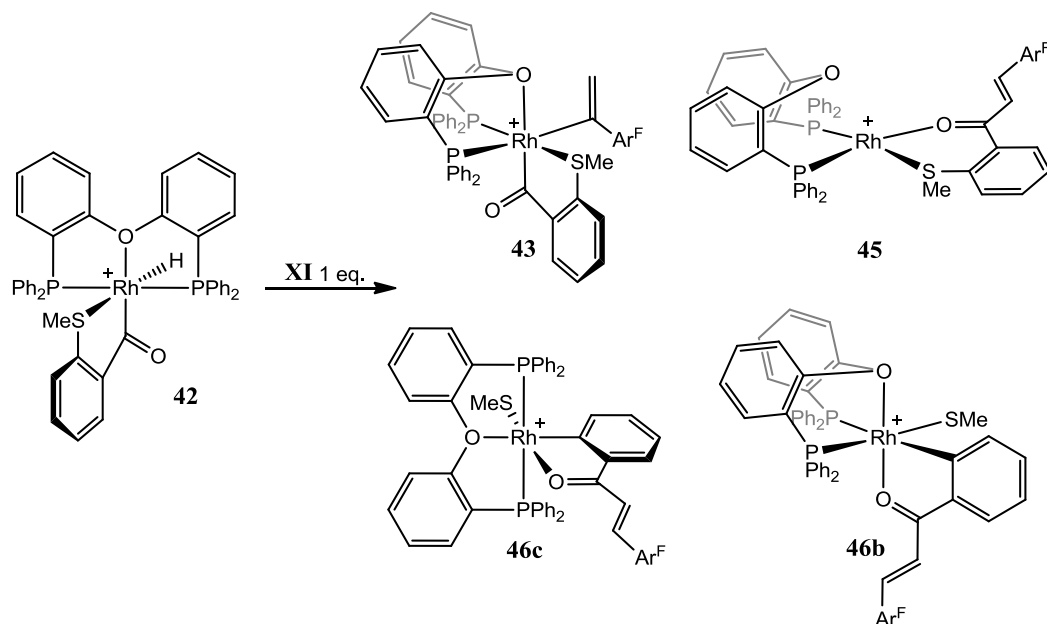


Scheme 4.12: Formation of coordinated linear product (**45**) and three isomers of the C-S activated species (**46a–c**). [*closo*-CB₁₁H₁₂][–] anions not shown.

Addition of isolated branched product (**XIII**) to the mixture of linear complexes (**45** and **46a – c**), leads to the formation of the coordinated branched complex (**44**) alongside the appearance of free linear product (**XII**) to give a ~1:1 mixture of linear:branched complexes (**45** and **46a – c**:**44**). The same equilibrium mixture is achieved by addition of isolated linear product (**XII**) to complex **44**, while addition of 1 equivalent each of isolated linear (**XII**) and branched (**XIII**) products to the bis-acetone complex (**42**) affords the same mixture of **44**, **45** and **46a – c**, indicating there is no strong preference over which complex is formed.

4.6 Stoichiometric reactions to elucidate the catalytic cycle

Retrospective assignment of NMR spectroscopy data for the stoichiometric addition of ~1 equivalent of alkyne **XI** to complex **42** is now possible, and identifies the species formed as the complexes **43**, **45**, **46b** and **46c**, as well as some unreacted **42** (Scheme 4.13 and Figure 4.11). These form in a ratio of 27:20:17:21:15 (**43**:**45**:**46b**:**46c**:**42**), or in terms of branched complex (**43**) to linear complexes (**45**, **46b** and **46c**), these form in a ratio of ~1:2.



Scheme 4.13: Addition of 1 eq. of alkyne **XI** to complex **42** forms a mixture of complexes **43**, **45** and **46b** and **46c**. [*closo*-CB₁₁H₁₂]⁻ anions not shown.

This provides some information about the relative rates of reductive elimination in the branched and linear reaction pathways, as well as the relative rates of hydride insertion to give the linear alkenyl and branched alkenyl intermediate complexes (**B** and complex **43**). The 2:1 ratio of the linear to branched complexes (formed on addition of ~1 equivalent of alkyne **XI** to **42**) suggests that the relative

rate of hydride insertion of the linear reaction is approx. twice as fast as that of the branched reaction. The linear reaction is complete by the time the first observation of the reaction mixture by NMR experiment can be taken (all of the linear complexes observed have undergone reductive elimination), indicating that the DPEphos system catalyses the linear reaction pathway rapidly at room temperature – turning over in less than 3 min. – while the branched reaction pathway effectively halts after the hydride insertion step. Extrapolating from the Eyring analysis of the rate of reductive elimination in complex **43** (to give complex **44**) gives a value of $1.2 \times 10^{-6} \text{ s}^{-1}$ for the rate of reductive elimination at 295 K, which is an order of magnitude slower than the observed rate at 313 K ($k_{\text{obs}} = 1.5 \times 10^{-5} \text{ s}^{-1}$), indicating that at room temperature this reaction (reductive elimination of **43** to **44**) is only very slowly taking place.

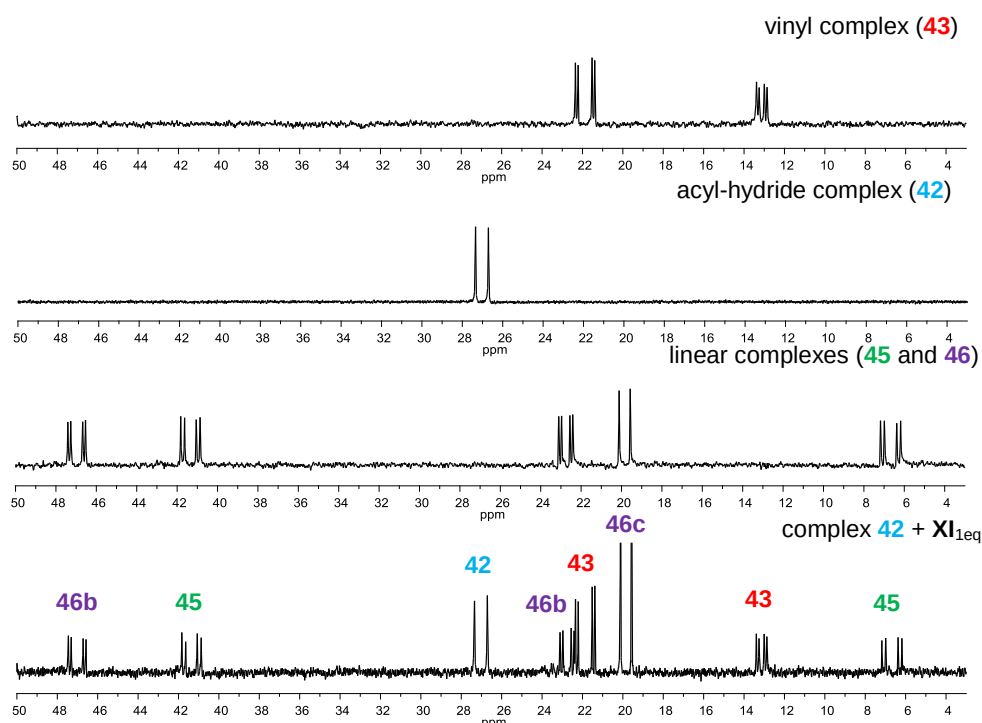
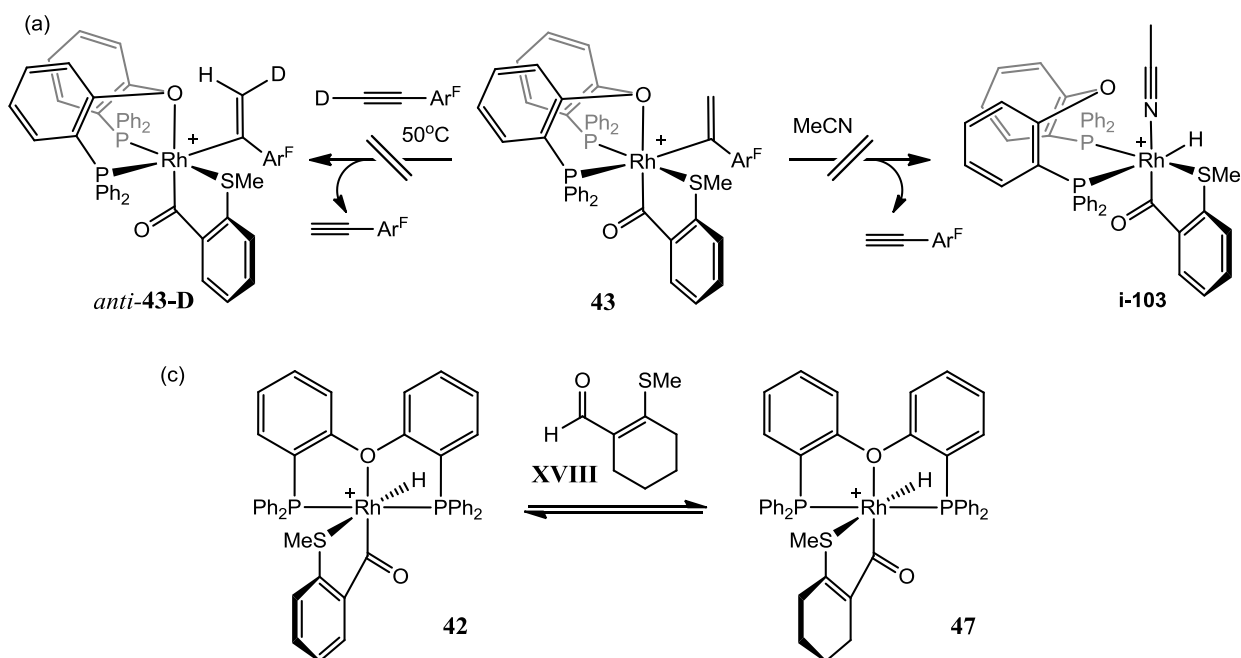


Figure 4.11: $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of 1eq. alkyne **XI** added to **42** (bottom), and its component parts (above). Integrals are 27:20:17:21:15 (**43:45:46b:46c:42**), i.e. 2:4:1 branched:linear:**42**.



Scheme 4.14: (a) Addition of alkyne **D-XI** or MeCN to complex **43** does not lead to exchange, or coordination of MeCN. (b) Addition of aldehyde **XVIII** to complex **42** forms a mixture of **42** and **47**. [*closo*-CB₁₁H₁₂]⁻ anions not shown.

Further stoichiometric reactions were undertaken to help elucidate the catalytic cycle. To determine if hydride insertion is reversible, one equivalent of deuterated alkyne **D-XI** was added to complex **43** in d₆-acetone. Reductive elimination is very slow at room temperature; consequently hydride de-insertion may have a similar energy barrier to overcome. Therefore the solution was heated to 50 °C and monitored by ¹H NMR spectroscopy over 12 hours. Over the course of the reaction complex **43** underwent reductive elimination to form **44**, with only negligible (<5%) incorporation of **D-XI**, effectively ruling out reversible hydride insertion coupled with alkyne exchange (Scheme 4.14a). Similar observations have been made for (PCP')Ru(PhC=CH₂)Cl;²² whereas (PCP)Ir(PhC=CH₂)(CCPh)(CO)⁸ does undergo this exchange. This of course only probes the branched reaction pathway, hydride insertion may be reversible in the linear pathway, as has been proposed

as a possible mechanism in the dpp2-*o*-iPr system described in the previous chapter.⁹ Further evidence against reversible hydride insertion is provided by the addition of excess (> 10 eq.) MeCN to complex **43**, which does not form the previously reported complex [Rh(DPEphos)(H)(COC₆H₄SMe)(MeCN)][*closo*-CB₁₁H₁₂] (**i-103**) (Scheme 4.14a).²¹ Addition of aldehyde **XVIII** to complex **42**, however, does lead to the immediate formation of a mixture of complexes; **42** and the related complex [Rh(*mer*- κ^3 (POP)-DPEphos)(H)(κ^1 (S)- σ^1 (C)-COC₆H₈SMe)][*closo*-CB₁₁H₁₂] (**47**), indicating that C-H activation is reversible as was observed in the previous chapter with the dpp2-*o*-iPr system (Scheme 4.14b).

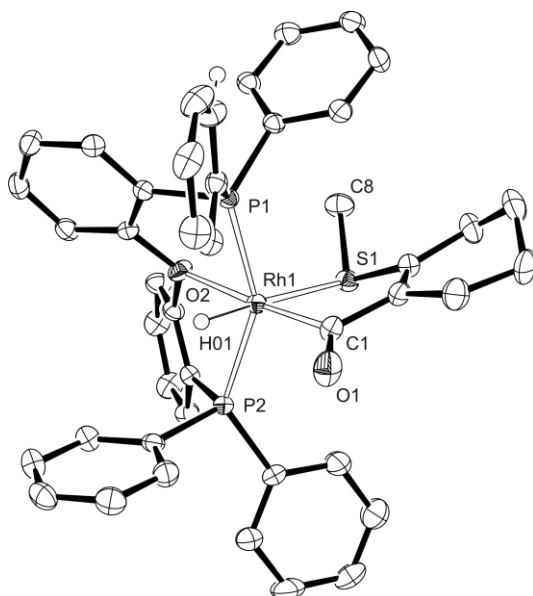
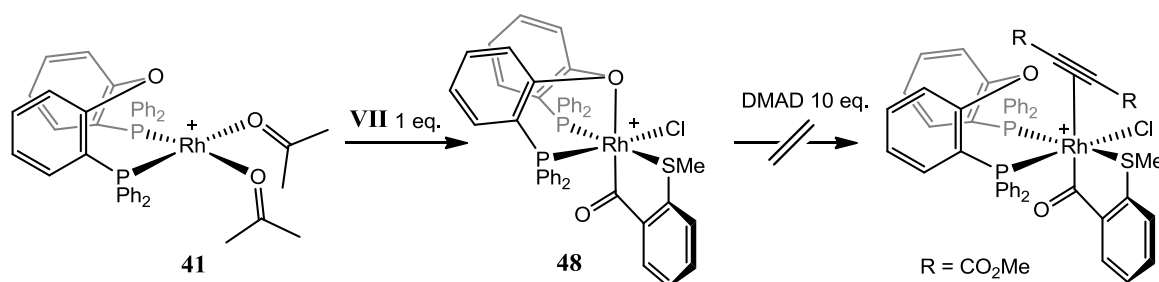


Figure 4.12: Molecular structures of the cationic portion of [Rh(κ^3 (POP)-DPEphos)(H)(κ^1 (S)- σ^1 (C)-COC₆H₈SCH₃)] [*closo*-CB₁₁H₁₂] (**47**) (major disordered component shown). Displacement ellipsoids are drawn at the 50% probability level. The anion and hydrogen atoms, apart from H01, are omitted for clarity. Selected bond lengths [Å]: Rh1-H01, 1.56(2); Rh1-P1, 2.3009(4); Rh1-P2, 2.3207(4); Rh1-O2, 2.2459(12); Rh1-C1, 1.9714(18); Rh1-S1, 2.4189(4). Selected bond angles [°]: P2-Rh1-P1, 149.256(16); C1-Rh1-S1, 83.14(5); H01-Rh1-S1, 173.8(8); C1-Rh1-O2, 175.91(6); (dihedral): C8/S1/Rh1/O2, 42.70(8).

Complex **47** is unknown and was characterised by NMR spectroscopy and X-ray crystallography. Solution data of **47** was consistent with the solid-state structure,

which was analogous to complexes **42**, **7** and **13** (Figure 4.12). One signal is observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at δ 127 [$J(\text{RhP}) = 127$], indicating a rhodium(III) oxidation state with equivalent phosphine environments. The alkyl backbone of the acyl group is masked by the carborane anion in the ^1H NMR spectrum. However, the SMe signal appears as an apparent doublet at δ 1.36 [$J(\text{HH}) = 1.6$], and a hydride is observed at δ -8.02 [$J(\text{RhH}) = 24$, $J(\text{PH}) = 4.6$, $J(\text{HH}) = 1.8$]. The bond lengths and angles observed in the solid-state structure of **47** are similar to those observed in **42**,²¹ **7** and **13**: the Rh1-O2 distance [2.2459(12) Å] indicates the oxygen is bound to the metal centre, and is within error of the distance observed in **42** [2.248(3) Å].



Scheme 4.15: Addition of acyl-chloride (**VII**) to complex **41** to give **48**.
Addition of DMAD to **48** does not form an isolable complex.
[*closo*-CB₁₁H₁₂]⁻ anions not shown.

In an attempt to form a complex analogous to the metal-acyl-hydride intermediate with coordinated alkyne (**A**, Scheme 4.6), the metal-acyl-chloride complex $[\text{Rh}(\text{fac-}\kappa^3(\text{POP})\text{-DPEphos})(\text{Cl})(\kappa^1(\text{S})\text{-}\sigma^1(\text{C})\text{-COC}_6\text{H}_8\text{SMe})][\text{closo-CB}_{11}\text{H}_{12}]$ (**48**) was first synthesised by addition of 1 eq. of acyl chloride **VII** to complex **41** in acetone (Scheme 4.15). Acyl-chlorides are useful analogues of acyl-hydride complexes, as they do not undergo migratory insertion. The DPEphos ligand adopts a *facial* geometry in this complex (**48**), in contrast to the *meridinal* geometry of the

DPEphos ligand **42**. Complex **48** was characterised by NMR spectroscopy, X-ray crystallography and ESI-MS. Two doublet of doublet signals are observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, at δ 29.08 [$J(\text{RhP}) = 133.2$, $J(\text{PP}) = 18.4$] and 16.70 [$J(\text{RhP}) = 139.7$, $J(\text{RhP}) = 18.3$], indicating *cis* inequivalent phosphine environments, *trans* to weak *trans* influence ligands. The analogous dpp2-*o*-ⁱPr and dpp2 complexes (**38** and **39** respectively) which can only adopt a *cis* configuration, also displayed two signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for inequivalent phosphines, with ^{103}Rh - ^{31}P coupling in the region of 127-149. A signal in the ^1H NMR spectrum of **48**, at δ 2.92 has been assigned as the SCH_3 protons, *trans* to the phosphine at δ 20.1, due to showing coupling (4.2 Hz) to the phosphine signal. This down field chemical shift, compared to the chemical shift of the SMe signal in **42** (at δ 1.68), is consistent with coordination *trans* to a lower *trans* influence phosphine ligand, as opposed to the high *trans* influence hydride ligand. The SMe chemical shift of **38** and **39** are δ 3.32 and 3.35 respectively. ESI-MS confirms the empirical formulation of $[\text{M}]^+ m/z = 827.27$ (calc. 827.06).

Crystals suitable for X-ray diffraction were obtained by diffusion of pentane into a solution of complex **48** in CH_2Cl_2 at room temperature (Figure 4.13). The solid-state structure is in agreement with the solution data. The complex adopts a psuedo-octahedral arrangement about the metal centre. The phosphine ligand is coordinated *fac*- κ^3 , with one phosphine *trans* to the chloride, and the other phosphine *trans* to the thioether. The P1-Rh1-P2 bond angle is $97.21(3)^\circ$, in contrast to the *mer*- κ^3 coordinated DPEphos ligand in **42**, which has a P-Rh-P bond angle of $155.93(5)^\circ$. The Rh1-O2 bond distance [$2.385(2) \text{ \AA}$] is longer than the

equivalent distance in complex **42** [2.248(3) Å],²¹ but similar to the distance observed in **43**, in which DPEphos is also coordinated *fac*- κ^3 [2.3458(17) Å].²

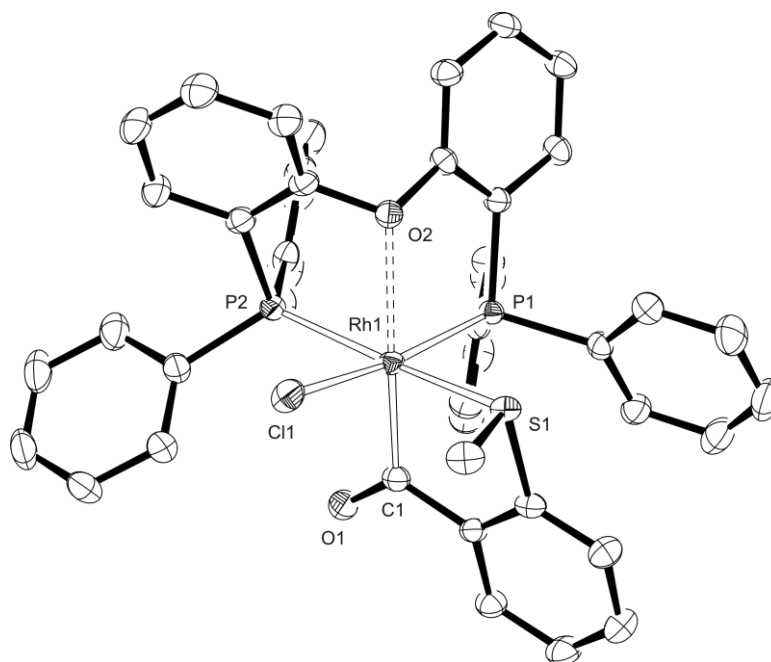


Figure 4.13: Molecular structures of the cationic portion of [Rh(κ^3 (POP)-DPEphos)(Cl)(κ^1 (S)- σ^1 (C)-COC₆H₄SCH₃)] [*closo*-CB₁₁H₁₂] (**48**). Displacement ellipsoids are drawn at the 50% probability level. The anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Rh1-C1, 1.977(3); Rh1-O2, 2.385(2); Rh1-P1, 2.2976(9); Rh1-P2, 2.3561(10); Rh1-S1, 2.3869(9); Rh1-Cl1, 2.3628(9); O1-C1, 1.207(5). Selected bond angles [°]: P1-Rh1-P2, 97.21(3).

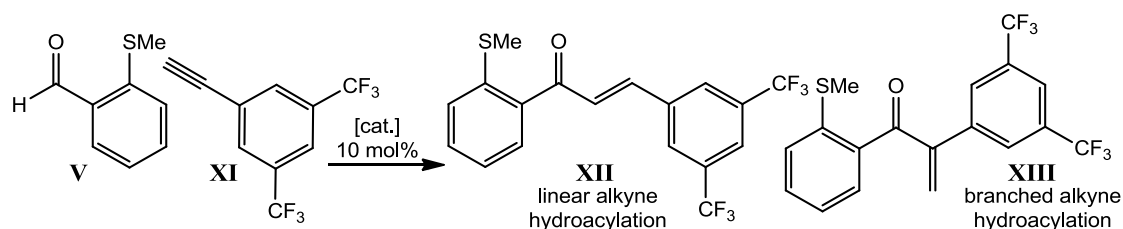
Unfortunately, addition of 10 equivalents of DMAD (MeO₂C-C≡C-CO₂Me) to **48** did not result in any observable change (Scheme 4.15), with the same species (**48**) observed by ¹H and ³¹P{¹H} NMR spectroscopy and ESI-MS.

^[2] A similar complex [Rh(*fac*- κ^3 (POP)-DPEphos-*o*-Me)(Cl)(κ^1 (S)- σ^1 (C)-COC₆H₈SMe)] [*closo*-CB₁₁H₁₂] [where DPEphos-*o*-Me = {P(C₆H₄Me)₂C₆H₄}₂O] has also been isolated and displays the same geometry. Details of the crystal structure are given in the appendix, but further studies with this ligand have not been undertaken.

4.7 Catalytic activity of the DPEphos system

Having identified the organometallic species observed throughout the catalytic cycle, investigations into the catalytic activity of the DPEphos system for the hydroacylation of alkyne **XI** by aldehyde **V** was readdressed. Due to the overlapping nature of the signals in the ^1H NMR spectra, meaning that there was difficulty in integrating the data unambiguously, the kinetic values derived from this data must be treated with caution and can only be discussed in general terms.

Table 4.2: Rates for the change in concentration of substrates for the hydroacylation of **V** and **XI** by DPEphos-based catalysts.^a



entry	catalyst	T (K)	aldehyde (V) $k \times 10^{-6} \text{ M s}^{-1}$	alkyne (XI) $k \times 10^{-6} \text{ M s}^{-1}$	linear (XII) $k \times 10^{-6} \text{ M s}^{-1}$	branched (XIII) $k \times 10^{-6} \text{ M s}^{-1}$
1 ^b	41	323	-2.54(8)	-2.31(9)	1.75(3)	0.96(7)
2 ^c	43	323	-2.91(5)	-2.63(3)	1.97(2)	1.03(1)
3 ^d	42	323	-2.51(1)	-1.77(2)	1.65(2)	0.913(2)
4 ^e	41	295	-0.132(7)	-0.094(8)	0.084(2)	0.040(1)

^aConditions: all manipulations under argon atmosphere, 0.18 M solution of complex in d_6 -acetone at stated temperatures, conversion determined by ^1H NMR spectroscopy. Rates determined by fitting zero order trendlines to data. ^bCatalyst:aldehyde ratio = 1:10, substrate ratio = 1:1 aldehyde:alkyne. ^cCatalyst:aldehyde ratio = 1:9, substrate ratio = 1:1 aldehyde:alkyne. ^dCatalyst:aldehyde ratio = 1:9, substrate ratio = 9:10 aldehyde:alkyne. ^eCatalyst:aldehyde ratio = 1:10, substrate ratio = 1:1 aldehyde:alkyne.

Under catalytic conditions (10 mol% bis-acetone complex **41**, 0.4 mL of d_6 -acetone, 323 K, 1:1 aldehyde **V**:alkyne **XI**) there is rapid catalysis of the linear reaction pathway (forming approx. two equivalents of linear product **XII**). However, by the time the first analysis is performed by NMR spectroscopy (~ 2

min.) the vinyl complex (**43**) is observed, and continues to be the only organometallic species evident during catalysis. After complex **43** has formed, the consumption of substrates (**V** and **XI**) and formation of products (**XII** and **XIII**) follow zero order kinetics, and the linear product (**XII**) grows in at a rate which is roughly twice as fast as the rate at which the branched product (**XIII**) grows in [$k_{\text{obs}} = 1.75(3) \times 10^{-6}$ and $0.96(7) \times 10^{-6} \text{ M s}^{-1}$ respectively] (entry 1, Table 4.2 and Figure 4.15). The observation of zero-order kinetics suggests that the rate-limiting step of the catalytic cycle is independent of the substrate concentration, i.e. hydride insertion is not rate determining and is irreversible.

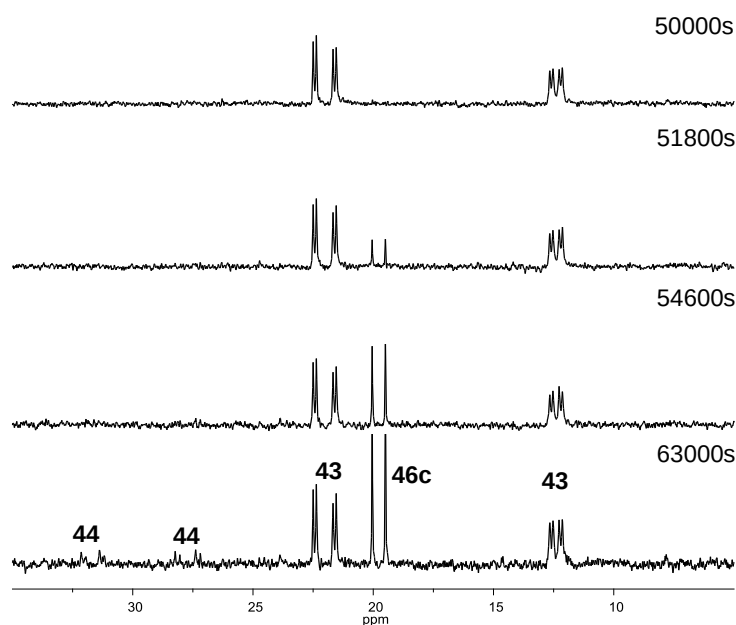


Figure 4.14: $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of catalytic reaction 10 mol% aldehyde **V** and alkyne **XI**, by complex **41**, over time.

Following catalysis by $^{31}\text{P}\{^1\text{H}\}$ as well as ^1H NMR spectroscopy (in a separate experiment, under the same conditions) shows that the co-ordinated branched complex (**44**) observed only after all substrate has been consumed and catalysis is complete ($\sim 50000 \text{ s}$) (Figure 4.14). Likewise, oxidative addition of the linear

product (**XII**) to form the C-S activated species (**46c**) is only observed after catalysis is complete. There is also no evidence of carbothiolation of the alkene hydroacylation product by alkyne (as has been reported to be catalysed by the DPEphos system),³¹ which indicates that C-S activation is not competitive with C-H activation of the aldehyde.

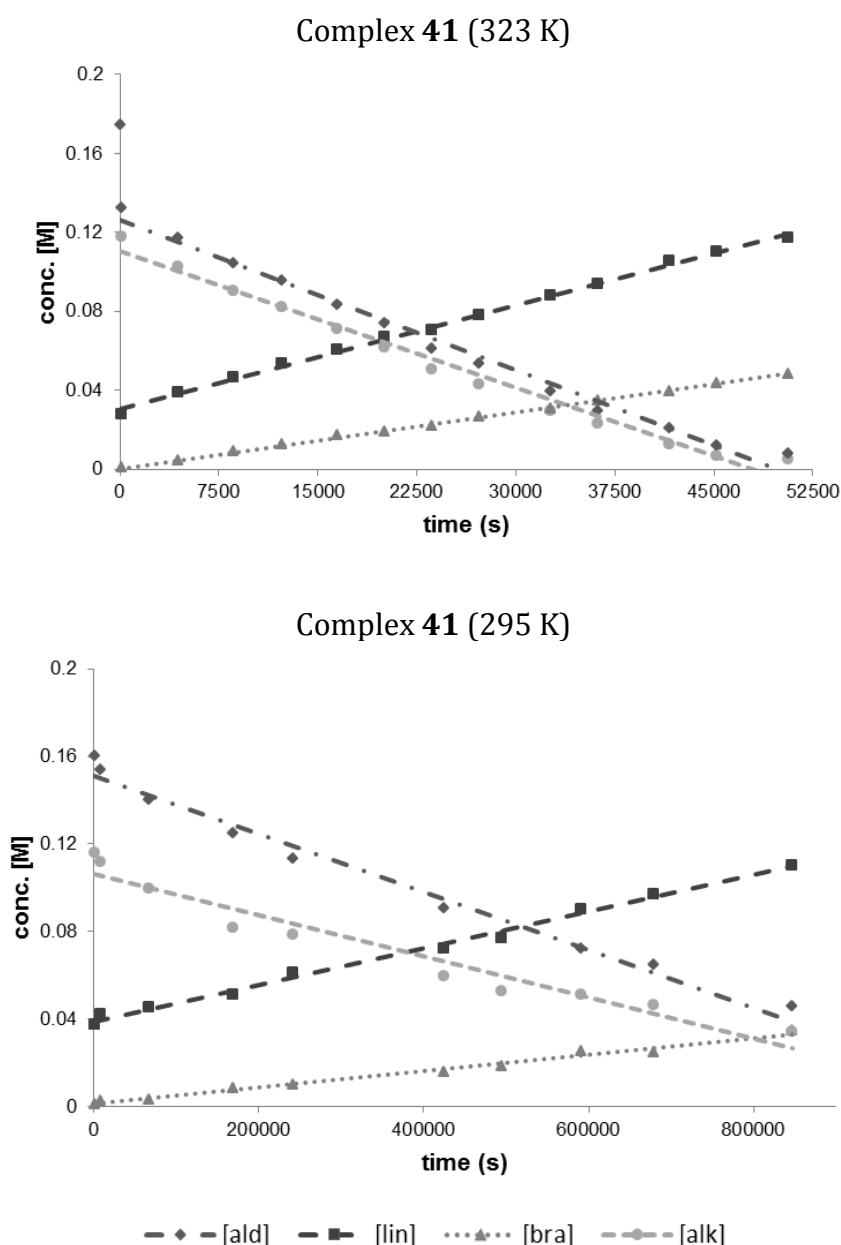


Figure 4.15: Concentration of substrates and products during catalysis of aldehyde **V** and alkyne **XI** by complex **41**, at 323 K and 295 K. See Table 4.2 for conditions. Plotted lines are linear fits.

Under catalytic conditions at room temperature (entry 4, Table 4.2 and Figure 4.15) the same initial rapid formation of linear product still occurs (forming ~ 2 eq. **XII**), and the only organometallic species observable by NMR spectroscopy is the vinyl complex (**43**). However, monitoring the reaction mixture over time shows that catalysis is taking place, albeit much more slowly than is observed at 323 K. Again product formation follows zero-order kinetics, and the linear product (**XII**) grows in at a rate which is roughly twice as fast as the rate at which branched product (**XIII**) grows in [$k_{\text{obs}} = 8.6(2) \times 10^{-8}$ and $4.0(1) \times 10^{-8} \text{ Ms}^{-1}$ respectively] (Figure 4.15).

This observation – even at room temperature – of an initial rapid reaction of the catalyst with substrates **V** and **XI** to form two eq. of the linear product (**XII**) and complex **43**, but no branched product (**XIII**), indicates that reductive elimination is a much lower energy process for the linear pathway than for the branched pathway. It also shows that once complex **43** has formed, it sits in a deep energy well and undergoes reductive elimination very slowly, i.e. it is comparatively inactive.

Figure 4.16 shows a hypothetical experiment in which the quantity of active catalyst is reduced by a percentage after each turnover. This models the partitioning of active (linear) and inactive (branched) catalytic pathways. If 20% of catalyst is lost each turnover (i.e. 80% of the catalyst remains active), then the apparent maximum number of catalyst turnovers achievable by the system is

approx. 4, i.e. the catalyst will turnover more than 4 times, but the cumulative total of product at the point at which all of the catalyst is inactive will be 4 equivalents of the original catalyst concentration.

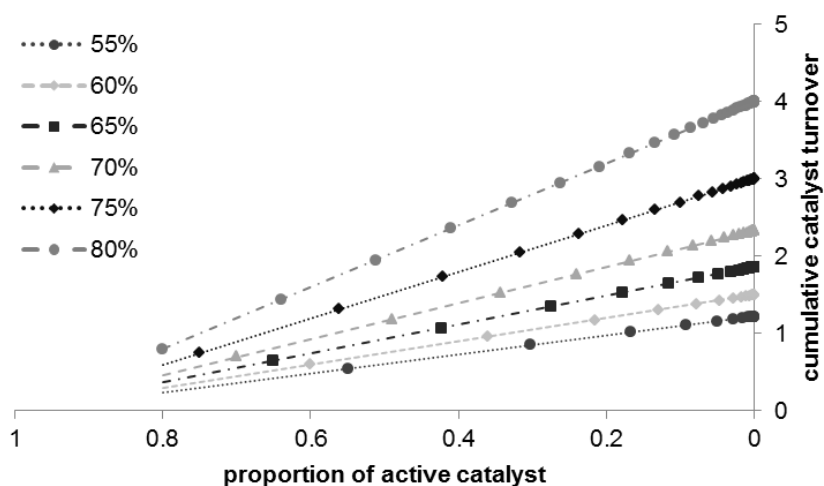


Figure 4.16: Cumulative total of catalytic turnover vs. proportion of active catalyst after each turnover. Demonstrating maximum cumulative catalyst turnover for a catalyst in which 55%-80% of the catalyst is still active after each turnover.

The fact that two turnovers of the linear reaction are observed at the start of catalysis in the DPEphos system (for the hydroacylation of **V** and **XI**), then catalytic activity effectively halts, indicates that only ~65% of the catalyst remains active after each turnover, i.e. 35% of the catalyst forms the (relatively) inactive vinyl complex **43** each turnover. This therefore is a partitioning ratio of ~2:1 in favour of the linear pathway. If a proportion of the catalyst $\{\text{Rh}(\text{DPEphos})\}^+$ pools as complex **43** each turnover, then eventually all of $\{\text{Rh}(\text{DPEphos})\}^+$ will be trapped as complex **43**, and then only through the much slower turnover of the branched reaction pathway (**43** to **44**) will the catalyst be released. This means that once all of the catalyst has pooled as complex **43**, its turnover in reductive elimination becomes effectively rate-controlling for the whole system. The zero

order consumption of substrates and formation of products is consistent with a rate which is concentration independent. The turnover of complex **43** is a first order process, dependent only on the concentration of complex **43**, therefore the concentration of the substrates has no effect on the rate. The sum of the branched and linear zero order rates at 323 K [rate = $k = 2.7 \times 10^{-6} \text{ M s}^{-1}$ for 0.018 M of catalyst] corresponds reasonably well with the first order kinetic data for the reductive elimination of complex **43** at 324 K. For a first order process rate = $k[A]$ M s^{-1} ; at 324 K the rate constant (k) was found to be $6.14(4) \times 10^{-5} \text{ s}^{-1}$ (at 0.024 M of complex **43**), which gives a rate of $1.5 \times 10^{-6} \text{ M s}^{-1}$. That the relative rates of linear (**XII**) and branched (**XIII**) product formation both show zero order kinetics is also consistent with the hydride-insertion step not being significantly reversible (Scheme 4.14a).

On starting catalysis with the vinyl complex (**43**) instead of the bis-acetone complex (**41**) under catalytic conditions (10 mol% complex **43**, 0.4 mL of d_6 -acetone, 323 K, 9 eq. of both substrates **V** and **XI**), no initial rapid catalysis of the linear reaction is observed; instead substrate consumption and product formation follow zero-order kinetics and the linear product (**XII**) grows in at a rate [$k_{\text{obs}} = 1.97(2) \times 10^{-6} \text{ M s}^{-1}$] which is roughly twice as fast as the branched product (**XIII**) [$k_{\text{obs}} = 1.03(1) \times 10^{-6} \text{ M s}^{-1}$] (entry 2, Table 4.2 and Figure 4.17). These rates are also essentially the same as the rates observed when starting with complex **41** – after the initial burst of catalytic activity – supporting the theory that the formation of complex **43** effectively controls the rate of the linear reaction.

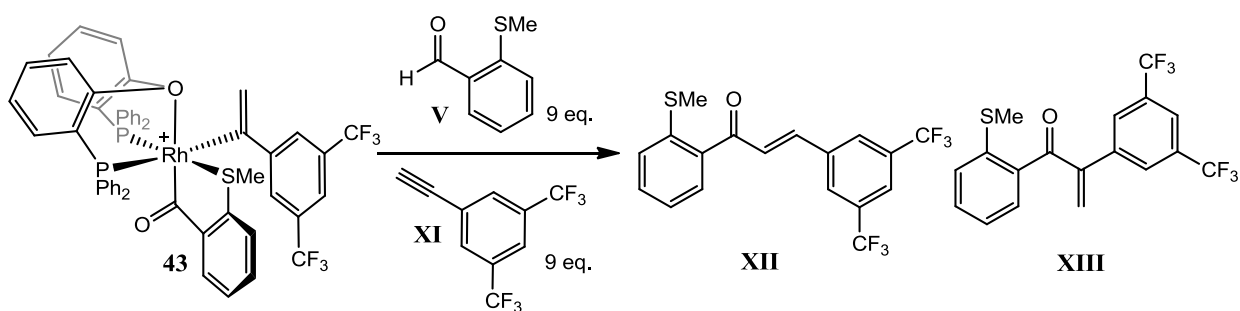
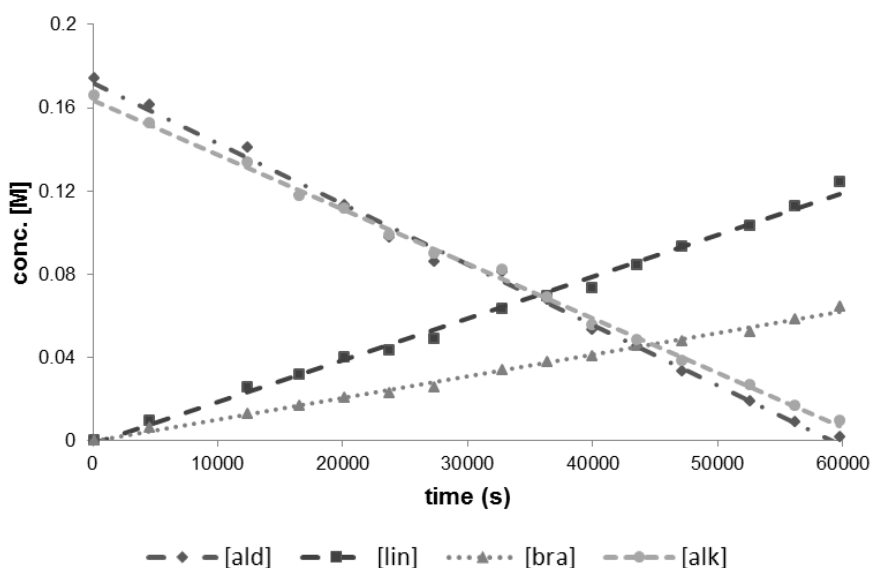
Complex **43** (323 K)

Figure 4.17: Concentration of substrates and products during catalysis of aldehyde **V** and alkyne **XI** by complex **43** at 323 K. See Table 4.2 for conditions.

To investigate if a different catalyst was forming from the bis-acetone complex (**41**) which was responsible for the initial catalytic activity of the linear reaction pathway, but then dying after the first minutes, the acyl-hydride complex (**42**) was chosen as a catalyst which is within the catalytic cycle but has not already selected for either linear or branched reaction pathways. Conditions were adjusted to 10 mol% complex **42**, 0.4 mL of d_6 -acetone, 323 K, 9 eq. of aldehyde **V** and 10 eq. of alkyne **XI**. Once again the initial rapid linear formation is observed, after which the two products grow at a rate which follows zero-order kinetics, and is roughly 2:1

linear (**XII**) to branched (**XIII**) [$k_{\text{obs}} = 1.65(2) \times 10^{-6}$ and $0.913(2) \times 10^{-6} \text{ M s}^{-1}$ respectively] (entry 3, Table 4.2 and Figure 4.18). Only complex **43** is observed during catalysis, and the rates of product formation are essentially the same as observed when starting with either complexes **41** or **43**. This strongly suggests that the bis-acetone complex (**41**), acyl-hydride complex (**42**) and branched alkenyl complex (**43**) lie within the same catalytic cycle.

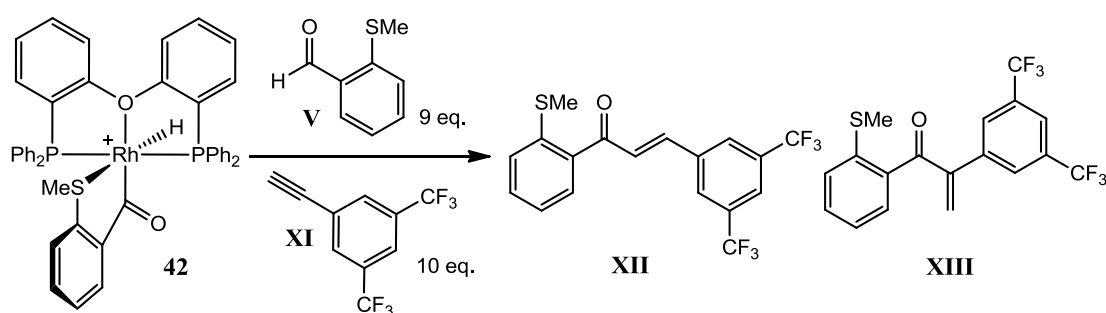
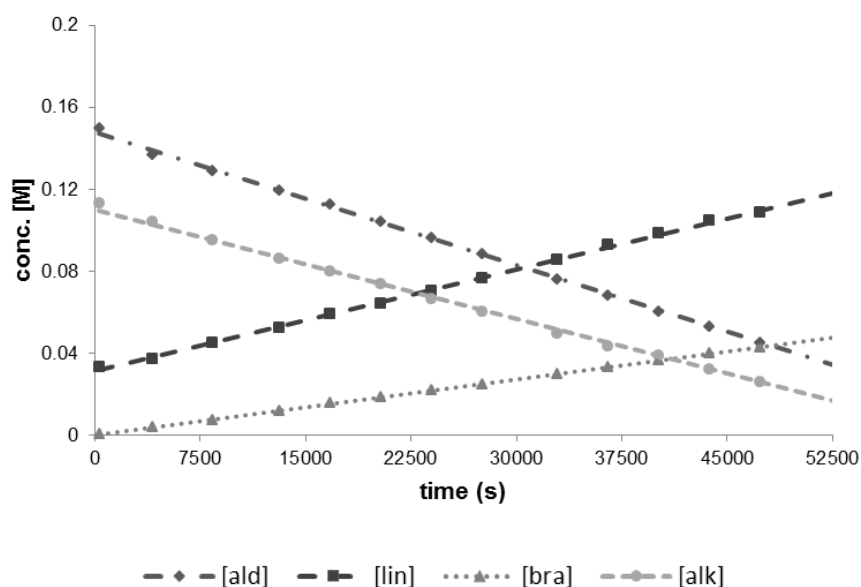
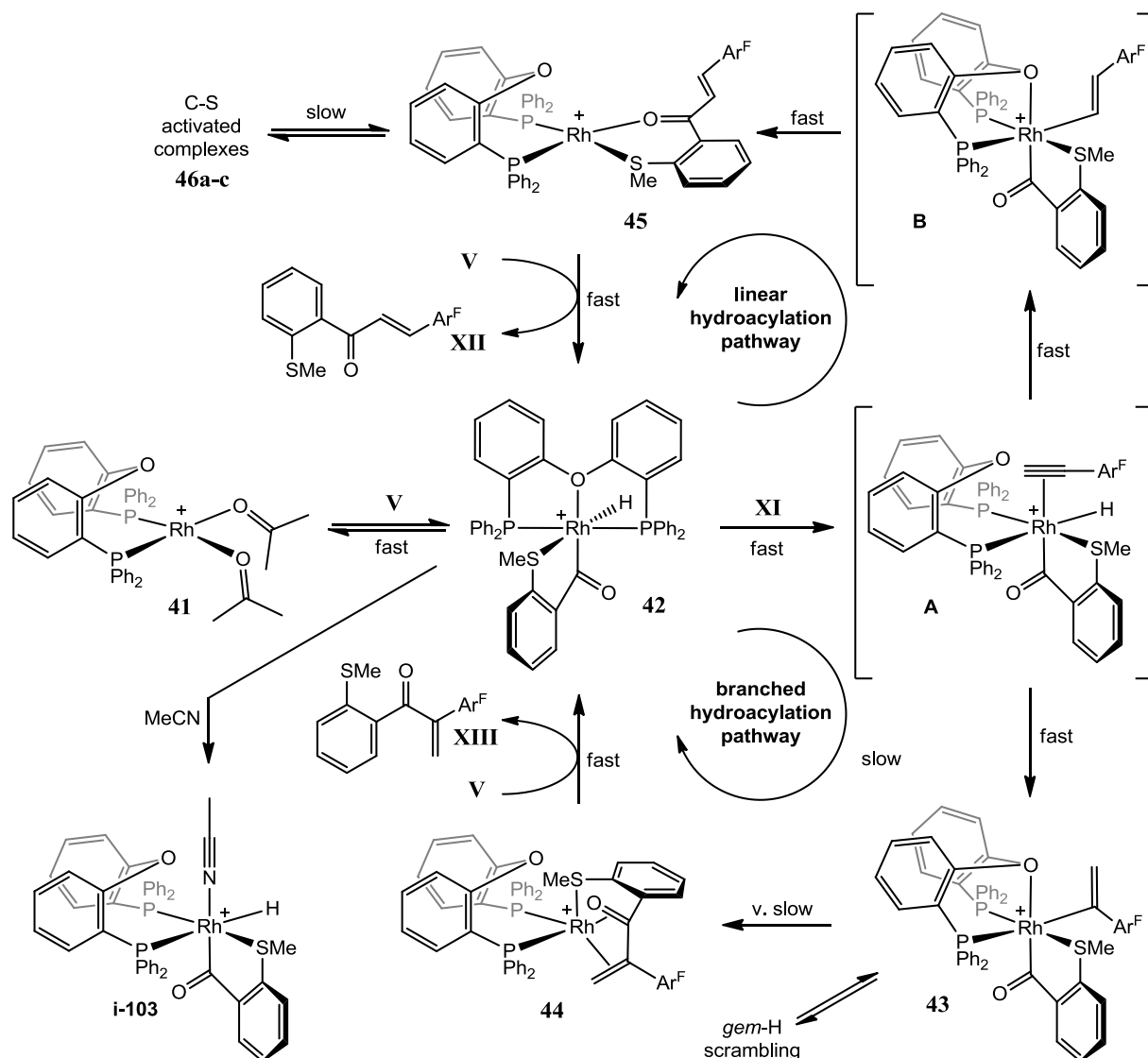
Complex **42** (323 K)

Figure 4.18: Concentration of substrates and products during catalysis of aldehyde **V** and alkyne **XI** by complexes **43** and **42** at 323 K. See Table 4.2 for conditions.

4.8 Proposed catalytic cycle



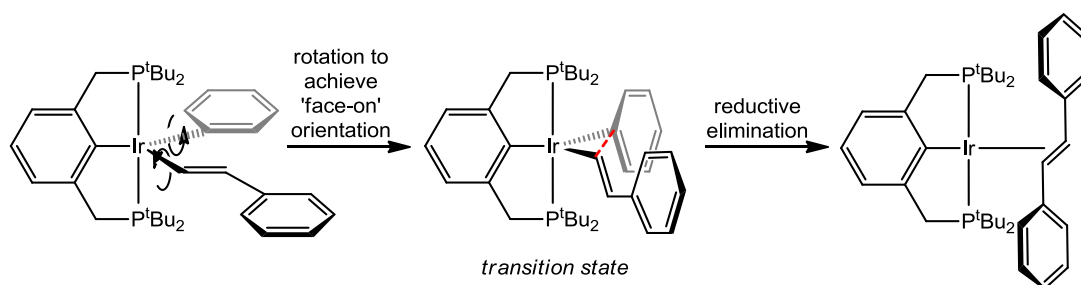
Scheme 4.16: Proposed mechanism for the catalytic hydroacylation of aldehyde **V** and alkyne **XI** to give linear (**XII**) and branched (**XIII**) products. [*closo*-CB₁₁H₁₂]⁻ anions not shown.

From this data, combined with the stoichiometric studies, the mechanism presented in Scheme 4.15 is proposed. Addition of aldehyde **V** to the precursor complex **41** leads to the rapid formation of an equilibrium with the acyl-hydride complex **42** in which only complex **42** is observed. Alkyne **XI** may coordinate, *via* the hemi-labile action of the DPEphos ligand, to give the proposed intermediate

complex **A**. Evidence for intermediate **A** is provided by the isolation of an MeCN analogue (**i-103**) of this complex by Gemma Moxham (Weller group) which demonstrates that the DPEphos oxygen donor may dissociate in the presence of an incoming ligand.²¹ This common intermediate (**A**) may then undergo hydride insertion to give a postulated linear alkenyl intermediate (complex **B**) or the branched alkenyl intermediate (**43**). It is proposed that the rate of hydride insertion in intermediate **A**, to give the linear intermediate (**B**) is approx. twice the rate of formation of the vinyl complex (**43**), on the basis of two linked observations: addition of one equivalent of alkyne **XI** to complex **42** leads to a ~2:1 mixture of linear to branched species (Figure 4.11, p.194); while the observation of approx. two turnovers of the linear reaction (forming two eq. of **XII**) on addition of excess **V** and **XI** to **41** (i.e. 5 eq. used to isolate **43**, and 10 eq. during catalysis), indicates the catalytic pathway is partitioning 2:1 linear to branched, and only the linear pathway is turning over with any observable rate (Figure 4.16).

Reductive elimination from the vinyl complex (**43**) and the linear intermediate (**A**) forms the coordinated branched and linear products (**44** and **45** respectively), which de-coordinate immediately in the presence of aldehyde to reform complex **42**. The stoichiometric addition of aldehyde **V** to **44** leads to the immediate formation of **42**; however, the addition of aldehyde **V** to the linear complexes **45** and **46a-c** does not lead to the immediate formation of **42**, and is instead a relatively slow process. This is accounted for on the basis that the equilibrium between the linear complexes (**45** and **46a-c**) lies towards complex **46c**; for the

linear product (**XII**) to de-coordinate, complex **45** must first reform from the C-S activated complexes (**46a-c**). The rate of this equilibrium must be the same in both directions; if the reductive elimination from **46a-c** to give **45** is slow, then the reverse (**45** to give **46a-c**) must also be slow, and therefore, if the rate of aldehyde coordination and C-H activation is fast – as is suggested by the immediate formation of **42** on addition of aldehyde **V** to **41** – this will occur more readily than C-S activation while there is free aldehyde **V** present. Evidence for this comes from the fact that no linear complexes (**45** and **46a-c**) are observed until aldehyde is no longer present in the mixture (Figure 4.11).



Scheme 4.17: A ‘face-on’ orientation is necessary for reductive elimination. When the groups are already appropriately orientated reductive elimination is rapid; where this is not the case, rotation of the groups is necessary.

Krogh-Jespersen and Goldman undertook DFT studies on systems such as $\text{Ir}(\text{PCP})\text{Ph}(\text{CH}=\text{CHPh})$, to investigate the relative barriers to reductive elimination to form C-C bonds of different hybridisation (sp , sp^2 , sp^3).⁷ These showed that before reductive elimination could take place, the alkenyl group must first twist (90°) away from its ground-state orientation so that it is perpendicular to the impending C-C bond (Scheme 4.17). This gives a ‘face-on’ orientation between the two groups about to undergo reductive elimination, which minimises the steric resistance during the sp^2 - sp^2 reductive elimination. In complex **43**, the alkenyl

group lies in line with the Rh1-O1 bond [dihedral angle is $8.9(3)^\circ$], and would need to twist around the Rh1-C1 axis so that it was in line with either the Rh1-S1 bond [dihedral angle in **43** is $-86.6(3)^\circ$] or the Rh1-P2 bond [dihedral angle in **43** is $88.5(3)^\circ$]. Although the structure of the linear intermediate (**A**) is unknown, experimental results suggest the barrier to C-C bond formation in this intermediate is lower than in complex **43**, possibly due to an orientation whereby the acyl and alkenyl groups are correctly orientated for reductive elimination in the ground state. Further evidence for this is provided by the same researchers,⁸ who showed that steric crowding in branched intermediates $[\text{Ir}(\text{PCP})(\text{CCP})(\text{CPh}=\text{CH}_2)]$ inhibited reductive elimination, even though the intermediates are higher in energy than the linear counterparts $[\text{Ir}(\text{PCP})(\text{CCP})(\text{CH}=\text{CHPh})]$ (Figure 1.18, p.41).

4.9 Simulation of kinetics

Kinetic modelling was undertaken by Prof. Guy Lloyd-Jones of Bristol University. His report is reproduced here *verbatim*.

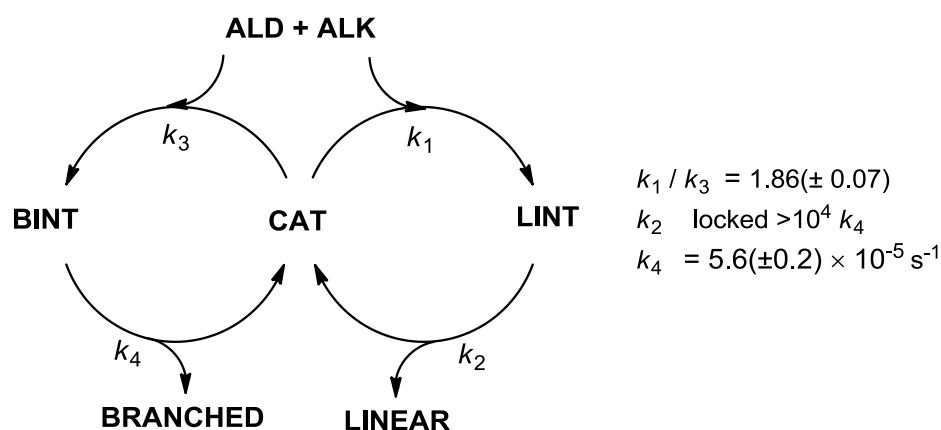


Figure 4.19: Model used for kinetic analysis.

Kinetic modelling supports the proposed mechanism with the rate of reductive elimination from **43** comparing well with experiment [modelled, $5.6(2) \times 10^{-5} \text{ s}^{-1}$; experiment, $6.14(4) \times 10^{-5}$]. When starting from **41** the y-intercept corresponds to $\{[\text{cat}] \times k_{\text{rel}}\}$, where k_{rel} is the partitioning at the hydride insertion step between **B** and **43**. This is 1.86(7) in favour of the linear pathway at 323 K, also consistent with our experimental observations. The linearity of the early-phase temporal evolution of the linear product confirms that the relative rate of reductive elimination is more than 3 orders of magnitude greater from linear (i.e. **B**) versus branched (**43**) intermediates. Moreover the sum of the rates of linear and branched [$2.71 \times 10^{-6} \text{ M s}^{-1}$ at 0.18 M] corresponds well to rate of reductive elimination in the branched isomer from **43**, which is thus the rate-limiting step in the overall catalytic cycle presented in Scheme 4.17. Figure 4.20 shows the kinetic modelling (lines) and the experimental data (points) for the concentration of substrates **V** and **XI**, and products **XII** and **XIII**, starting with complexes **41** and **43** respectively.

The simplified model presented [in Figure 4.19], in which many steps have been telescoped, some to nominal termolecularity, is intended solely to provide a quantitative fit of substrate and product temporal concentration data in support of the partitioning of resting states in the hydroacylation reaction. The model should not be interpreted in isolation or indeed in any quantitative manner other than the magnitude of the rate constant associated with reductive elimination in the branched manifold (k_4 ; s^{-1}), and the global partitioning between linear and branched manifolds (k_1 / k_3 ; dimensionless).

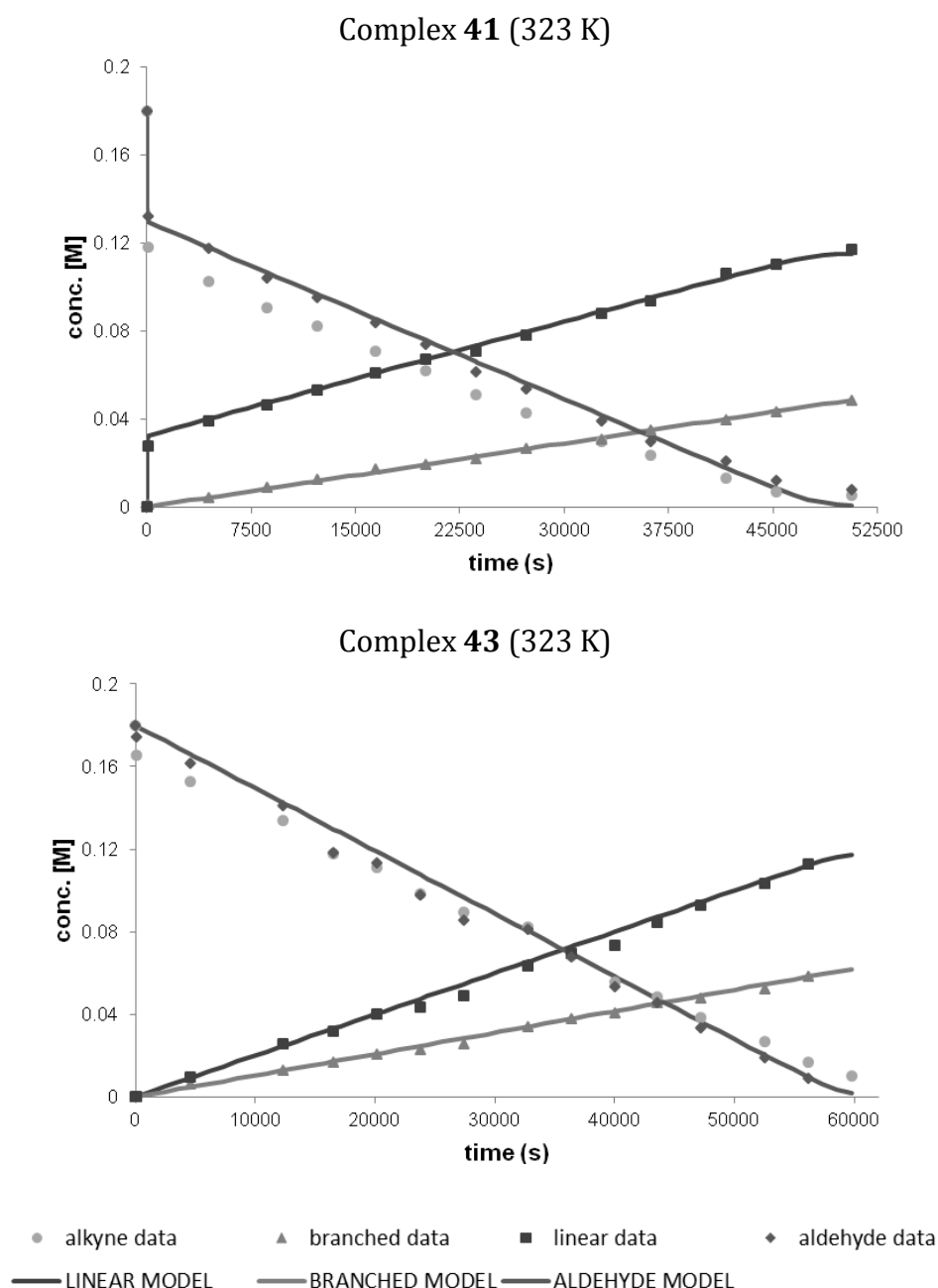


Figure 4.20: Plotted points show experimentally observed concentration of substrates and products during catalysis of aldehyde **V** and alkyne **XI** by complexes **41** and **43** at 323 K. Solid lines show kinetic modelling.

The model was simulated by iteration of two rate constants (k_1 and k_4) using Dynochem software (Scale-up Systems Ltd, Dublin, Eire) with rate constants k_2 and k_3 locked at values for which the model was insensitive to, within the data-density explored, and with equal weighting to the temporal concentration data for

aldehyde ("Ald"), and both hydroacylation products ("Branched" and "Linear"). Two datasets were simulated conducted, both with $[ALK]_0 = [ALD]_0 = 0.18\text{ M}$, and one starting with $[CAT]_0 = 0.018\text{ M}$ the other with $[BINT]_0 = 0.018\text{ M}$; affording satisfactory fits within the range of rate constants indicated.

4.10 Conclusion

The isolation of complex **43** is the first time that the intermediate which directly precedes the reductive elimination step in any hydroacylation reaction has been isolated. This allowed the mechanism to be probed, determining for this system that hydride insertion rather than acyl migration occurs. Furthermore, hydride insertion to give the branched alkenyl is irreversible, in contrast to the reversible hydride insertion proposed for the catalysis of the alkene hydroacylation reaction by the diphosphine catalysts described in the previous chapter. An isomerisation process is also taking place between the branched alkenyl protons, which is proposed to occur *via* a metallacyclopropenyl intermediate complex.

This DPEphos system catalyses both the linear and branched reaction pathways, which allows insight into factors affecting selectivity within this catalytic cycle, which can inform investigations into other catalytic systems. Kinetic modelling correlated well with the experimental observations, and provided support for the proposed overall catalytic cycle. In this system, bifurcation of the reaction pathway occurs at the hydride insertion step, which partitions 1:1.86(7) in favour of the linear pathway, at 323 K. Reductive elimination from the linear alkenyl

intermediate (**B**) is at least 10^3 times faster than reductive elimination from the branched alkenyl intermediate (**43**). A possible explanation for this difference in rates of reductive elimination comes from arguments put forward by Krogh-Jespersen and Goldman,^{7, 8} who showed that steric crowding in branched complexes can disfavour the orientation necessary for reductive elimination to take place, and so slow the rate of this reaction, despite being higher energy complexes than the analogous linear alkenyl complex.

4.11 References

1. L. W. Chung, O. Wiest and Y. D. Wu, *The Journal of Organic Chemistry*, 2008, **73**, 2649-2655.
2. Z. Shen, P. K. Dornan, H. A. Khan, T. K. Woo and V. M. Dong, *Journal of the American Chemical Society*, 2009, **131**, 1077-1091.
3. I. F. D. Hyatt, H. K. Anderson, A. T. Morehead and A. L. Sargent, *Organometallics*, 2008, **27**, 135-147.
4. A. C. Cooper, E. Clot, J. C. Huffman, W. E. Streib, F. Maseras, O. Eisenstein and K. G. Caulton, *Journal of the American Chemical Society*, 1998, **121**, 97-106.
5. J. T. Poulton, M. P. Sigalas, O. Eisenstein and K. G. Caulton, *Inorganic Chemistry*, 1993, **32**, 5490-5501.
6. Q. Meng, W. Shen, R. He and M. Li, *Transition Metal Chemistry*, **36**, 793-799.
7. R. Ghosh, T. J. Emge, K. Krogh-Jespersen and A. S. Goldman, *Journal of the American Chemical Society*, 2008, **130**, 11317-11327.
8. R. Ghosh, X. Zhang, P. Achord, T. J. Emge, K. Krogh-Jespersen and A. S. Goldman, *Journal of the American Chemical Society*, 2007, **129**, 853-866.
9. C. González-Rodríguez, R. J. Pawley, A. B. Chaplin, A. L. Thompson, A. S. Weller and M. C. Willis, *Angewandte Chemie International Edition*, **50**, 5134-5138.
10. M. M. Coulter, K. G. M. Kou, B. Galligan and V. M. Dong, *Journal of the American Chemical Society*, 2010, **132**, 16330-16333.
11. G. L. Moxham, H. Randell-Sly, S. K. Brayshaw, A. S. Weller and M. C. Willis, *Chemistry – A European Journal*, 2008, **14**, 8383-8397.
12. C. P. Lenges, P. S. White and M. Brookhart, *Journal of the American Chemical Society*, 1998, **120**, 6965-6979.
13. A. H. Roy, C. P. Lenges and M. Brookhart, *Journal of the American Chemical Society*, 2007, **129**, 2082-2093.
14. I. F. D. Hyatt, H. K. Anderson, A. T. Morehead and A. L. Sargent, *Organometallics*, 2007, **27**, 135-147.
15. K. Kundu, J. V. McCullagh and A. T. Morehead, *Journal of the American Chemical Society*, 2005, **127**, 16042-16043.
16. A. C. Cooper, E. Clot, J. C. Huffman, W. E. Streib, F. Maseras, O. Eisenstein and K. G. Caulton, *Journal of the American Chemical Society*, 1998, **121**, 97-106.
17. G. L. Moxham, H. Randell-Sly, E. , S. Brayshaw, K., R. L. Woodward, A. S. Weller and M. Willis, C., *Angewandte Chemie International Edition*, 2006, **45**, 7618-7622.
18. C. A. Reed, *Accounts of Chemical Research*, 2009, **43**, 121-128.
19. W. E. Buschmann, J. S. Miller, K. Bowman-James and C. N. Miller, in *Inorganic Syntheses*, ed. C. Dimitri, 2002, vol. 33, p. 83.
20. W. Reilly, MChem, *Hydroacylation: New catalysts for combined C-H activation and C-C bond formation*, University of Oxford, 2011.
21. G. L. Moxham, H. Randell-Sly, S. K. Brayshaw, A. S. Weller and M. C. Willis, *Chemistry - A European Journal*, 2008, **14**, 8383-8397.
22. W. Weng, S. Parkin and O. V. Ozerov, *Organometallics*, 2006, **25**, 5345-5354.
23. M. Portnoy and D. Milstein, *Organometallics*, 1994, **13**, 600-609.
24. T. Foo and R. G. Bergman, *Organometallics*, 1992, **11**, 1811-1819.
25. L. Benhamou, V. César, N. Lugan and G. Lavigne, *Organometallics*, 2007, **26**, 4673-4676.
26. R. S. Tanke and R. H. Crabtree, *Journal of the American Chemical Society*, 1990, **112**, 7984-7989.
27. C.-H. Jun and R. H. Crabtree, *Journal of Organometallic Chemistry*, 1993, **447**, 177-187.
28. K. Tanaka and G. C. Fu, *Journal of the American Chemical Society*, 2001, **123**, 11492-11493.
29. J. Cid, J. J. Carbó and E. Fernández, *Chemistry – A European Journal*, **18**, 1512-1521.
30. A. B. Chaplin, J. F. Hooper, A. S. Weller and M. C. Willis, *Journal of the American Chemical Society*, 2012, **134**, 4885-4897.
31. J. F. Hooper, A. B. Chaplin, C. González-Rodríguez, A. L. Thompson, A. S. Weller and M. C. Willis, *Journal of the American Chemical Society*, **134**, 2906-2909.

5.1 General

All manipulations, unless otherwise stated, were performed under an atmosphere of argon, using standard Schlenk-line and glove-box techniques. Glassware was oven dried at 130 °C overnight and flamed under vacuum prior to use. CH₂Cl₂, CH₃CN, Et₂O, THF, toluene, benzene, hexane, and pentane were dried using a Grubbs-type solvent purification system (MBraun SPS-800) and degassed by successive freeze-thaw degas cycles.¹ Acetone and d₆-acetone were dried over Ba₂O₃ and vacuum distilled twice.² CD₂Cl₂, C₆H₅F and 1,2-C₆H₄F₂ were distilled under vacuum from CaH₂ and stored over 3 Å molecular sieves. Methanol and ethanol were dried over sodium; vacuum distilled and stored over 3 Å molecular sieves. Microanalyses were performed by Elemental Microanalysis Ltd or London Metropolitan University.

5.2 Nuclear Magnetic Resonance spectroscopy

NMR spectra were recorded on Varian Unity 500 MHz, Varian Mercury 300 MHz, Varian Venus 300 MHz, Bruker DRX 500 or Bruker AVC 500 MHz spectrometers at room temperature, unless otherwise stated. Residual protio solvent was used as reference for ¹H and ¹³C NMR spectra in deuterated solvent samples. In 1,2-C₆H₄F₂, C₆H₅F and (CH₃)₂CO, ¹H NMR spectra were referenced to the centre of the high frequency solvent multiplet or singlet (δ = 7.07, 7.11 and 2.09 respectively). ³¹P NMR spectra were referenced against 85 % H₃PO₄ (external). Chemical shifts are quoted in ppm and coupling constants in Hz.

5.3 Mass spectrometry

MicrOTOF instrument directly connected to a modified Innovative Technology glove box.³ The mass spectrometer was calibrated in positive ion mode using a 10 ng/mL mixture of tetra(alkyl)ammonium bromides $[N(C_nH_{2n+1})_4]Br$ ($n = 2, 3, 4, 5, 6, 7, 8, 12, 16, 18$) in CH_2Cl_2 . Typical acquisition parameters were: sample flow rate 4 $\mu L/min$; nebuliser gas pressure 0.4 bar; drying gas (argon) at 60 $^{\circ}C$, flowing at 4 L/min; capillary voltage 4.5 kV; funnel voltage 200 Vpp; and the solvents: CH_2Cl_2 , C_6H_5F , 1,2- $C_6H_4F_2$ or $(CH_3)_2CO$. MS samples were diluted to a concentration of 1×10^{-6} M before running.

5.4 X-ray crystallography

Structure determinations were carried out by Dr. Adrian B. Chaplin, Dr. Miguel A. Huertos Mansilla, Dr. Simon K. Brayshaw, Dr. Amber L. Thompson or myself. Relevant crystallographic data for complexes **4**, **5**, **7**, **8**, **11**, **13**, **14**, **21**, **29**, **32**, **33**, **38**, **43**, **44**, **47** and **48** can be found in Tables 6.1-6.6 in the Appendix. Data was acquired on a Nonius Kappa CCD diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and a low-temperature device.⁴ All non-hydrogen atoms were refined anisotropically. Data has been deposited in CCDC and can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif. Graphical representations of X-ray structures were made using ORTEP3.⁵

5.5 Starting materials

The starting materials: $Na[BAr^F_4]$,⁶ $Na[BAr^{Cl}_4]$,⁷ $[Rh(NBD)Cl]_2$,⁸ $[Rh(COD)Cl]_2$,⁹ $[Rh(\kappa^2_{(PP)}-dpp2)Cl]_2$,¹⁰ $Cs[closo-CB_{11}H_6Br_6]$ ¹¹ and $Cs[closo-CB_{11}H_{12}]$;¹¹ the phosphine ligands: POP',¹² dpp2-*o*-Me¹³ and dpp2-*o*-^{*i*}Pr;¹⁴ the catalyst precursors: $[Rh(\kappa^2_{(PP)}-diphosphine)(NBD)][X]$ (complexes **1**,¹⁵ **20**,¹⁶ **21**,¹⁷ **22**¹⁷ and **40**¹⁸); the

solvent complexes: $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-diphosphine})(\text{acetone})_2][\text{X}]$ (**25**,¹⁷ **26**,¹⁷ **27**¹⁷ and **41**¹⁹) and $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-dpp5})(\eta^6\text{-FB})][\text{BAr}^{\text{F}}_4]$;²⁰ and the acyl-hydride complex **42**;¹⁹ were all prepared by published literature methods, or variations thereof using $\text{Na}[\text{BAr}^{\text{F}}_4]$, $\text{Na}[\text{BAr}^{\text{Cl}}_4]$, $\text{Cs}[\text{closo-CB}_{11}\text{H}_6\text{Br}_6]$ or $\text{Cs}[\text{closo-CB}_{11}\text{H}_{12}]$ as the chloride extracting agent. Acyl chloride **VII**²¹ and aldehyde **XVIII**¹⁴ were prepared according to literature preparations. Aldehydes **I** and **V**; alkene **II** and alkyne **XI** were obtained from a commercial source and purified by distillation before use. All other chemicals were used as received from Sigma-Aldrich, Acros, Fisher, Fluka, Fluorochem or Strem Chemicals.

5.6 Synthesis of new complexes

$[\text{Rh}(\kappa^3_{\text{(POP)}}\text{-POP}')(\text{H})_2(\text{acetone})][\text{BAr}^{\text{F}}_4]$ (**2**)

The title compound was prepared *in situ* by placing a solution of $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-POP}')(\text{NBD})][\text{BAr}^{\text{F}}_4]$ (10 mg, 6.7×10^{-3} mmol) in d_6 -acetone (0.3 mL) under 4 atmospheres of hydrogen (298/77 K = 3.9). The compound was characterised by NMR spectroscopy and ESI-MS.

¹H NMR (500 MHz, d_6 -acetone, 295 K): δ 8.09–6.96 [m, 32H, Ar-H + BAr^{F}_4 ; {7.79 (8H, BAr^{F}_4), 7.67 (4H, BAr^{F}_4)}, 4.27 (br, 4H, O-CH₂), 3.18 (br, 4H, P-CH₂), -19.84 (br, 2H, fwhm = 106 Hz, Rh-H) (co-ordinated d_6 -acetone is not observed).

¹H NMR (500 MHz, d_6 -acetone, 225 K): δ 8.02–7.38 [m, 32H, Ar-H + BAr^{F}_4 ; {7.82 (8H, BAr^{F}_4), 7.73 (4H, BAr^{F}_4)}, 4.35 (m, 2H, O-CH₂), 4.16 (m, 2H, O-CH₂'), 3.42 (m, 2H, P-CH₂), 2.94 (m, 2H, P-CH₂'), -19.25 [dtd, 1H, $J(\text{RhH}) = 24.5$, $J(\text{PH}) = 13.9$, $J(\text{HH}) = 10.7$, Rh-H], -20.27 [dtd, 1H, $J(\text{RhH}) = 24.3$, $J(\text{PH}) = 13.4$, $J(\text{HH}) = 10.7$, Rh-H].

³¹P{¹H} NMR (202 MHz, d_6 -acetone, 295 K): δ 48.39 [d, $J(\text{RhP}) = 121$].

³¹P{¹H} NMR (202 MHz, d_6 -acetone, 225 K): δ 49.0 [d, $J(\text{RhP}) = 121$].

ESI-MS (acetone, 60 °C, 4.5 kV) positive ion: (minor peak) $[\text{M}]^+$ $m/z = 605.1118$

(calc. 605.1240); (major peak) $[M - \text{acetone}]^+ m/z = 547.0706$ (calc. 547.0821).

[Rh($\kappa^3_{\text{(POP)}}\text{-POP}')(\text{H})_2][\text{BAr}^{\text{F}}_4]$ (3)

The title compound was prepared *in situ* by placing a solution of $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-POP}')(\text{NBD})][\text{BAr}^{\text{F}}_4]$ (10 mg, 6.7×10^{-3} mmol) in CD_2Cl_2 (0.3 mL) under 4 atmospheres of hydrogen. The compound was characterised by NMR spectroscopy and ESI-MS.

^1H NMR (300 MHz, CD_2Cl_2): δ 7.79–7.19 [m, 32H, Ar-H + BAr^{F}_4 ; {7.73 (8H, BAr^{F}_4), 7.53 (4H, BAr^{F}_4)}], 3.90 (br, 4H, O- CH_2), 3.00 (br, 4H, P- CH_2), -19.10 [dt, 2H, $J(\text{RhH}) = 32$, $J(\text{PH}) = 12$, Rh-H].

$^{31}\text{P}\{^1\text{H}\}$ NMR (122 MHz, CD_2Cl_2): δ 44.04 [d, $J(\text{RhP}) = 119$].

ESI-MS (fluorobenzene, 60 °C, 4.5 kV) positive ion: $[M]^+ m/z = 547.0860$ (calc. 547.0821).

[Rh($\kappa^3_{\text{(POP)}}\text{-POP}')(\text{H})_2(\text{CH}_3\text{CN})][\text{BAr}^{\text{F}}_4]$ (4)

$[\text{Rh}(\kappa^3_{\text{(POP)}}\text{-POP}')(\text{H})_2][\text{BAr}^{\text{F}}_4]$ was formed *in situ* by placing a solution of $[\text{Rh}(\kappa^2_{\text{(PP)}}\text{-POP}')(\text{NBD})][\text{BAr}^{\text{F}}_4]$ (22.5 mg, 1.5×10^{-2} mmol, 1 eq.) in CD_2Cl_2 (0.3 mL) under 4 atmospheres of hydrogen. The solution was shaken for 30 mins. at room temperature. Acetonitrile (7.8 μL , 1.5×10^{-1} mmol, 10 eq.) was added under an atmosphere of argon and the solution shaken for 30 mins. The solution was transferred into a Young's crystallisation tube. Solvent was removed *in vacuo* and the resulting residue washed with pentane (3 x 2 mL), then recrystallised by diffusion of hexane into a fluorobenzene solution of the crude product to yield colourless crystals. Yield = 43 %, 9.3 mg. The compound was characterised by NMR spectroscopy, ESI-MS and elemental analysis.

^1H NMR (500 MHz, CD_2Cl_2): δ 7.85–7.30 [m, 32 H, Ar-H + BAr^{F}_4 ; {7.72 (8H, BAr^{F}_4), 7.56 (4H, BAr^{F}_4)}], 4.10 (m, 2H, O- CH_2), 3.53 (m, 2H, O- CH_2'), 2.92 (m, 4H, P- CH_2), -16.69 [dtd, 1H, $J(\text{RhH}) = 21.3$, $J(\text{PH}) = 12.3$, $J(\text{HH}) = 8.9$, Rh-H], -19.39 [dtd, 1H, $J(\text{RhH}) = 21.9$, $J(\text{PH}) = 13.1$, $J(\text{HH}) = 8.8$, Rh-H].

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2): δ 47.1 [d, $J(\text{RhP}) = 120$].

ESI-MS (fluorobenzene, 60 °C, 4.5 kV) positive ion: (minor peak) $[\text{M}]^+$ $m/z = 588.0922$ (calc. 588.1087); (major peak) $[\text{M} - \text{CH}_3\text{CN}]^+$ $m/z = 547.0705$ (calc. 547.0821).

Microanalysis: $\text{C}_{62}\text{H}_{45}\text{BF}_{24}\text{NOP}_2\text{Rh}$ (1451.65) requires: C 51.30, H 3.12, N 0.96; found: C 51.42, H 3.00, N 1.08.

$[\text{Rh}(\kappa^3(\text{POP})\text{-POP}')\{\eta^2\text{-H}_2\text{C=CHCO}_2\text{CH}_3\}][\text{BAr}^{\text{F}}_4]$ (5)

The title compound was prepared by placing a solution of $[\text{Rh}(\kappa^2(\text{PP})\text{-POP}')(\text{NBD})][\text{BAr}^{\text{F}}_4]$ (55.2 mg, 3.7×10^{-2} mmol, 1 eq.) in CH_2Cl_2 (3 mL) under 4 atmospheres of hydrogen for 5 mins, followed by addition of methyl acrylate (**II**) (6.6 μL , 7.4×10^{-2} mmol, 2 eq.) under an atmosphere of argon. The solution was added dropwise to a stirring solution of pentane (30 mL) to give a suspension of a bright yellow solid. The solution was filter-decanted off and the solid washed with pentane (5 x 5 mL). The resulting pale yellow solid was dried *in vacuo*. Yield = 62 %, 34.0 mg. The compound was characterised by NMR spectroscopy, ESI-MS and elemental analysis. Yellow crystals suitable for single crystal x-ray diffraction were grown by diffusion of pentane into a solution of the crude product in CD_2Cl_2 .

^1H NMR (500 MHz, CD_2Cl_2 , 295 K): δ 7.95-7.50 [m, 32H, Ar-H + BAr^{F}_4 ; {7.72 (8H, BAr^{F}_4), 7.55 (4H, BAr^{F}_4)}], 4.04 (m, 2H, O- CH_2), 3.97 (m, 2H, O- CH'_2), 3.66 (m, 1H, $\text{H}_2\text{C=CH}$), 3.33 (s, 3H, O- CH_3), 3.20 (m, 1H, $\text{H}_2\text{C=CH}$), 2.76 (m, 2 + 1H, P- CH_2 + $\text{H}'_2\text{C=CH}$), 2.60 (m, 2H, P- CH'_2).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CD_2Cl_2 , 295 K): δ 38.9 [d, $J(\text{RhP}) = 133$].

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, d_6 -acetone, 200 K) ABX coupling pattern observed: δ 40.70 [dd, $J(\text{PP}) = 384$, $J(\text{RhP}) = 119$], 32.91 [dd, $J(\text{PP}) = 384$, $J(\text{RhP}) = 127$].

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2 , 295 K): δ 162.14 [q, $J(\text{BC}) = 50$, BAr^{F}_4], 135.19 (s, BAr^{F}_4), 133.94 [t, $J(\text{CC}) = 6.5$, Ph], 133.18 [t, $J(\text{CC}) = 6.5$, Ph'], 132.60 (s, Ph), 132.41 (s, Ph'), 129.27 (m, Ph + Ph'), 129.24 [qq, $J(\text{FC}) = 31$, $J(\text{BC}) = 3.4$, BAr^{F}_4], 127.54

(app. t, $J = 22.1$, Ph), 126.98 (app. t, $J = 23.3$, Ph'), 124.98 [q, $J(\text{FC}) = 272$, BAr^{F}_4], 117.87 (m, BAr^{F}_4), 75.74 (s, O-CH₂), 52.12 (s, O-CH₃), 52.00 [d, $J(\text{RhC}) = 15.9$, CH₂=CH], 47.63 [d, $J(\text{RhC}) = 15.9$, CH₂=CH], 34.52 (s, C=O), 33.03 [app. t, $J(\text{PC}) = 10.9$, P-CH₂].

¹H-¹H COSY NMR (500 MHz, CD₂Cl₂, 295 K): Correlation observed between alkene protons at δ 3.66 and 3.20; and between alkene protons at δ 3.66 and 2.79. Correlations observed between all ligand backbone protons at δ 4.04, 3.97, 2.76 and 2.60.

¹H-¹³C HSQC NMR (500 MHz, CD₂Cl₂, 295 K): O-CH₂ protons at δ 4.04 and 3.97 correlate to one carbon (δ 75.74), P-CH₂ protons at δ 2.76 and 2.60 correlate to one carbon (δ 33.03), and CH₂=CH alkene protons at δ 3.20 and 2.79 correlate to one carbon (δ 52.00).

ESI-MS (acetone, 60 °C, 4.5 kV) positive ion: $[\text{M}]^+$ $m/z = 631.1283$ (calc. 631.1038).

Microanalysis: C₆₄H₄₆BF₂₄O₃P₂Rh (1494.67) requires: C 51.43, H 3.10; found: C 51.49, H 2.95.

[Rh($\kappa^3(\text{POP})\text{-POP}'$)($\eta^2\text{-COE}$)] [BAr^{F}_4] (6)

The title compound was prepared by placing a solution of [Rh($\kappa^2(\text{PP})\text{-POP}'$)(NBD)] [BAr^{F}_4] (52.7 mg, 3.5×10^{-2} mmol, 1 eq.) and *cis*-cyclooctene (10.1 μL , 7.7×10^{-2} mmol, 2 eq.) in CH₂Cl₂ (3 mL) under 4 atmospheres of hydrogen for 2 mins, before returning the solution to an argon atmosphere. The solution was stirred for 1 h, then the solvent removed and the residue agitated in pentane to give a pale yellow solid, which was collected by filtration. Yield = 80 %, 42.6 mg. The compound was characterised by NMR spectroscopy, ESI-MS and elemental analysis.

¹H NMR (500 MHz, CD₂Cl₂): δ 7.85-7.50 [m, 32H, Ar-H + BAr^{F}_4 ; {7.72 (8H, BAr^{F}_4), 7.55 (4H, BAr^{F}_4)}], 3.74 (m, 4H, O-CH₂), 3.66 (m, 2H, COE HC=CH), 2.61 (m, 4H, P-

CH₂), 2.02 (m, 2H, COE HC=CH-CH₂), 1.35-1.03 (m, 6H, COE CH₂), 0.99-0.76 (m, 2 + 2H, COE CH₂ + HC=CH-CH₂).

³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ 35.9 [d, *J*(RhP) = 143].

¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 162.32 [q, *J*(BC) = 50, BAr^F₄], 135.19 (s, BAr^F₄), 133.57 [t, *J*(CC) = 5.7, Ph], 132.12 (s, Ph), 129.82 [t, *J*(CC) = 4.6, Ph], 129.79 (m, Ph), 129.43 [qq, *J*(FC) = 31, *J*(BC) = 3.1, BAr^F₄], 125.19 [q, *J*(FC) = 274, BAr^F₄], 117.87 (m, BAr^F₄), 73.74 (s, O-CH₂), 69.45 [d, *J*(RhC) = 15, HC=CH], 33.30 [app. t, *J*(CC) = 4.2, HC=CH-CH₂], 32.98 [app. t, *J*(CC) = 10.7, P-CH₂], 31.31 (s, COE CH₂), 26.46 (s, COE CH₂).

ESI-MS (fluorobenzene, 60 °C, 4.5 kV) positive ion: [M]⁺ *m/z* = 655.1924 (calc. 655.1760).

Microanalysis: C₆₈H₅₄BF₂₄OP₂Rh (1518.78) requires: C 53.78, H 3.58; found: C 53.51, H 3.47.

[Rh(κ³(POP)-POP')(H){κ¹(S)-σ¹(C)-C(O)CH₂CH₂SCH₃}] [BAr^F₄] (7)

[Rh(κ²(PP)-POP')(NBD)] [BAr^F₄] (91.5 mg, 6.1 x 10⁻² mmol, 1 eq.) in acetone (3 mL) was hydrogenated (4 atm). The solution was stirred for 1 h at room temperature. Methyl acrylate (**II**) (8.2 μL, 9.2 x 10⁻² mmol, 1.5 eq.) was added under an atmosphere of argon and the solution stirred for 4 h. Aldehyde **I** (9.1 μL, 9.2 x 10⁻² mmol, 1.5 eq.) was added and the solution stirred for a further h. The solvent was removed *in vacuo* and the resulting residue washed with pentane (2 x 3 mL), then recrystallised by diffusion of pentane into a fluorobenzene solution of the crude product to yield colourless crystals. Yield = 63 %, 69.4 mg. The compound was characterised by NMR spectroscopy and ESI-MS.

¹H NMR (500 MHz, d₆-acetone, 295 K): δ 8.23 - 7.30 [m, 32 H, Ar-H + BAr^F₄; {7.72 (8H, BAr^F₄), 7.61 (4H, BAr^F₄)}], 4.01 (m, 2H, CH₂), 3.05 - 2.79 (m, 6H, CH₂), 2.37 (br m, 2H, CH₂), 1.79 [d, *J*(HH) = 1.8, 3H, S-CH₃], 1.67 (br m, 2H, CH₂), -9.58 [br d, 1H, *J*(RhH) = 24, Rh-H].

^1H NMR (500 MHz, d_6 -acetone, 225 K, selected data): δ -9.55 [dd, 1H, $J(\text{RhH}) = 24$, $J(\text{PH}) = 6.5$].

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, d_6 -acetone, 295 K): δ 31.1 (br s, fwhm = 513 Hz).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, d_6 -acetone, 225 K): ABX coupling pattern observed: δ 34.30 [dd, $J(\text{PP}) = 308$, $J(\text{RhP}) = 127$], 28.19 [dd, $J(\text{PP}) = 308$, $J(\text{RhP}) = 130$].

^1H - ^1H COSY NMR (500 MHz, d_6 -acetone, 295 K): Correlation observed between S- CH_3 (δ 1.79) and Rh-H (δ -9.58).

ESI-MS (acetone, 60 $^\circ\text{C}$, 4.5 kV) positive ion: m/z $[\text{M}]^+ = 649.1022$ (calc. 649.0961).

$[\text{Rh}(\kappa^2(\text{PP})\text{-XANTphos})(\text{NBD})][\text{BAr}^{\text{F}}_4]$ (8)

XANTphos (125.5 mg, 2.17×10^{-1} mmol, 2 eq.) in CH_2Cl_2 (13 mL) was added dropwise over 30 mins to $[\text{Rh}(\text{NBD})\text{Cl}]_2$ (50 mg, 1.08×10^{-1} mmol, 1 eq.) in CH_2Cl_2 (1 mL). The resulting reaction mixture was then added dropwise to $\text{Na}[\text{BAr}^{\text{F}}_4]$ (192.2 mg, 2.17×10^{-1} mmol, 2 eq.) in CH_2Cl_2 (1 mL) and the mixture was stirred for 2 h. The solution was filtered, and the filtrate solvent was reduced to ~ 5 mL. Pentane was added to the filtrate until the solution began to precipitate, then the solution was layered with pentane (15 mL). The solution was stored overnight at -18 $^\circ\text{C}$ to give orange crystals, yield = 53 %, 189 mg. The compound was characterised by NMR spectroscopy, ESI-MS and elemental analysis.

^1H NMR (300 MHz d_6 -acetone): δ 7.79 (m, 8H, BAr^{F}_4), 7.68 (s, 4H, BAr^{F}_4), 7.46-6.82 (m, 26H, Ar-H), 3.78 (s, 4H, NBD $\text{CH}=\text{CH}$), 3.52 (s, 2H, NBD CH), 1.70 (s, 6H, CH_3), 1.16 (s, 2H, NBD CH_2).

$^{31}\text{P}\{^1\text{H}\}$ NMR (122 MHz d_6 -acetone): δ 9.74 [d, $J(\text{RhP}) = 142$].

ESI-MS (acetone, 60 $^\circ\text{C}$, 4.5 kV) positive ion: $[\text{M}]^+ m/z = 773.1505$ (calc. 773.1604).

Microanalysis: $\text{C}_{78}\text{H}_{52}\text{BF}_{24}\text{OP}_2\text{Rh}$ (1636.87) requires: C 57.23, H 3.20; found: C 57.51, H 3.19.

[Rh(κ^3 (POP)-XANTphos)(H)₂(acetone)][BAr^F₄] (9)

The title compound was prepared *in situ* by placing a solution of [Rh(κ^2 (PP)-XANTphos)(NBD)][BAr^F₄] (10 mg, 6.1 x 10⁻³ mmol) in d₆-acetone (0.3 mL) under 4 atmospheres of hydrogen. These compounds were characterised by NMR spectroscopy and ESI-MS.

¹H NMR (500 MHz, d₆-acetone, 295 K): δ 8.34–6.85 [m, 38H, Ar-H + BAr^F₄; {7.79 (8H, BAr^F₄), 7.68 (4H, BAr^F₄)}], 2.25–1.54 (br m, 6H, CH₃), -18.89 (br, 2H, Rh-H).

¹H NMR (500 MHz, d₆-acetone, 225 K): δ 8.26–7.20 [m, 38H, Ar-H + BAr^F₄; {7.83 (8H, BAr^F₄), 7.73 (4H, BAr^F₄)}], 1.94 (s, 3H, CH₃), 1.70 (s, 3H, CH₃'), -18.44 [dtd, 1H, *J*(RhH) = 22.1, *J*(PH) = 12.8, *J*(HH) = 9.5, Rh-H], -19.17 [dtd, 1H, *J*(RhH) = 31.4, *J*(PH) = 14.5, *J*(HH) = 9.5, Rh-H].

³¹P{¹H} NMR (202 MHz, d₆-acetone, 295 K): δ 45.4 [d, *J*(RhP) = 121].

³¹P{¹H} NMR (202 MHz, d₆-acetone, 225 K): δ 46.0 [d, *J*(RhP) = 121].

ESI-MS (acetone, 60 °C, 4.5 kV) positive ion: (minor peak) [M]⁺ *m/z* = 741.1499 (calc. 741.1553); (major peak) [M – acetone]⁺ *m/z* = 683.1134 (calc. 683.1067).

[Rh(κ^3 (POP)-XANTphos)(H)₂][BAr^F₄] (10)

The title compound was prepared *in situ* by placing a solution of [Rh(κ^2 (PP)-XANTphos)(NBD)][BAr^F₄] (10 mg, 6.1 x 10⁻⁶ mol) in CD₂Cl₂ (0.3 mL) under 4 atmospheres of hydrogen. The compound was characterised by NMR spectroscopy and ESI-MS.

¹H NMR (300 MHz, CD₂Cl₂): δ 7.84–7.38 [m, 38H, Ar-H + BAr^F₄; {7.72 (8H, BAr^F₄), 7.55 (4H, BAr^F₄)}], 1.73 (br s, 6H, CH₃), -18.28 [dt, 2H, *J*(RhH) = 33, *J*(PH) = 12, Rh-H].

³¹P{¹H} NMR (122 MHz, CD₂Cl₂): δ 41.50 [d, *J*(RhP) = 117].

ESI-MS (fluorobenzene, 60 °C, 4.5 kV) positive ion: [M]⁺ *m/z* = 683.1250 (calc. 683.1134).

[Rh(κ^3 (POP)-XANTphos)(H)₂(CH₃CN)][BAr^F₄] (11)

[Rh(κ^3 (POP)-XANTphos)(H)₂][BAr^F₄] was prepared *in situ* from [Rh(κ^2 (PP)-XANTphos)(NBD)][BAr^F₄] (24.5 mg, 1.5 x 10⁻² mmol) hydrogenated (4 atm) in CD₂Cl₂ (0.3 mL). The solution was shaken for 30 mins. Acetonitrile (7.8 μ L, 1.5 x 10⁻¹ mmol, 10 eq.) was added under an atmosphere of argon and the solution shaken for 30 mins. Solvent was removed *in vacuo* and the resulting residue washed with pentane (3 x 2 mL), then recrystallised by diffusion of hexane into a fluorobenzene solution of the crude product to yield colourless crystals. Yield = 73 %, 17.4 mg. The compound was characterised by NMR spectroscopy, ESI-MS and elemental analysis.

¹H NMR (500 MHz, CD₂Cl₂): δ 7.92-7.29 [m, 38H, Ar-H + BAr^F₄; {7.72 (8H, BAr^F₄), 7.55 (4H, BAr^F₄)}], 1.91 (s, 3H, CH₃), 1.51 (s, 3H, CH₃'), 1.16 (s, 3H, co-ordinated CH₃CN CH₃), -15.36 [dtd, 1H, *J*(RhH) = 20.3, *J*(PH) = 12.3, *J*(HH) = 7.8, Rh-H], -19.36 [dtd, 1H, *J*(RhH) = 30.8, *J*(PH) = 13.9, *J*(HH) = 7.8, Rh-H].

³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ 44.8 [d, *J*(RhP) = 117].

ESI-MS (fluorobenzene, 60 °C, 4.5 kV) positive ion: (minor peak) [M]⁺ *m/z* = 724.0896 (calc. 724.1400); (major peak) [M - CH₃CN]⁺ *m/z* = 683.0745 (calc. 683.1134).

Microanalysis: C₇₃H₄₉BF₂₄NOP₂Rh (1587.80) requires: C 55.22, H 3.11, N 0.88; found: C 55.14, H 3.01, N 0.97.

[Rh(κ^3 (POP)-XANTphos){ η^2 -H₂C=CHCO₂CH₃)][BAr^F₄] (12)

The title compound was prepared by placing a solution of [Rh(κ^2 (PP)-XANTphos)(NBD)][BAr^F₄] (35 mg, 2.1 x 10⁻² mmol, 1 eq.) in acetone (3 mL) under 4 atmospheres of hydrogen, followed by addition of methyl acrylate (**II**) (4.2 μ L, 4.3 x 10⁻² mmol, 2 eq.) under an atmosphere of argon. The solution was stirred for 1 h, then the solvent removed *in vacuo*, and the residue agitated in pentane for 1 h. The complex was collected as a pale yellow solid by filtration, and characterised by NMR spectroscopy and ESI-MS. Yield = 47 %, 16.4 mg.

^1H NMR (500 MHz, CD_2Cl_2): δ 7.94-7.34 [m, 38H, Ar-H + BAr^{F_4} ; {7.72 (8H, BAr^{F_4}), 7.55 (4H, BAr^{F_4})}, 3.97 (m, 1H, $\text{H}_2\text{C}=\text{CH}$), 3.45 (m, 1H, $\text{H}_2\text{C}=\text{CH}$), 3.24 (s, 3H, O- CH_3), 2.91 (m, 1H, $\text{H}'_2\text{C}=\text{CH}$), 1.77 (s, 6H, CH_3).

$^{31}\text{P}\{^1\text{H}\}$ NMR (122 MHz, CD_2Cl_2): δ 32.66 [d, $J(\text{RhP}) = 124$].

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2): δ 173.43 (s, XANTphos), 162.30 [q, $J(\text{BC}) = 49$, BAr^{F_4}], 154.96 [t, $J(\text{CC}) = 8.2$, XANTphos], 135.35 (s, BAr^{F_4}), 134.97 (s, XANTphos), 134.70 [t, $J(\text{CC}) = 6.0$, XANTphos], 133.93 [t, $J(\text{CC}) = 6.5$, XANTphos], 133.22 (s, XANTphos), 133.10 [t, $J(\text{CC}) = 6.8$, XANTphos], 132.81 (s, XANTphos), 132.39 (s, XANTphos), 130.03 [t, $J(\text{CC}) = 3.5$, XANTphos], 130.13 (m, XANTphos), 129.43 [qq, $J(\text{FC}) = 31$, $J(\text{BC}) = 2.8$, BAr^{F_4}], 128.38 [t, $J(\text{CC}) = 3.2$, XANTphos], 127.61 [t, $J(\text{CC}) = 26$, XANTphos], 125.17 [q, $J(\text{FC}) = 273$, BAr^{F_4}], 121.77 [t, $J(\text{CC}) = 18$, XANTphos], 118.03 (m, BAr^{F_4}), 55.75 [d, $J(\text{RhC}) = 20$, $\text{CH}_2=\text{CH}$], 52.37 (s, O- CH_3), 47.88 [d, $J(\text{RhC}) = 18$, $\text{CH}_2=\text{CH}$], 34.77 (s, C=O), 34.26 [s, $\text{C}(\text{CH}_3)_2$], 34.08 [s, $\text{C}(\text{CH}_3)_2$].

ESI-MS (fluorobenzene, 60 °C, 4.5 kV) positive ion: $[\text{M}]^+$ m/z , 767.0934 (calc. 767.1351).

$[\text{Rh}(\kappa^3(\text{POP})\text{-XANTphos})(\text{H})\{\kappa^1(\text{S})\text{-}\sigma^1(\text{C})\text{-C}(\text{O})\text{CH}_2\text{CH}_2\text{SCH}_3\}][\text{BAr}^{\text{F}_4}]$ (13)

$[\text{Rh}(\kappa^2(\text{PP})\text{-XANTphos})(\text{NBD})][\text{BAr}^{\text{F}_4}]$ (10 mg, 6.1×10^{-2} mmol, 1 eq.) in acetone (3 mL) was hydrogenated and stirred for 1 h at room temperature. Methyl-acrylate (**II**) (8.2 μL , 9.2×10^{-2} mmol, 1.5 eq.) was added under an atmosphere of argon and the solution stirred for 4 h. Aldehyde **I** (9.1 μL , 9.2×10^{-2} mmol, 1.5 eq.) was added and the solution stirred for a further h. The solvent was removed *in vacuo* and the resulting residue washed with pentane (2 x 3 mL), then recrystallised by diffusion of pentane into a fluorobenzene solution of the crude product to yield colourless crystals. Yield = 35 %, 31.8 mg. The compound was characterised by NMR spectroscopy, ESI-MS and elemental analysis.

^1H NMR (500 MHz, d_6 -acetone, 295 K): δ 8.48-7.36 [m, 38H, Ar-H + BAr^{F_4} ; {7.79 (8H, BAr^{F_4}), 7.68 (4H, BAr^{F_4})}, 2.62 (br s, 2H, fwhm = 77 Hz, CH_2), 2.04 (br, 2H,

CH₂, coincident with CD₂HCOCD₃ peak) 1.97 (s, 3H, CH₃), 1.51 (s, 3H, CH₃'), 1.47 [d, 3H, $J(\text{HH}) = 1.8$, S-CH₃], -8.72 [br d, 1H, $J(\text{RhH}) = 23$, Rh-H].

¹H NMR (500 MHz, d₆-acetone, 240 K): δ 8.58-7.24 [m, 38H, Ar-H + BAr^F₄; {7.81 (8H, BAr^F₄), 7.72 (4H, BAr^F₄)}], 2.80 (m, 1H, CH₂), 2.37 (m, 1H, CH₂), 2.10 (m, 1H, CH₂), 1.94 (s, 3H, CH₃), 1.82 (m, 1H, CH₂), 1.47 (s, 3H, CH₃'), 1.38 (s, 3H, S-CH₃), -8.65 [br dd, 1H, $J(\text{RhH}) = 23$, $J(\text{PH}) = 7$, Rh-H].

³¹P{¹H} NMR (202 MHz, d₆-acetone, 295 K): δ 32.8 (br s, fwhm = 478 Hz).

³¹P{¹H} NMR (202 MHz, d₆-acetone, 257 K): ABX coupling pattern observed: δ 35.22 [dd, $J(\text{PP}) = 300$, $J(\text{RhP}) = 124$], 32.04 [dd, $J(\text{PP}) = 300$, $J(\text{RhP}) = 127$].

¹H-¹H COSY NMR (500 MHz, d₆-acetone, 295 K): Correlation observed between S-CH₃ (δ 1.97) and Rh-H (δ -8.72).

ESI-MS (acetone, 60 °C, 4.5 kV) positive ion: [M]⁺ $m/z = 785.1221$ (calc. 785.1274).

Microanalysis: C₇₅H₅₂BF₂₄NO₂P₂RhS (1648.90) requires: C 54.63, H 3.18; found: C 54.57, H 3.10.

5,5'-oxybis(1-bromo-2,4-dimethylbenzene)

To a stirred solution of 4,4'-oxybis(1,3-dimethylbenzene) (1.0g, 4.4 mmol) in CH₂Cl₂ (20 mL) at 0 °C was added bromine (0.45 mL, 8.8 mmol) dropwise. The reaction mixture was stirred at 0 °C for 1.5 h and quenched by the addition of saturated aqueous Na₂S₂O₃ solution (20 mL). The aqueous phase was extracted with CH₂Cl₂ (2 × 20 mL) and the combined organic extracts were dried (MgSO₄), reduced and the crude product purified by column chromatography (petrol) to yield the product as a white crystalline solid (1.10 g, 65 %).

¹H NMR (400 MHz, CDCl₃): δ 7.12 (s, 2H), 6.93 (s, 2H), 2.37 (s, 6H), 2.23 (s, 6H).

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 153.9, 133.6, 133.0, 128.3, 122.2, 121.7, 22.5, 16.2.

Xphos

To a stirred solution of 5,5'-oxybis(1-bromo-2,4-dimethylbenzene) (0.47 g, 1.22 mmol) in THF (2 mL) at -78 °C was added *n*-butyl lithium solution (1.7 mL, 1.6 M in hexane, 2.7 mmol) dropwise. After 5 minutes Ph₂PdCl (0.5 mL, 2.7 mmol) was added dropwise, and the solution allowed to warm to room temperature overnight. Water (10 mL) was added, the aqueous phase was extracted with CH₂Cl₂ (2 × 20 mL) and the combined organic extracts were dried (Mg₂SO₄) and reduced *in vacuo*. The crude product purified by column chromatography (2 % Et₂O/petrol) to yield the product as a white solid (340 mg, 47 %)

¹H NMR (500 MHz, d₆-acetone): δ 7.35 (m, 4H, P-Ph), 7.30 (m, 8H, P-Ph), 7.14 (m, 8H, P-Ph), 7.00 [d, 2H, *J* = 4.9, Ar-H], 5.91 [d, 2H, *J* = 4.2, Ar-H], 2.28 (s, 6H, Ar-Me), 2.02 (s, 6H, Ar-Me).

¹³C{¹H} NMR (125 MHz, d₆-acetone): δ 153.19, 136.7, 136.4 (d, *J* = 9.1), 134.1 (d, *J* = 12.6), 133.6, 133.1, 133.0, 128.9, 128.6, 128.5, 128.4, 121.9, 20.2 (d, *J* = 19.5), 15.8.

³¹P NMR (122 MHz, d₆-acetone): δ 13.6 (s).

[Rh(κ²_(PP)-Xphos)NBD]₂[BAr^F₄]₂ (14)

Xphos (594.7 mg, 0.217 mmol, 2 eq.) in CH₂Cl₂ (13mL) was added dropwise over 30 mins to [Rh(NBD)Cl]₂ (50 mg, 0.108 mmol, 1 eq.) in CH₂Cl₂ (1 mL). The resulting reaction mixture was then added dropwise to Na[BAr^F₄] (192.2 mg, 0.217 mmol, 2 eq.) in CH₂Cl₂ (1 mL) and the mixture was stirred for 2 h. The solution was filtered, and pentane added to the filtrate until the solution became opaque, then layered with pentane (15 mL). The solution was stored overnight at -18 °C to give an orange oil. The solvent was decanted off, and the oil agitated *in vacuo* to give a fine orange powder, yield = 85 %, 294 mg. The compound was characterised by NMR spectroscopy, ESI-MS and elemental analysis.

¹H NMR (500 MHz, d₆-acetone): δ 9.20 [d, 1H, *J*(PH) = 15.5, Ar-H], 8.95 [d, 1H, *J*(PH) = 18.4, Ar-H], 7.79 (m, 8H, BAr^F₄), 7.72-6.74 [m, 26H, Ar-H + BAr^F₄; {7.67

(4H, BAr^F₄)}, 4.79 (m, 1H, NBD), 4.65 (m, 1H, NBD), 4.01 (m, 1H, NBD), 3.85 (m, 1H, NBD), 3.61 (m, 1H, NBD), 2.65 (m, 1H, NBD), 2.39 (s, 3H, Xphos CH₃), 2.22 (s, 3H, Xphos CH₃), 1.52 (s, 3H, Xphos CH₃), 1.43 (s, 3H, Xphos CH₃), 1.39 (m, 2H, NBD CH₂).

³¹P{¹H} NMR (202 MHz, d₆-acetone): δ 36.06 [dd, *J*(RhP) = 162.3, *J*(PP) = 28.8], 24.22 [dd, *J*(RhP) = 156.7, *J*(PP) = 28.8].

ESI-MS (fluorobenzene, 60 °C, 4.5 kV) positive ion: [M]₂²⁺ *m/z*, = 789.6950 (calc. 789.6934).

Microanalysis: C₁₅₈H₁₁₂B₂F₄₈O₂P₄Rh₂ (3305.83) requires: C 57.40, H 3.41; found: C 57.77, H 3.42.

[Rh(κ²_(PP)-Xphos)(η⁶-C₆H₅F)]₂[BAr^F₄]₂ (15)

The title compound was prepared *in situ* by hydrogenation (4 atm) of a solution of [Rh(κ²_(PP)-Xphos)(NBD)]₂[BAr^F₄]₂ (15.0 mg, 4.54 × 10⁻³ mmol) in C₆H₅F (0.3 mL). The solution was shaken for 30mins, and darkened in colour. The compound was characterised *in situ* by NMR spectroscopy and ESI-MS.

¹H NMR (500 MHz, C₆H₅F): δ 8.92 [d, 1H, *J*(PH) = 16.8, Ar-H], 8.85 [d, 1H, *J*(PH) = 18.5, Ar-H], 8.33 (m, 8H, BAr^F₄), 7.62 (s, 4H, BAr^F₄), 7.43 [app. t, 1H, *J* = 8.7, Ar-H], 7.34 [app. t, 1H, *J* = 7.7, Ar-H], 6.68 [app. t, 1H, *J* = 8.1, Ar-H], 6.43 [app. t, 1H, *J* = 7.5, Ar-H], 6.16 [app. q, 1H, *J* = 6.1, η⁶-C₆H₅F F-CCHCH], 5.56 [app. q, 1H, *J* = 6.1, η⁶-C₆H₅F F-CCH'CH'], 5.42 [app. t, 1H, *J* = 5.6, η⁶-C₆H₅F F-CCH'], 4.79 [app. t, 1H, *J* = 5.7, η⁶-C₆H₅F F-CCH], 4.52 [app. t, 1H, *J* = 6.1, η⁶-C₆H₅F F-CCHCHCH], 2.28 (s, 3H, Xphos CH₃), 2.06 (s, 3H, Xphos CH₃), 1.30 (s, 3H, Xphos CH₃), 1.22 (s, 3H, Xphos CH₃). (Ar-H peaks obscured by solvent peak).

³¹P{¹H} NMR (202 MHz C₆H₅F): δ 49.00 [dd, *J*(RhP) = 218.4, *J*(PP) = 33.9], 38.79 [dd, *J*(RhP) = 208.3, *J*(PP) = 33.9].

¹⁹F NMR (283 MHz, C₆H₅F): δ -64.78 (s, BAr^F₄), -124.28 (s, η⁶-C₆H₅F).

¹H{³¹P_{39ppm}} NMR (500 MHz, C₆H₅F, selective data): δ 8.93 (s, Ar-H).

$^1\text{H}\{^{31}\text{P}_{49\text{ppm}}\}$ NMR (500 MHz, $\text{C}_6\text{H}_5\text{F}$, selective data): δ 8.86 (s, Ar-H).

^1H - ^1H COSY NMR (500 MHz, $\text{C}_6\text{H}_5\text{F}$): Correlations between peaks at δ 6.16, 5.56, 5.42, 4.79 and 4.52 indicate the peaks due to the $\eta^6\text{-C}_6\text{H}_5\text{F}$ protons, while the peaks at δ 7.43, 7.34, 6.68 and 6.43 correlate with each other, but not the $\eta^6\text{-C}_6\text{H}_5\text{F}$ proton peaks.

ESI-MS (fluorobenzene, 60 °C, 4.5 kV) positive ion: (minor peak) $[\text{M-C}_6\text{H}_5\text{F}]^{2+}$ m/z , = 697.1446 (calc. 697.1291); (major peak) $[\text{M}]^{2+}$ m/z = 793.6740 (calc. 793.6683).

$[\text{Rh}(\kappa^2_{(\text{PP})}\text{-Xphos})(\eta^6\text{-benzene})]_2[\text{CB}_{11}\text{H}_6\text{Br}_6]_2$ (16)

The title compound was prepared *in situ* by hydrogenation (4 atm) of a solution of $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-Xphos})(\text{NBD})]_2[\text{CB}_{11}\text{H}_6\text{Br}_6]_2$ (16.0 mg, 5.69×10^{-3} mmol, 1 eq.) and 10 equivalents – per rhodium atom – of benzene (10.2 μL , 5.69×10^{-2} mmol, 20 eq.) in CD_2Cl_2 (0.3 mL). The solution was shaken for 30mins, and characterised *in situ* by NMR spectroscopy and ESI-MS.

^1H NMR (300 MHz, CD_2Cl_2): δ 8.89 [d, 1H, J = 16.8, Ar-H], 8.78 [d, 1H, J = 18.6, Ar-H], 7.60-6.48 (m, 22H, Ar-H), 5.46 (s, 6H, $\eta^6\text{-benzene}$), 2.72-1.23 (br, $\text{CB}_{11}\text{H}_6\text{Br}_6$), 2.30 (s, 3H, Xphos CH_3), 2.19 (s, 3H, Xphos CH_3), 1.35 (s, 3H, Xphos CH_3), 1.29 (s, 3H, Xphos CH_3). Free benzene observed at δ 7.37.

$^{31}\text{P}\{^1\text{H}\}$ NMR (122 MHz CD_2Cl_2): δ 48.37 [dd, $J(\text{RhP})$ = 211.8, $J(\text{PP})$ = 33.2], 38.74 [dd, $J(\text{RhP})$ = 202.9, $J(\text{PP})$ = 33.3].

ESI-MS (fluorobenzene, 60 °C, 4.5 kV) positive ion: $[\text{M}]^{2+}$ m/z , = 775.7165 (calc. 775.6777).

$[\text{Rh}(\kappa^2_{(\text{PP})}\text{-Xphos})]_2[\text{BAr}^{\text{F}}_4]_2$ (17)

The title compound was prepared *in situ* by hydrogenation (4 atm) of a solution of $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-Xphos})(\text{NBD})]_2[\text{BAr}^{\text{F}}_4]_2$ (8.3 mg, 2.51×10^{-3} mmol) in CD_2Cl_2 (0.3 mL).

The solution was shaken for 30mins, and the compound characterised *in situ* by NMR spectroscopy and ESI-MS.

^1H NMR (500 MHz, CD_2Cl_2): δ 9.82 [d, 1H, $J = 19.2$, Ar-H], 9.01 (m, 1H, Ar-H), 8.69 [d, 1H, $J = 18.7$, Ar-H], 8.50 (br s, 1H, Ar-H), 7.82-6.71 [m, 28H, Ar-H + BAr^{F_4} ; {7.67 (8H, BAr^{F_4})}; {7.56 (4H, BAr^{F_4})}; {7.20 (app t, 1H, $J = 6.7$, $\eta^6\text{-P-CHCH}$)}], 6.53 [app. t, 1H, $J = 8.4$, Ar-H], 6.03 [app. t, 1H, $J = 5.9$, $\eta^6\text{-P-CHCHCH}$], 5.97 [app. t, 1H, $J = 5.9$, $\eta^6\text{-P-CH'}$], 5.84 [app. t, 1H, $J = 7.4$, $\eta^6\text{-P-CH}$], 4.32 [app. t, 1H, $J = 5.4$, $\eta^6\text{-P-CH'CH'}$], 2.62 (s, 3H, Xphos CH_3), 2.34 (s, 3H, Xphos CH_3), 1.50 (s, 3H, Xphos CH_3), 0.73 (s, 3H, Xphos CH_3).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz CD_2Cl_2): δ 51.13 [ddm, $J(\text{RhP}) = 227.67$, $J(\text{PP}) = 31.2$], 42.15 [dd, $J(\text{RhP}) = 208.8$, $J(\text{PP}) = 31.2$].

ESI-MS (di-fluorobenzene, 60 °C, 4.5 kV) positive ion: $[\text{M}]_2^{2+}$ m/z , = 697.1656 (calc. 697.1291).

Microanalysis: $\text{C}_{82}\text{H}_{96}\text{B}_{22}\text{O}_2\text{P}_4\text{Rh}_2$ (1681.19) requires: C 58.58, H 5.76; found: C 58.49, H 5.78.

$[\text{Rh}(\kappa^2_{(\text{PP})}\text{-dpp5})(\text{acetone})_2][\text{BAr}^{\text{F}_4}]$ (24)a, $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-dpp5})(\text{H})_2(\text{acetone})_2][\text{BAr}^{\text{F}_4}]$ (24)b and $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-}\sigma^1(\text{C})\text{-PPh}_2(\text{CH}_2)_2\text{CH}(\text{CH}_2)_2\text{PPh}_2)(\text{H})(\text{acetone})_2][\text{BAr}^{\text{F}_4}]$ (24)c

The title compounds were prepared *in situ* by placing a solution of $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-dpp5})(\text{NBD})][\text{BAr}^{\text{F}_4}]$ (10 mg, 6.7×10^{-3} mmol) in d_6 -acetone (0.3 mL) under 4 atmospheres of hydrogen. These compounds were characterised by NMR spectroscopy and ESI-MS.

^1H NMR (500 MHz, d_6 -acetone): δ 7.91-7.31 [m, 32H, Ar-H + BAr^{F_4} ; {7.80 (8H, BAr^{F_4}), 7.68 (4H, BAr^{F_4})}], 2.92 (m, 2H, $\text{P-CH}_2\text{CH}_2\text{CH}_2$), 2.47 (m, 4H, $\text{P-CH}_2\text{CH}_2$), 1.86 (m, 4H, P-CH_2), -21.68 [dt, $J(\text{RhH}) = 27$, $J(\text{PH}) = 16$, Rh-H, **24c**], -22.30 [dt, $J(\text{RhH}) = 35$, $J(\text{PH}) = 11$, Rh-H, **24b**] (co-ordinated d_6 -acetone is not observed)

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, $\text{d}_6\text{-acetone}$): δ 55.3 [d, relative 0.8 P, $J(\text{RhP}) = 133$, **24b**], 37.3 [d, relative 10P, $J(\text{RhP}) = 201$, **24a**], 35.8 [d, relative 2P, $J(\text{RhP}) = 115$, **24c**].

ESI-MS (acetone, 60 °C, 4.5 kV) positive ion: (minor peak) $[\text{M}_{(24a)}]^+$ $m/z = 659.1647$ (calc. 659.1710); (major peak) $[\text{M}_{(24a)} - \text{acetone}]^+$ $m/z = 601.1252$ (calc. 601.1291); (major peak) $[\text{M}_{(24a)} - (\text{acetone})_2]^+$ $m/z = 543.0844$ (calc. 543.0872).

$[\text{Rh}(\kappa^2_{(\text{PP})}\text{-}\eta^2_{(\text{CH})}\text{-dpp5})(\text{H})\{\kappa^1_{(\text{S})}\text{-}\sigma^1_{(\text{C})}\text{-C(O)C}_6\text{H}_4\text{SCH}_3\)][\text{BAR}^{\text{F}}_4]$ (28**)**

The compound was prepared *in situ* by addition of $\text{HOCOC}_6\text{H}_4\text{SCH}_3$ (**V**) (1.3 μL , 9.9×10^{-3} mmol, 1.1 eq.) to a solution of $[\text{Rh}(\kappa^2_{(\text{PP})}\text{-dpp5})(\eta^6\text{-C}_6\text{H}_5\text{F})][\text{BAR}^{\text{F}}_4]$ (13.5 mg, 8.9×10^{-3} mmol, 1 eq.) in $\text{d}_6\text{-acetone}$ (0.4 mL). The compound was characterised by NMR spectroscopy and ESI-MS.

^1H NMR (500 MHz, $\text{d}_6\text{-acetone}$, 295 K): δ 8.24 [qd, 2H, $J = 6.4$, $J = 1.8$, Ar-H], 7.79 (m, 8H, BAR^{F}_4), 7.69-7.17 [m, 22H, Ar-H + BAR^{F}_4 ; {7.67 (4H, BAR^{F}_4)}], 3.11 (br, 1H, $\text{P-CH}_2\text{CH}_2\text{CH}_2$) 3.07 (obscured m, 4H, P-CH_2), 2.26 (br, 2H, $\text{P-CH}_2\text{CH}_2$), 2.11 [d, 3H, $J = 1.4$, S- CH_3], 1.42 (m, 2H, $\text{P-CH}_2\text{CH}_2'$), -5.05 (m, 1H, $\text{P-CH}_2\text{CH}_2\text{CH}_2'$), -8.00 [d, $J(\text{RhH}) = 25$, Rh-H].

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, $\text{d}_6\text{-acetone}$, 295 K): δ 37.32 [br d, $J(\text{RhP}) = 128$].

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, $\text{d}_6\text{-acetone}$, 200 K): ABX coupling pattern observed: δ 42.39 [dd, $J(\text{PP}) = 292$, $J(\text{RhP}) = 130$], 32.04 [dd, $J(\text{PP}) = 292$, $J(\text{RhP}) = 133$].

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{d}_6\text{-acetone}$, 295 K): δ 209.3 [d, $J(\text{RhC}) = 13.3$, Rh-C=O], 162.58 [q, $J(\text{BC}) = 47.8$, BAR^{F}_4], 139.44 (s, Ar), 135.52 (s, BAR^{F}_4), 135.43 (s, Ar-H), 134.27 (s, Ph), 132.57 (s, Ar-H), 132.01 [t, $J(\text{CC}) = 5.5$, Ph], 131.51 (s, Ar-H), 131.32 (s, Ar-H), 129.24 [qq, $J(\text{FC}) = 31.6$, $J(\text{BC}) = 2.5$, BAR^{F}_4], 129.99-129.37 (m, Ph), 127.11 (s, Ar-H), 125.35 [q, $J(\text{FC}) = 267$, BAR^{F}_4], 117.87 [sept, $J(\text{FC}) = 4.3$, BAR^{F}_4], 45.93 (s, $\text{P-CH}_2\text{CH}_2\text{CH}_2$), 37.00 [app. t, $J(\text{PC}) = 13.7$, P-CH_2], 27.21 (s, $\text{P-CH}_2\text{CH}_2$), 22.65 [app. t, $J(\text{PC}) = 3.1$, S- CH_3].

$^1\text{H}\text{-}^1\text{H}$ COSY NMR (500 MHz, $\text{d}_6\text{-acetone}$, 295 K): Correlation observed between signals S- CH_3 (δ 2.11) and Rh-H (δ -8.00). Correlation observed between $\text{P-CH}_2\text{CH}_2\text{CH}_2$ protons (agostic C-H δ -5.05 and δ 3.11), and between agostic C-H (δ -5.05) and one $\text{P-CH}_2\text{CH}_2$ (δ 1.42) proton. Correlation observed between $\text{P-CH}_2\text{CH}_2$

protons (δ 1.42 and 2.26). Correlation observed between P-CH₂ (δ 3.07) and one P-CH₂CH₂ proton (δ 2.26).

¹H-¹³C HSQC NMR (500 MHz, d₆-acetone): Protons at δ -5.05 and 3.12 correlate to the same carbon (δ 45.93), protons at δ 2.26 and 1.42 correlate to the same carbon (δ 27.21).

¹H-¹³C HMBC NMR (500 MHz, d₆-acetone): Correlation between Rh-H (δ -8.00) and Rh-C=O (δ 209.3).

ESI-MS (acetone, 60 °C, 4.5 kV) positive ion: [M]⁺ m/z = 695.1819 (calc. 695.1168).

dpp2-Mes

A 250 mL round-bottomed flask was charged with a stirrer bar and MesMgBr (20 mL, 0.0198 mol, 4.6 eq.) in Et₂O (20 mL). (Cl₂PCH₂)₂ (1 g, 4.3 x 10⁻³ mol, 1 eq.) in Et₂O (30 mL) was added dropwise over 30 mins. at 0 °C. The orange solution was stirred overnight at room temperature. NH₄Cl_(aq) (60 mL) was added to the reaction mixture. The ethereal layer was extracted three times with Et₂O (3 x 30 mL). The extracted layers were dried over anhydrous Na₂SO₄, and then filtered into a schlenk. The ether was reduced *in vacuo* to ~20 mL and MeOH (10 mL) added to give a white precipitate. The solid was collected by filtration, redissolved in THF (30 mL), then layered with MeOH (15 mL) and stored overnight at -18 °C to give a white solid, yield = 25 %, 611 mg. The compound was characterised by NMR spectroscopy.

¹H NMR (300 MHz, CDCl₃): δ 6.67 (s, 8H, C₆H₂), 2.30 (s, 4H, CH₂), 2.18 (s, 12H, *p*-CH₃), 2.09 (s, 24H, *o*-CH₃).

³¹P{¹H} NMR (122 MHz, CDCl₃): δ -19.15 (s).

[Rh($\kappa^2_{(PP)}$ -dpp2-Mes)(NBD)][BAR^F₄] (29)

[Rh(NBD)Cl]₂ (50 mg, 0.1085 mmol, 1 eq.) and dpp2-Mes (122.9 mg, 0.2169 mmol, 2 eq.) were dissolved together in CH₃OH (5 mL) and stirred for 30 min, then added dropwise to a stirring suspension of Na[BAR^F₄] (192.2 mg, 0.2169 mmol, 2 eq.) in CH₂Cl₂ (2 mL), out of which an orange precipitate rapidly formed. The suspension was stirred for 2 h, then evaporated to dryness *in vacuo* and the resulting residue partially redissolved in CH₂Cl₂ (5 mL). The solution was filtered and enough pentane added to the filtrate to observe a precipitate (~ 15 mL). The solution was stored overnight at -18 °C to give orange crystals, yield = 89 %, 299 mg. The compound was characterised by NMR spectroscopy.

¹H NMR (300 MHz, d₆-acetone): δ 7.79 (m, 8H, BAR^F₄), 7.68 (m, 4H, BAR^F₄), 7.01 (m, 8H, Mes-H), 4.76 (m, 4H, NBD CH=CH), 3.97 (m, 2H, NBD CH), 2.77 [app. d, 4H, *J*(PH) = 21, P-CH₂), 2.42 (s, 24H, *o*-Mes), 2.29 (s, 12H, *p*-Mes), 1.58 (s, 2H, NBD CH₂).

³¹P{¹H} NMR (122 MHz, d₆-acetone): δ 36.80 [d, *J*(RhP) = 154].

[Rh($\kappa^2_{(PP)}$ -dpp2-*o*-Me)(NBD)][BAR^F₄] (30)

[Rh(NBD)Cl]₂ (50 mg, 0.1085 mmol, 1 eq.) and dpp2-*o*-Me (98.6 mg, 0.2169 mmol, 2 eq.) were dissolved together in CH₃OH (5 mL) and stirred for 30 min, then added dropwise to a stirring suspension of Na[BAR^F₄] (192.2 mg, 0.2169 mmol, 2 eq.) in CH₂Cl₂ (2 mL), out of which an orange precipitate rapidly formed. The suspension was stirred for 2 h, then evaporated to dryness *in vacuo* and the resulting residue partially redissolved in CH₂Cl₂ (5 mL). The solution was filtered and enough pentane added to the filtrate to observe a precipitate (~ 15 mL). The solution was stored overnight at -18 °C to give orange crystals, yield = 99 %, 265 mg. The compound was characterised by NMR spectroscopy, ESI-MS and elemental analysis.

¹H NMR (500 MHz, d₆-acetone): δ 7.92 (m, 4H, Ar-H), 7.80 (m, 8H, BAR^F₄), 7.68 (m, 4H, BAR^F₄), 7.50 (m, 4H, Ar-H), 7.42-7.34 (m, 8H, Ar-H), 5.11 (m, 4H, NBD

CH=CH), 4.14 (m, 2H, NBD CH), 2.80 [app. d, 4H, $J(\text{PH}) = 19$, P-CH₂], 2.26 (s, 12H, *o*-Me), 1.70 (s, 2H, NBD CH₂).

³¹P{¹H} NMR (122 MHz, d₆-acetone): δ 54.73 [d, $J(\text{RhP}) = 160$].

ESI-MS (acetone, 60 °C, 4.5 kV) positive ion: $[\text{M}]^+ m/z = 649.1794$ (calc. 649.1655).

Microanalysis: C₆₉H₅₂BF₂₄P₂Rh (1512.78) requires: C 54.78, H 3.46; found: C 54.32, H 3.61.

[Rh($\kappa^2_{\text{(PP)}}\text{-dpp2-}o\text{-Me}$)(acetone)₂][BAr^F₄] (31)

The title compound was prepared *in situ*, by addition of hydrogen (4 atm) to a solution of [Rh($\kappa^2_{\text{(PP)}}\text{-dpp2-}o\text{-Me}$)(NBD)][BAr^F₄] (25.2 mg, 0.017 mmol) in d₆-acetone (0.4 mL). A colour change from yellow-orange to red-orange was observed. The compound was characterised *in situ* by NMR spectroscopy and ESI-MS.

¹H NMR (500 MHz, d₆-acetone): δ 8.17 (m, 4H, Ar-H), 7.80 (m, 8H, BAr^F₄), 7.68 (m, 4H, BAr^F₄), 7.42 (m, 4H, Ar-H), 7.33-7.22 (m, 8H, Ar-H), 2.64 [app. d, 4H, $J(\text{PH}) = 17$, P-CH₂], 2.35 (s, 12H, *o*-Me).

³¹P{¹H} NMR (122 MHz, d₆-acetone): δ 78.99 [d, $J(\text{RhP}) = 208$].

ESI-MS (acetone, 60 °C, 4.5 kV) positive ion: $[\text{M-(acetone)}_2]^+ m/z = 557.0466$ (calc. 557.1029); $[\text{M-(acetone)}]^+ m/z = 615.0841$ (calc. 615.1447).

[Rh($\kappa^2_{\text{(PP)}}\text{-dpp2}$)(NBD)][BAr^F₄] (23) (improved synthetic route)¹⁷

[Rh($\kappa^2_{\text{(PP)}}\text{-dpp2}$)Cl]₂ (50 mg, 4.9 x 10⁻² mmol, 1 eq.) and Na[BAr^F₄] (86.8 mg, 9.8 x 10⁻² mmol, 2 eq.) were stirred together in C₆H₄F₂ (10 mL) for 20 min. C₇H₈ (norbornadiene) (24.9 μ L, 2.5 x 10⁻¹ mmol, 5 eq.) was added to the mixture, and the mixture stirred for 2 h. The mixture was filtered and pentane (25 mL) added to the filtrate. The solution was stored overnight at -18 °C. The solution was

reduced to 10 mL, filtered, and hexane (25 mL) added to the filtrate. The solvent was removed *in vacuo* leaving an orange powder. Yield = 45 %, 65 mg. The compound was characterised by NMR spectroscopy.

^1H NMR (300 MHz, d_6 -acetone): δ 7.50-7.88 (m, 32H, BAr^{Cl_4} + Ar-H), 5.51 (m, 4H, NBD $\text{CH}=\text{CH}$), 4.26 (m, 2H, NBD CH), 2.58 (m, 4H, P- CH_2), 1.82 (s, 2H, NBD CH_2).

$^{31}\text{P}\{^1\text{H}\}$ NMR (122 MHz, d_6 -acetone): δ 55.9 [d, $J(\text{RhP}) = 157$].

$[\text{Rh}(\kappa^2_{(\text{PP})}\text{-dpp2})(\text{Cl})\{\kappa^2_{(\text{C,S})}\text{-C(O)C}_6\text{H}_4\text{SCH}_3\}][\text{BAr}^{\text{Cl}_4}]$ (39)

A solution of $[\text{Rh}(\text{dpp2})(\text{NBD})][\text{BAr}^{\text{Cl}_4}]$ (103 mg, 0.0863 mmol, 1 eq.) in acetone (8 mL) was placed under 4 atm of hydrogen and stirred for 1 h. Acyl-chloride (**VII**) $\text{ClC(O)C}_6\text{H}_4\text{SCH}_3$ (18 mg, 0.0949 mmol, 1.1 eq.) was added under an atmosphere of argon and the solution stirred for 2 h. A colour change to pale yellow was observed. The solvent was removed *in vacuo* and the resultant residue agitated in pentane (10 mL) to give a pale yellow solid, yield = 94 %, 104 mg. The compound was characterised by NMR spectroscopy, ESI-MS and elemental analysis.

^1H NMR (300 MHz, d_6 -acetone): δ 8.32-7.01 (m, 36H, Ar-H + BAr^{Cl_4}), 3.94-3.40 (m, 3H, P- CH_2), 3.35 [br d, 3H, $J(\text{RhH}) = 4.3$, S- CH_3], 3.18 (m, 1H, P- CH_2').

$^{31}\text{P}\{^1\text{H}\}$ NMR (122 MHz, d_6 -acetone): δ 61.26 [br dd, $J(\text{RhP}) = 143$, $J(\text{PP}) = 7.3$, P *trans* SCH_3], 54.21 [br dd, $J(\text{RhP}) = 135$, $J(\text{PP}) = 8.1$, P *trans* Cl].

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, d_6 -acetone): δ 209.2 (m, Rh-C=O), 165.5 [q, $J(\text{BC}) = 49$, BAr^{Cl_4}], 145.0-126.8 [Ar-H + BAr^{Cl_4} { 134.0 (br, BAr^{Cl_4}), 133.9 (m, BAr^{Cl_4})}], 124.0 (s, BAr^{Cl_4}), 27.6 [dd, $J(\text{PC}) = 35$, $J(\text{P}'\text{C}) = 12$, P- CH_2], 25.9 [dd, $J(\text{P}'\text{C}) = 35$, $J(\text{PC}) = 8$, P- CH_2'], 20.0 (s, S- CH_3).

$^1\text{H}\{^{31}\text{P}_{62\text{ppm}}\}$ NMR (500 MHz, d_6 -acetone, selective data): δ 3.35 (s, SCH_3).

^1H - ^{13}C HSQC NMR (500 MHz, d_6 -acetone): Sixteen $^1J(\text{CH})$ environments observed for ligand + acyl Ar-H, indicating free rotation of ligand phenyl groups: δ 135.1 [d, $J(\text{PC}) = 8.5$, Ar-H], 134.7 (s, Ar-H), 134.6 [d, $J(\text{PC}) = 8.5$, Ar-H], 133.2 (m, Ar-H), 133.1 [d, $J(\text{PC}) = 8.5$, Ar-H], 132.3 (m, Ar-H), 132.1 (m, Ar-H, two $^1J(\text{CH})$

environments observed), 131.8 [d, $J(\text{PC}) = 8.5$, Ar-H], 131.0 (m, Ar-H), 130.6 (s, Ar-H), 130.1 [d, $J(\text{PC}) = 10$, Ar-H], 129.8 [d, $J(\text{PC}) = 10$, Ar-H], 129.4 [d, $J(\text{PC}) = 10$, Ar-H], 129.1 [d, $J(\text{PC}) = 10$, Ar-H], 126.8 (s, Ar-H).

ESI-MS (fluorobenzene, 60 °C, 4.5 kV) positive ion: $[\text{M}]^+$ $m/z = 687.0506$ (calc. 687.0309).

Microanalysis: $\text{C}_{35}\text{H}_{37}\text{B}_{11}\text{Br}_6\text{ClOP}_2\text{RhS}$ (1304.38) requires: C 32.23, H 2.86; found: C 32.12, H 2.82.

[Rh($\kappa^2(\text{PP})$ -dpp2-*o*-iPr)(NBD)][BAr^F₄] (32)

[Rh(NBD)Cl]₂ (20 mg, 0.0434 mmol, 1 eq.) and dpp2-*o*-iPr (49.2 mg, 0.0868 mmol, 2 eq.) were dissolved together in CH₃OH (5 mL) and stirred for 30 min, then added dropwise to a stirring suspension of Na[BAr^F₄] (75.2 mg, 0.0868 mmol, 2 eq.) in CH₃OH (2 mL), out of which an orange precipitate rapidly formed. The suspension was stirred for 2 h, then evaporated to dryness *in vacuo* and the resulting residue partially redissolved in CH₂Cl₂ (5 mL). The solution was filtered and enough pentane added to the filtrate to observe a precipitate (~ 15 mL). The solution was stored overnight at -18 °C to give orange crystals, yield = 78 %, 110 mg. The compound was characterised by NMR spectroscopy, ESI-MS and elemental analysis.

¹H NMR (300 MHz, d₆-acetone): δ 8.03-7.33 [m, 28H, Ar-H + BAr^F₄; {7.79 (8H, BAr^F₄), 7.67 (4H, BAr^F₄)}, 5.15 (s, 4H, NBD CH=CH), 4.23 (s, 2H, NBD CH), 3.09 [sept, 4H, $J(\text{HH}) = 6.6$, Ar-CH(CH₃)₂], 2.73 [app. d, 4H, $J(\text{PH}) = 22$, P-CH₂], 1.74 (s, 2H, NBD CH₂), 1.14 [app. d, 12H, $J(\text{PH}) = 6.9$, Ar-CH(CH₃)(CH₃')], 1.05 [app. d, 12H, $J(\text{PH}) = 6.8$, Ar-CH(CH₃)(CH₃')].

³¹P{¹H} NMR (122 MHz, d₆-acetone): δ 50.92 [br d, $J(\text{RhP}) = 157$].

ESI-MS (fluorobenzene, 60 °C, 4.5 kV) positive ion: $[\text{M}]^+$ $m/z = 761.2912$ (calc. 761.2907).

Microanalysis: $\text{C}_{77}\text{H}_{68}\text{BF}_{24}\text{P}_2\text{Rh}$ (1625.0) requires: C 56.91, H 4.22; found: C 56.72, H 4.26.

[Rh($\kappa^2_{(PP)}$ -dpp2-*o*-iPr)(acetone)₂][BAr^F₄] (33)

A solution of [Rh($\kappa^2_{(PP)}$ -dpp2-*o*-iPr)(NBD)][BAr^F₄] (200 mg, 0.123 mmol) in acetone (8 mL) was placed under 4 atmospheres of hydrogen and stirred for 1 h. A slow colour change from yellow-orange to red-orange was observed. The solvent was removed *in vacuo* and the resultant residue agitated in hexane (10 mL) to give an orange solid, yield = 87 %, 176 mg. The compound was characterised by NMR spectroscopy, ESI-MS and elemental analysis.

¹H NMR (300 MHz, d₆-acetone): δ 8.01-7.19 [m, 28H, Ar-H + BAr^F₄; {7.79 (8H, BAr^F₄), 7.67 (4H, BAr^F₄)}, 3.70 [sept, 4H, *J*(HH) = 6.6, Ar-CH(CH₃)₂], 2.63 [app. dd, 4H, *J*(PH) = 17, *J*(HH) = 1.0, P-CH₂], 1.18 [app. d, 12H, *J*(PH) = 6.7, Ar-CH(CH₃)(CH₃')], 1.12 [app. d, 12H, *J*(PH) = 6.7, Ar-CH(CH₃)(CH₃')].

³¹P{¹H} NMR (122 MHz, d₆-acetone): δ 79.24 [br d, *J*(RhP) = 205].

ESI-MS (acetone, 60 °C, 4.5 kV) positive ion: [M]⁺ *m/z* = 785.3158 (calc. 785.3118); [M-acetone]⁺ *m/z* = 727.2766 (calc. 727.2699); [M-(acetone)₂]⁺ *m/z* = 669.2284 (calc. 669.2281).

Microanalysis: C₇₆H₇₂BF₂₄O₂P₂Rh (1649.01) requires: C 55.36, H 4.40; found: C 55.58, H 4.72.

[Rh($\kappa^2_{(PP)}$ -dpp2-*o*-iPr)(MeCN)₂][BAr^F₄] (37)

A solution of [Rh($\kappa^2_{(PP)}$ -dpp2-*o*-iPr)(NBD)][BAr^F₄] (16 mg, 0.099 mmol) and MeCN (3 μ L) in d₆-acetone (0.4 mL) was placed under 4 atmospheres of hydrogen and stirred for 1 h. A colour change from yellow-orange to bright yellow was observed. The complex was characterised *in situ* by NMR spectroscopy and ESI-MS.

¹H NMR (300 MHz, d₆-acetone): δ 7.80 (m, 8H, BAr^F₄), 7.68 (m, 4H, BAr^F₄), 7.57-7.41 (m, 12H, Ar-H), 7.15 (m, 4H, Ar-H), 3.95 [br s, 4H, Ar-CH(CH₃)₂], 2.61 [app. d, 4H, *J*(PH) = 17, P-CH₂], 1.26 [br s, 24H, Ar-CH(CH₃)₂]. MeCN is observed at δ 2.05.

³¹P{¹H} NMR (122 MHz, d₆-acetone): δ 67.09 (br s).

ESI-MS (acetone, 60 °C, 4.5 kV) positive ion: $[M-(MeCN)_2]^+$ $m/z = 669.2385$ (calc. 669.2281).

$[Rh(\kappa^2_{(PP)}-dpp2-o-iPr)\{\kappa^2_{(O,S)}-HC(O)C_6H_4SCH_3\}][BAr^F_4]$ (34** and **34'**) and $[Rh(\kappa^2_{(PP)}-dpp2-o-iPr)(H)(\kappa^1_{(S)}-\sigma^1_{(C)}-COC_6H_4SCH_3)][BAr^F_4]$ (**35**)**

The title compounds were characterized *in situ* by addition of $HC(O)C_6H_4SCH_3$ (**V**) (0.8 μ L, 6.3×10^{-3} mmol, 1 eq.) to a solution of $[Rh(\kappa^2_{(PP)}-dpp2-o-iPr)(acetone)_2][BAr^F_4]$ (10.3 mg, 6.3×10^{-3} mmol, 1 eq.) in d_6 -acetone (0.4 mL). An immediate colour change from orange to brown was observed. **34** is formed as an interconverting mixture of two isomers: **34** and **34'**, in the ratio 1:0.37 at 200 K.

^1H NMR (500 MHz, d_6 -acetone, 200 K): (selected data) δ 10.25 [br d, $J(RhH) = 6.1$, C-H **34**], 10.18 [br d, $J(RhH) = 6.1$, C-H **34'**], 3.68 (br s, S-CH₃ **35**), 1.92 (br s, S-CH₃ **34'**), 1.85 (br s, S-CH₃ **34**), -7.04 [dd, $J(PH) = 169$, $J(RhH) = 16$, Rh-H **35**].

$^{31}P\{^1H\}$ NMR (202 MHz, d_6 -acetone, 200 K): δ 84.36 [dd, $J(RhP) = 187$, $J(PP) = 20$, **34'**], 78.90 [dd, $J(RhP) = 189$, $J(PP) = 32$, **34**], 70.72 [d, $J(RhP) = 160$, **35**], 55.98 [dd, $J(RhP) = 168$, $J(PP) = 20$, **34'**], 44.96 [br d, $J(RhP) = 172$, **34**], 31.37 [d, $J(RhP) = 87$, **35**].

ESI-MS (acetone, 60 °C, 4.5 kV) positive ion: $[M]^+$ $m/z = 821.3013$ (calc. 821.2577); $[M-HCOC_6H_4SCH_3]^+$ $m/z = 669.2635$ (calc. 669.2281).

$[Rh(\kappa^2_{(PP)}-dpp2-o-iPr)(Cl)\{\kappa^1_{(S)}-\sigma^1_{(C)}-C(O)C_6H_4SCH_3\}][BAr^{Cl}_4]$ (38**)**

A solution of $[Rh(\kappa^2_{(PP)}-dpp2-o-iPr)(NBD)][BAr^{Cl}_4]$ (113 mg, 8.3×10^{-2} mmol) in acetone (8 mL) was placed under 4 atmospheres of hydrogen and stirred for 1 h. A slow colour change from yellow-orange to red-orange was observed. The solution was placed under an atmosphere of argon by successive freeze-thaw degas cycles, acyl-chloride $ClCOC_6H_4SCH_3$ **VII** (17 mg, 9.16×10^{-2} mmol, 1.1 eq.) was added and the solution stirred for 2 h. A rapid colour change to pale yellow was observed. The solvent was removed *in vacuo* and the resultant residue agitated in pentane

(10 mL) to give a pale yellow solid, yield = 88 %, 106 mg. Crystal suitable for x-ray diffraction formed on diffusion of pentane into a solution of the complex in acetone, at 4 °C. The compound was characterised by NMR spectroscopy, ESI-MS and elemental analysis.

¹H NMR (300 MHz, CD₂Cl₂, 295 K): δ 8.17 (br, fwhm = 33 Hz, 1H, Ar-H), 7.65-6.90 [m, 31H, Ar-H + BAr^{Cl}₄; {7.04 (8H, BAr^{Cl}₄), 6.99 (4H, BAr^{Cl}₄)}], 3.77-3.25 (m, 2H, P-CH₂), 3.20 [br d, *J*(RhH) = 3.6, 3H, S-CH₃], 3.15-2.32 [m, 6H, P-CH₂' + Ar-CH(CH₃)₂], 1.36-0.50 [m, 24H, Ar-CH(CH₃)₂].

¹H NMR (500 MHz, d₆-acetone, 200 K): δ 8.47-8.31 (m, 1H, Ar-H), 7.86-6.88 (m, 31H, Ar-H + BAr^{Cl}₄), 4.19 (br, 1H, P-CH₂^a), 3.93-3.72 (br m, 1H, P-CH₂^b), 3.56-3.34 [br m, 3H, P-CH₂^a + Ar-CH(CH₃)₂^c], 3.32 [br d, *J*(RhH) = 3.5, 3H, S-CH₃], 2.93 [br m, 1H, Ar-CH(CH₃)₂^d], 2.84 [br m, 1H, Ar-CH(CH₃)₂^e], 2.76 [br m, 1H, Ar-CH(CH₃)₂^f], 2.23 (br, 1H, P-CH₂^b), 1.27 [br m, 6H, Ar-CH(CH₃)₂^d], 1.20 [br m, 3H, Ar-CH(CH₃)(CH₃)^e], 1.10 [br m, 3H, Ar-CH(CH₃)(CH₃)^e], 1.01 [br m, 3H, Ar-CH(CH₃)(CH₃)^f], 0.61 [br m, 3H, Ar-CH(CH₃)(CH₃)^e], 0.45 [br m, 3H, Ar-CH(CH₃)(CH₃)^f], 0.13 [br m, 3H, Ar-CH(CH₃)(CH₃)^c].

³¹P{¹H} NMR (202 MHz, d₆-acetone, 200 K): δ 62.03 [d, *J*(RhP) = 127, P *trans* Cl], 59.89 [d, *J*(RhP) = 149, P *trans* SCH₃].

ESI-MS (acetone, 60 °C, 4.5 kV) positive ion: [M]⁺ *m/z* = 855.2491 (calc. 855.2187).

Microanalysis for C₇₀H₆₇BCl₉OP₂RhS (1451.09) requires: C 57.94, H 4.65; found: C 58.05, H 4.90.

[Rh(κ²_(PP)-dpp2-*o*-iPr){κ²_(OS)-SCH₃C₆H₄C(O)C(=CH₂)C₆H₃(CF₃)₂}[BAr^F₄] (36)

The title compound was characterized *in situ* by addition of isolated branched product SCH₃C₆H₄C(O)C(=CH₂)C₆H₃(CF₃)₂ (**XIII**) (2.3 mg, 0.0059 mmol, 1.1 eq.) to a solution of [Rh(dpp2-*o*-iPr)(acetone)₂][BAr^F₄] (8.7 mg, 0.0053 mmol, 1 eq.) in d₆-acetone (0.4 mL). An immediate colour change from orange to brown was observed. The compound was characterised by NMR spectroscopy and ESI-MS.

^1H NMR (300 MHz, d_6 -acetone): δ 8.91 (br s, 1H, Ar-H), 8.17-6.89 [br m, 34H, ligand Ar-H + bound product Ar-H + BAr^{F_4} ; {7.79 (8H, BAr^{F_4}), 7.67 (4H, BAr^{F_4})}, 6.86 (s, 1H, $\text{C}=\text{CH}_2^{\text{a}}$), 6.24 (s, 1H, $\text{C}=\text{CH}_2^{\text{b}}$), 4.69-2.55 [br, 6H, P- CH_2 + Ar- $\text{CH}(\text{CH}_3)_2$], 2.26 (s, 3H, S- CH_3), 1.34-0.82 [br m, 24H, Ar- $\text{CH}(\text{CH}_3)_2$].

$^{31}\text{P}\{^1\text{H}\}$ NMR (122 MHz, d_6 -acetone): δ 81.01 [br dd, $J(\text{RhP}) = 198$, $J(\text{PP}) = 32$], 51.63 (br s).

ESI-MS (fluorobenzene, 60 °C, 4.5 kV) positive ion: $[\text{M}]^+$ $m/z = 1059.2968$ (calc. 1059.2794).

$[\text{Rh}(\kappa^3(\text{POP})\text{-DPEphos})\{\kappa^1(\text{S})\text{-}\sigma^1(\text{C})\text{-C}(\text{O})\text{C}_6\text{H}_4\text{SCH}_3\}\{\sigma^1(\text{C})\text{-C}(\text{=CH}_2)\text{C}_6\text{H}_3(\text{CF}_3)_2\}][\text{closo-CB}_{11}\text{H}_{12}]$ (43)

$[\text{Rh}(\kappa^2(\text{PP})\text{-DPEphos})(\text{acetone})_2][\text{closo-CB}_{11}\text{H}_{12}]$ is formed *in situ* on hydrogenation (4 atm) of $[\text{Rh}(\kappa^2(\text{PP})\text{-DPEphos})\text{NBD}][\text{closo-CB}_{11}\text{H}_{12}]$ (100.9 mg, 0.12 mmol, 1 eq.) in acetone (5 mL). $\text{HC}(\text{O})\text{C}_6\text{H}_4\text{SCH}_3$ (**V**) (74.2 μL , 0.6 mmol, 5 eq.) and $\text{HC}\equiv\text{CC}_6\text{H}_3(\text{CF}_3)_2$ (**XI**) (101.8 μL , 0.6 mmol, 5 eq.) were added and the solution stirred for 1 h. There was a colour change from dark red through dark brown and finally to bright yellow. The solution was added dropwise to a stirring solution of pentane (30 mL) to give a suspension of a pale solid in bright yellow solution. The solution was filter-decanted off and the solid washed with pentane (5 x 5 mL). The resulting pale yellow solid was dried *in vacuo* (yield = 86 %, 117 mg). The compound was characterised by NMR spectroscopy, ESI-MS and elemental analysis.

^1H NMR (500 MHz, d_6 -acetone): δ 8.53 [app. dd, 1H, $J(\text{HH}) = 8.1$, $J(\text{PH}) = 4.9$, Ar-H], 8.34 [app. dd, 1H, $J(\text{HH}) = 8.5$, $J(\text{PH}) = 5.3$, Ar-H], 8.09-8.00 (m, 4H, Ar-H), 7.80-7.24 (m, 20H, Ar-H), 7.12 [app. t, 1H, $J = 7.6$, Ar-H], 7.02 [app. t, 1H, $J = 7.4$, Ar-H], 6.94 [app. d, 1H, $J = 7.8$, Ar-H], 6.65 [app. td, 2H, $J = 8.2$, $J(\text{PH}) = 2.6$, Ar-H], 6.42 (s, 2H, Ar-H), 6.30 [app. ddd, 2H, $J(\text{PH}) = 10.9$, $J = 8.2$, $J = 1.0$, Ar-H], 5.72 [d, 1H, $J(\text{PH}) = 8.9$, $\text{C}=\text{CH}_2$], 5.50 [d, 1H, $J(\text{PH}) = 18.1$, $\text{C}=\text{CH}_2'$], 2.59 (br s, 3H, S- CH_3), 2.27-1.11 (br m, 12H, $\text{CB}_{11}\text{H}_{12}$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, d_6 -acetone): δ 21.87 [dd, $J(\text{RhP}) = 166.5$, $J(\text{PP}) = 27.0$], 13.12 [dd, $J(\text{RhP}) = 78.7$, $J(\text{PP}) = 27.0$].

^{19}F NMR (282 MHz, d_6 -acetone): δ 62.92 (br s, fwhm = 2.6, CF_3).

$^1\text{H}\{^{31}\text{P}_{22\text{ppm}}\}$ NMR (500 MHz, d_6 -acetone, selective data): δ 8.34 [app. d, 1H, $J = 8.5$, Ar-H], 2.59 (sharp s, 3H, S- CH_3).

$^1\text{H}\{^{31}\text{P}_{13\text{ppm}}\}$ NMR (500 MHz, d_6 -acetone, selective data): δ 8.53 [app. d, 1H, $J(\text{HH}) = 8.1$, Ar-H], 6.65 [app. t, 2H, $J = 8.2$, Ar-H], 6.30 [app. dd, 2H, $J = 8.2$, $J = 1.0$, Ar-H], 5.72 (s, $\text{C}=\text{CH}_2$), 5.50 (s, $\text{C}=\text{CH}_2'$).

^1H - ^1H COSY NMR (500 MHz, d_6 -acetone): Correlation observed between $\text{C}=\text{CH}_2$ proton peaks at δ 5.72 and 5.50.

^1H - ^{13}C HSQC NMR (500 MHz, d_6 -acetone): Twenty-six $^1J(\text{CH})$ environments observed for ligand + acyl Ar-H + alkyl Ar-H, indicating free rotation of alkyl group, and the phenyl groups. Two $^1J(\text{CH})$ environments are observed for the $\text{C}=\text{CH}_2$ protons, on the same carbon.

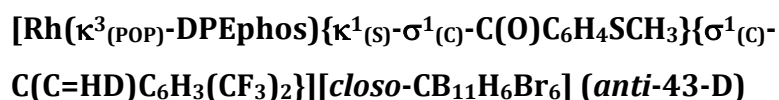
ESI-MS (fluorobenzene, 60°C, 4.5 kV) positive ion: $[\text{M}]^+$ $m/z = 1031.1497$ (calc. 1031.1178).

Microanalysis: $\text{C}_{55}\text{H}_{52}\text{B}_{11}\text{F}_6\text{O}_2\text{P}_2\text{RhS}$ (1174.8291) requires: C 56.23, H 4.46; found: C 56.31, H 4.44.

$[\text{Rh}(\kappa^3(\text{POP})\text{-DPEphos})\{\kappa^1(\text{S})\text{-}\sigma^1(\text{C})\text{-C}(\text{O})\text{C}_6\text{H}_4\text{SCH}_3\}\{\sigma^1(\text{C})\text{-C}(\text{C}=\text{D}_2)\text{C}_6\text{H}_3(\text{CF}_3)_2\}][\text{closo-CB}_{11}\text{H}_6\text{Br}_6]$ (43-D₂**)**

The complex was synthesised according to the method above (using **D-V** and **D-XI**) to give an off-white coloured solid (yield = 93 %, 24.6 mg). NMR characterisation showed the same spectrum as for **43**, except for selected data, shown below.

^2H NMR (76.7 MHz, acetone): δ 5.72 (s, CD_2), 5.54 (s, CD_2').

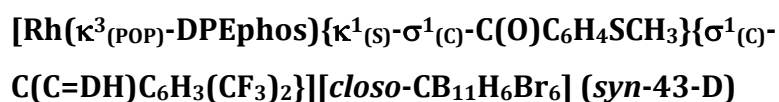


The complex was synthesised according to the method above (with **V** and **D-XI**) to give an off-white coloured solid (yield = 96 %, 18.0 mg). NMR characterisation showed the same spectrum as for **43**, except for selected data, shown below.

¹H NMR (500 MHz, acetone, selected data): δ 5.72 [d, 1H, $J(\text{PH}) = 8.9$, C=CHD].

²H NMR (76.7 MHz, acetone): δ 5.60 (s, CHD).

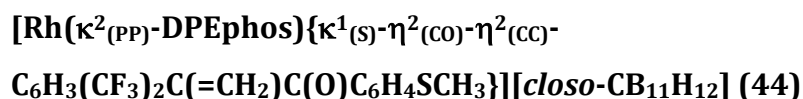
Microanalysis: C₅₅H₅₁B₁₁F₆O₂P₂RhS (1175.83) requires: C 56.18, H 4.54; found: C 56.27, H 4.42.



The complex was synthesised according to the method above (with **D-V** and **XI**) to give an off-white coloured solid (yield = 87 %, 19.7 mg). NMR characterisation showed the same spectrum as for **6**, except for selected data, shown below.

¹H NMR (500 MHz, acetone, selected data): δ 5.50 [d, 1H, $J(\text{PH}) = 18.1$, C=CDH].

²H NMR (76.7 MHz, acetone): δ 5.73 (s, CDH).



Isolated branched product C₆H₃(CF₃)₂C(=CH₂)C(O)C₆H₄SCH₃ (**XIII**) (7.4 mg, 0.018 mmol, 1 eq.) was added to a solution of [Rh(κ²(PP)-DPEphos)(acetone)₂][closo-CB₁₁H₁₂] (16.6 mg, 0.018 mmol, 1 eq.) in CH₂Cl₂ (5 mL). A colour change from dark red to orange-yellow was observed, while the mixture was stirred for 1 h. Crystals suitable for x-ray diffraction were obtained by diffusion of pentane into a solution of the complex in CH₂Cl₂ (yield = 87 %, 15.8 mg). The compound was characterised by NMR spectroscopy and ESI-MS.

¹H{³¹P} NMR (500 MHz, d₆-acetone, selected data): δ 2.25 [app. t, *J* = 1.65, C=CH₂'].

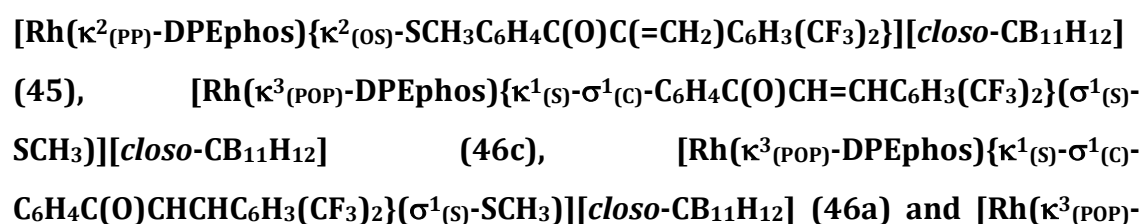
$^1\text{H}\{^{31}\text{P}_{32\text{ppm}}\}$ NMR (500 MHz, $\text{d}_6\text{-acetone}$, selected data): δ 7.34 (t, 2H, $J = 7.8$, Ar-H), 7.15 (app. d, 1H, $J = 7.5$, Ar-H), 6.94 (app. d, 2H, $J = 7.5$, Ar-H), 6.39 (app. d, 1H, $J = 7.5$, Ar-H), 3.60 (sharp s, 1H, $\text{C}=\text{CH}_2$), 2.25 [app. dt, 1H, $J(\text{PH}) = 11.5$, $J = 1.65$, $\text{C}=\text{CH}_2$].

$^1\text{H}\{^{31}\text{P}_{28\text{ppm}}\}$ NMR (500 MHz, d_6 -acetone, selected data): δ 7.08 (app. d, 1H, J = 7.5, Ar-H), 2.25 (m, 1H, C=CH₂'),

¹H-¹H COSY NMR (500 MHz, d₆-acetone): Correlation observed between C=CH₂ proton signals at δ 3.60 and 2.25.

¹H-¹³C HSQC NMR (500 MHz, d₆-acetone): Correlation observed between C=CH₂ peaks, and one carbon signal at δ 41.2.

ESI-MS (fluorobenzene, 60°C, 4.5 kV) positive ion: $[M]^+$ $m/z = 1031.1505$ (calc. 1031.8021).



DPEphos){ $\kappa^1_{(S)}$ - $\sigma^1_{(C)}$ -C₆H₄C(O)CH=CHC₆H₃(CF₃)₂}($\sigma^1_{(S)}$ -SCH₃)][*closo*-CB₁₁H₁₂] (46b).

The title compounds are formed *in situ* on addition of isolated linear product C₆H₃(CF₃)₂CHCHC(O)C₆H₄SCH₃ (**XII**) (4.9 mg, 0.01 mmol, 1 eq.) to a solution of [Rh($\kappa^2_{(PP)}$ -DPEphos)(acetone)₂][*closo*-CB₁₁H₁₂] (11.4 mg, 0.01 mmol, 1 eq.) in d₆-acetone (0.4 mL). A colour change from dark red to dark brown was observed. The compound was characterised by NMR spectroscopy and ESI-MS.

¹H NMR (500 MHz, d₆-acetone, 295 K, selected data): δ 8.34 (dt, *J*(Rh) = 8.5, *J*(PH) = 2.5, Ar-H, **46c**) 2.46 (s, S-CH₃, **45**), 1.61 [br d, *J* = 6.9, S-CH₃, **46a**], 0.60 (s, S-CH₃, **46c**), -1.03 [br d, *J* = 5.4, S-CH₃, **46b**].

³¹P{¹H} NMR (202 MHz, d₆-acetone, 295 K): δ 46.01 [dd, *J*(RhP) = 148.3, *J*(PP) = 28.9, **46b**], 41.36 [dd, *J*(RhP) = 155.3, *J*(PP) = 38.6, **45**], 22.76 [dd, *J*(RhP) = 111.8, *J*(PP) = 28.5, **46b**], 19.84 [d, *J*(RhP) = 111.1, **46c**], 6.68 [dd, *J*(RhP) = 162.7, *J*(PP) = 38.6, **45**]

³¹P{¹H} NMR (202 MHz, d₆-acetone, 200 K): δ 48.58 [dd, *J*(RhP) = 147.5, *J*(PP) = 28.3, **46b**], 42.12 [dd, *J*(RhP) = 153.5, *J*(PP) = 38.4, **45**], 35.01 [dd, *J*(RhP) = 151.5, *J*(PP) = 24.2, **46a**], 23.97 [dd, *J*(RhP) = 107.1, *J*(PP) = 24.2, **46a**], 22.99 [dd, *J*(RhP) = 111.1, *J*(PP) = 28.3, **46b**], 20.13 [dd, *J*(RhP) = 111.1, *J*(PP) = 22.2, **46c**], 6.92 [dd, *J*(RhP) = 163.6, *J*(PP) = 40.4, **45**].

ESI-MS (fluorobenzene, 60°C, 4.5 kV) positive ion: [M]⁺ *m/z* = 1031.1576 (calc. 1031.1178).

[Rh($\kappa^3_{(POP)}$ -DPEphos)(H){ $\kappa^1_{(S)}$ - $\sigma^1_{(C)}$ -C(O)C₆H₈SCH₃}] [*closo*-CB₁₁H₁₂] (47)

A solution of [Rh($\kappa^2_{(PP)}$ -DPEphos)(acetone)₂][*closo*-CB₁₁H₁₂] was prepared *in situ* from [Rh($\kappa^2_{(PP)}$ -DPEphos)(NBD)][*closo*-CB₁₁H₁₂] (50 mg, 5.7 x 10⁻² mmol) hydrogenated in acetone (5 mL). The aldehyde **XVIII** (10.7 mg, 6.8 x 10⁻² mmol, 1.2 eq.) was added under an atmosphere of argon, and the solution stirred for 2 h. The solvent was removed *in vacuo* and the resultant residue agitated in pentane (10 mL) to give a pale yellow solid, yield = 79 %, 42.4 mg. Crystal suitable for x-ray

diffraction formed on diffusion of hexane into a solution of the complex in CD_2Cl_2 , at room temperature. The compound was characterised by NMR spectroscopy.

^1H NMR (300 MHz, CD_2Cl_2): δ 8.01 (m, 4H, Ar-H), 7.56-7.42 (m, 14H, Ar-H), 7.40-7.33 (m, 4H, Ar-H), 7.26 (m, 2H, Ar-H), 7.13 (m, 4H, Ar-H), 2.37-0.61 [br, 12H + 13H, $\text{CB}_{11}\text{H}_{12}$ + 4 CH_2 + SCH_3 {1.87 (m, 2H, CH_2), 1.77 (m, 2H, CH_2), 1.36 [app. d, 3H, $J(\text{HH}) = 1.6$, SCH_3], 1.34-1.24 (m, 2H, CH_2), 1.22-1.12 (m, 2H, CH_2)}, -8.02 [app. dtd, 1H, $J(\text{RhH}) = 24$, $J(\text{PH}) = 4.6$, $J(\text{HH}) = 1.8$, Rh-H].

$^{31}\text{P}\{^1\text{H}\}$ NMR (122 MHz, CD_2Cl_2): δ 127 [d, $J(\text{RhP}) = 127$].

$[\text{Rh}(\kappa^3(\text{POP})\text{-DPEphos})(\text{Cl})(\kappa^1(\text{S})\text{-}\sigma^1(\text{C})\text{-CO}\text{C}_6\text{H}_4\text{SCH}_3)][\text{closo-CB}_{11}\text{H}_{12}]$ (48)

The title compound was synthesised *in situ* on addition of $\text{Cl}(\text{CO})\text{C}_6\text{H}_4\text{SCH}_3$ (**VII**) (4.3 mg, 0.023 mmol, 1 eq.) to a solution of $[\text{Rh}(\kappa^2(\text{PP})\text{-DPEphos})(\text{acetone})_2][\text{closo-CB}_{11}\text{H}_{12}]$ (20.8 mg, 0.023 mmol, 1 eq.) in d_6 -acetone (0.4 mL). There was a colour change from dark red to orange. The compound was characterised by NMR spectroscopy and ESI-MS.

^1H NMR (500 MHz, d_6 -acetone): δ 8.21 [app. dd, 1H, $J = 8.8$, $J = 5.6$, Ar-H], 8.11 [app. dd, 1H, $J = 8.0$, $J = 5.1$, Ar-H], 8.05-7.92 (m, 4H, Ar-H), 7.84 [t, 1H, $J = 7.7$, Ar-H], 7.72-7.24 (m, 16H, Ar-H), 7.16-7.08 (m, 3H, Ar-H), 7.00 [app. dd, 2H, $J = 11.5$, $J = 8.6$, Ar-H], 6.65 [app. td, 2H, $J = 8.3$, $J = 2.4$, Ar-H], 6.44 [app. dd, 2H, $J = 11.3$, $J = 8.3$, Ar-H], 2.92 [app. dd, 3H, $J(\text{PH}) = 4.2$, $J = 1.1$, S- CH_3], 2.28-1.12 (br, 12H, $\text{CB}_{11}\text{H}_{12}$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, d_6 -acetone): δ 29.72 [dd, $J(\text{RhP}) = 134.6$, $J(\text{PP}) = 18.5$], 20.09 [dd, $J(\text{RhP}) = 143.1$, $J(\text{RhP}) = 18.5$].

$^1\text{H}\{^{31}\text{P}_{20\text{ppm}}\}$ NMR (500 MHz, d_6 -acetone, selective data): δ 2.92 [app. d, 3H, $J = 1.1$, S- CH_3].

ESI-MS (fluorobenzene, 60°C, 4.5 kV) positive ion: $[\text{M}]^+$ $m/z = 827.2683$ (calc. 827.0571).

5.7 NMR experiments

[Rh(κ^3 (POP)-DPEphos)(H)(κ^1 (S)- σ^1 (C)-(CO)C₆H₄SCCH₃)] [*closo*-CB₁₁H₁₂] and HC $\equiv$ CC₆H₃(CF₃)₂ (XI) (1 eq.)

Alkyne HC $\equiv$ CC₆H₃(CF₃)₂ (XI) (16.8 μ L, 0.01 mmol, 1 eq.) was added to a solution of [Rh(κ^3 (POP)-DPEphos)(H)(κ^1 (S)- σ^1 (C)-(CO)C₆H₄SCCH₃)] [*closo*-CB₁₁H₁₂] (10.4 mg, 0.01 mmol, 1 eq.) in d₆-acetone (0.4 mL). A colour change from dark red to dark brown was observed. The compound was characterised by NMR spectroscopy and ESI-MS.

¹H NMR (500 MHz, d₆-acetone, 295 K, selected data): δ 2.59 (br s, S-CH₃, **x-2**), 2.46 (s, S-CH₃, **x**), 1.89 (app. dd, $J = 1.8, J = 0.49$, S-CH₃, **x-3**), 1.61 (br d, $J = 6.8$, **x+1-fac A**), 0.60 (m, S-CH₃, **x+1-mer**), -1.03 (br d, $J = 5.5$, S-CH₃, **x+1-fac B**), -8.21 [dtd, $J(\text{RhH}) = 25, J(\text{PH}) = 5, J(\text{HH}) = 1.7$, Rh-H, **x-3**].

³¹P{¹H} NMR (202 MHz, d₆-acetone, 295 K): δ 47.01 [dd, $J(\text{RhP}) = 148.3, J(\text{PP}) = 28.9$, **x+1-fac B**], 41.36 [dd, $J(\text{RhP}) = 155.3, J(\text{PP}) = 38.6$, **x**], 27.03 [d, $J(\text{RhP}) = 127.3$, **x-3**], 35.01 [dd, $J(\text{RhP}) = 151.5, J(\text{PP}) = 24.2$, **x+1-fac A**], 23.97 [dd, $J(\text{RhP}) = 107.1, J(\text{PP}) = 24.2$, **x+1-fac A**], 22.76 [dd, $J(\text{RhP}) = 111.8, J(\text{PP}) = 28.5$, **x+1-fac B**], 21.87 [dd, $J(\text{RhP}) = 166.5, J(\text{PP}) = 27.0$, **x-2**], 19.84 [d, $J(\text{RhP}) = 111.1$, **x+1-mer**], 13.12 [dd, $J(\text{RhP}) = 78.7, J(\text{PP}) = 27.0$, **x-2**], 6.68 [dd, $J(\text{RhP}) = 162.7, J(\text{PP}) = 38.6$, **x**].

ESI-MS (fluorobenzene, 60°C, 4.5 kV) positive ion: [M]⁺ $m/z = 1031.1241$ (calc. 1031.1178).

5.8 References

1. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518-1520.
2. D. R. Burfield and R. H. Smithers, *The Journal of Organic Chemistry*, 2002, **43**, 3966-3968.
3. A. T. Lubben, J. S. McIndoe and A. S. Weller, *Organometallics*, 2008, **27**, 3303-3306.
4. J. Cosier and A. M. Glazer, *Journal of Applied Crystallography*, 1986, **19**, 105-107.
5. L. J. Farrugia, *Journal of Applied Crystallography*, 1997, **30**, 565-565.
6. W. E. Buschmann, J. S. Miller, K. Bowman-James and C. N. Miller, in *Inorganic Syntheses*, ed. C. Dimitri, 2002, vol. 33, p. 83.
7. A. B. Chaplin and A. S. Weller, *European Journal of Inorganic Chemistry*, **2010**, 5124-5128.
8. M. Kranenburg, Y. E. M. van der Burgt, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz and J. Fraanje, *Organometallics*, 1995, **14**, 3081-3089.
9. G. Giordano and R. H. Crabtree, *Inorganic Syntheses* 1990, **28**, 88.
10. A. Uehara and J. C. Bailar, *Journal of Organometallic Chemistry*, 1982, **239**, 11-15.
11. C. A. Reed, *Accounts of Chemical Research*, 2009, **43**, 121-128.
12. D. H. M. W. Thewissen, K. Timmer, J. G. Noltes, J. W. Marsman and R. M. Laine, *Inorganica Chimica Acta*, 1985, **97**, 143-150.
13. J. Chatt, W. Hussain, G. J. Leigh, H. M. Ali, C. J. Picket and D. A. Rankin, *Journal of the Chemical Society, Dalton Transactions*, 1985, **6**, 1131-1136.
14. C. González-Rodríguez, R. J. Pawley, A. B. Chaplin, A. L. Thompson, A. S. Weller and M. C. Willis, *Angewandte Chemie International Edition*, **50**, 5134-5138.
15. J. M. Brown, S. J. Cook and A. G. Kent, *Tetrahedron*, 1986, **42**, 5097-5104.
16. J. M. Brown, P. A. Chaloner, A. G. Kent, B. A. Murrer, P. N. Nicholson, D. Parker and P. J. Sidebottom, *Journal of Organometallic Chemistry*, 1981, **216**, 263-276.
17. D. P. Fairlie and B. Bosnich, *Organometallics*, 1988, **7**, 936-945.
18. G. L. Moxham, H. Randell-Sly, E. , S. Brayshaw, K., R. L. Woodward, A. S. Weller and M. Willis, C., *Angewandte Chemie International Edition*, 2006, **45**, 7618-7622.
19. G. L. Moxham, H. Randell-Sly, S. K. Brayshaw, A. S. Weller and M. C. Willis, *Chemistry - A European Journal*, 2008, **14**, 8383-8397.
20. R. Dallanegra, A. P. M. Robertson, A. B. Chaplin, I. Manners and A. S. Weller, *Chemical Communications*, 2011, **47**, 3763-3765.
21. J. J. Donleavy and J. English, *Journal of the American Chemical Society*, 1940, **62**, 220-221.

6.1 Crystal data

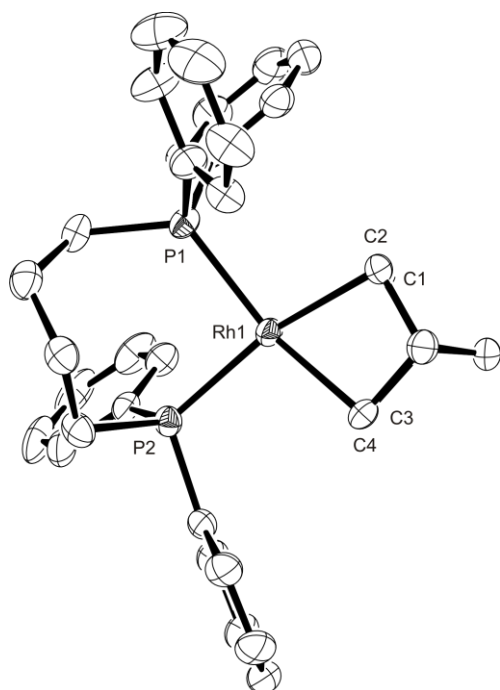


Figure 6.1: Molecular structure of the cationic portion of $[\text{Rh}(\kappa^2_{\text{ppp}}\text{-dpp4})(\text{NBD})][\text{BARF}_4]$ (**21**). Displacement ellipsoids are drawn at the 50% probability level. The anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Rh1-C1, 2.224(3); Rh1-C2, 2.213(3); Rh1-C3, 2.207(3); Rh1-C4, 2.193(3); Rh1-P1, 2.3111(8); Rh1-P2, 2.2957(8); C1-C2, 1.375(4); C3-C4, 1.382(4). Selected bond angles [°]: P2-Rh1-P1, 94.37(3).

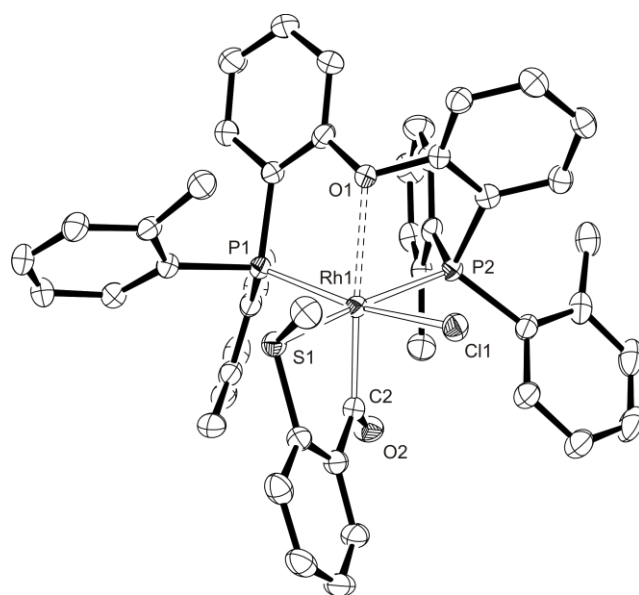


Figure 6.2: Molecular structures of the cationic portion of $[\text{Rh}(\kappa^3_{\text{POP}}\text{-DPEphos-}o\text{-Me})(\text{Cl})(\kappa^1_{\text{(S)}}\text{-}\sigma^1_{\text{(C)}}\text{-COC}_6\text{H}_4\text{SCH}_3)][\text{closo-CB}_{11}\text{H}_{12}]$. Displacement ellipsoids are drawn at the 50% probability level. The anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Rh1-C2, 1.977(3); Rh1-O1, 2.432(2); Rh1-P1, 2.3342(8); Rh1-P2, 2.4266(8); Rh1-S1, 2.3823(7); Rh1-Cl1, 2.3721(7); O2-C2, 1.205(4). Selected bond angles [°]: P1-Rh1-P2, 99.58(3).

Table 6.1: Crystallographic data for **4**, **5** and **7**.

	4	5	7
CCDC	802778	841413	802779
Formula	C ₆₂ H ₄₅ BF ₂₄ NOP ₂ Rh	C ₆₄ H ₄₆ BF ₂₄ O ₃ P ₂ Rh	C ₆₄ H ₄₈ BF ₂₄ O ₂ P ₂ Rh S
<i>M</i>	1451.65	1494.68	1512.74
Crystal System	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>T</i> [K]	200(2)	150(2)	150(2)
<i>a</i> [Å]	12.99920(10)	13.8681(5)	18.7068(1)
<i>b</i> [Å]	15.16770(10)	28.8045(9)	12.8436(1)
<i>c</i> [Å]	18.2568(2)	16.6233(6)	26.7507(2)
α [deg]	107.5945(4)	90	90
β [deg]	98.7135(4)	106.893(3)	95.3777(2)
γ [deg]	99.3630(6)	90	90
<i>V</i> [Å ³]	3307.59(5)	6353.9(4)	6398.90(8)
<i>Z</i>	2	4	4
Density [gcm ⁻³]	1.458	1.562	1.570
μ (mm ⁻¹)	0.414	0.435	0.464
θ range [deg]	5.12 $\leq \theta \leq$ 26.37	1.49 $\leq \theta \leq$ 32.15	4.08 $\leq \theta \leq$ 32.04
Refl ^{ns} collected	24923 [<i>R</i> _{int} = 0.0200]	85103 [<i>R</i> _{int} = 0.135]	146901 [<i>R</i> _{int} = 0.0458]
Completeness	99.2 %	96.0%	99.6
No. of data/restr/ param	13396 / 1017 / 979	13243 / 1026 / 1578	22186 / 1024 / 90
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0500	0.0643	0.0383
<i>wR</i> ₂ [all data]	0.1413	0.1509	0.0971
<i>GoF</i>	1.040	0.9308	1.024
Largest diff. pk and hole [eÅ ⁻³]	0.860, -0.666	1.25, -1.76	0.834, -0.519

Table 6.2: Crystallographic data for **8**, **11** and **13**.

	8	11	13
CCDC	-	802780	802781
Formula	C ₇₈ H ₅₂ BF ₂₄ OP ₂ Rh	C ₇₃ H ₄₉ BF ₂₄ NOP ₂ Rh	C ₇₅ H ₅₂ BF ₂₄ O ₂ P ₂ RhS
<i>M</i>	1636.86	1587.79	1648.89
Crystal System	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>T</i> [K]	150(2)	150(2)	150(2)
<i>a</i> [Å]	12.69990(10)	14.20090(10)	15.1944(2)
<i>b</i> [Å]	15.5324(2)	15.6702(2)	16.4866(2)
<i>c</i> [Å]	20.4619(3)	18.5173(2)	18.8553(2)
α [deg]	72.4123(4)	90.6979(5)	76.1397(4)
β [deg]	85.7290(4)	108.6901(5)	66.5680(4)
γ [deg]	85.8063(5)	115.1028(6)	89.9595(5)
<i>V</i> [Å ³]	3831.51(8)	3481.59(6)	4183.85(9)
<i>Z</i>	2	2	2
Density [gcm ⁻³]	1.419	1.515	1.309
μ (mm ⁻¹)	0.366	0.401	0.361
θ range [deg]	5.11 $\leq \theta \leq$ 25.03	5.13 $\leq \theta \leq$ 26.37	5.10 $\leq \theta \leq$ 25.03
Refl ^{ns} collected	25133 [<i>R</i> _{int} = 0.0295]	25263 [<i>R</i> _{int} = 0.0340]	26649 [<i>R</i> _{int} = 0.0207]
Completeness	99.0 %	99.2 %	99.0
No. of data/restr/ param	13416 / 1078 / 534	14134 / 1021 / 426	14645 / 2001 / 1258
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0451	0.0418	0.0442
<i>wR</i> ₂ [all data]	0.1299	0.1023	0.1328
<i>GoF</i>	1.067	1.038	1.072
Largest diff. pk and hole [eÅ ⁻³]	0.773, -0.672	0.670, -0.666	0.833, -0.585

Table 6.3: Crystallographic data for **14**, **21** and **29**.

	14	21	29
CCDC	-	-	-
Formula	C ₁₉₆ B ₃₈ Cl ₈ O ₄ P ₈ Rh ₄	C ₆₈ H ₅₀ BCl ₂ F ₂₄ P ₂ Rh	C ₇₇ H ₆₈ BF ₂₄ P ₂ Rh
<i>M</i>	3771.74	1569.64	1624.97
Crystal System	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
<i>T</i> [K]	293(2)	150(2)	150(2)
<i>a</i> [Å]	17.9(10)	18.2523(2)	13.9289(2)
<i>b</i> [Å]	24(2)	19.1762(2)	14.2670(3)
<i>c</i> [Å]	26(2)	19.0854(2)	19.3455(4)
α [deg]	85(3)	90.00	74.2321(7)
β [deg]	72(3)	95.3280(5)	83.1462(8)
γ [deg]	74(3)	90.00	81.9151(8)
<i>V</i> [Å ³]	10399(1305)	6651.21(12)	3649.67(12)
<i>Z</i>	2	4	2
Density [gcm ⁻³]	1.205	1.568	1.479
μ (mm ⁻¹)	0.525	0.494	0.383
θ range [deg]	5.10 $\leq \theta \leq$ 27.49	5.12 $\leq \theta \leq$ 26.37	5.097 $\leq \theta \leq$ 27.485
Refl ^{ns} collected	79760 [<i>R</i> _{int} = 0.0438]	26288 [<i>R</i> _{int} = 0.0253]	23744 [<i>R</i> _{int} = 0.0254]
Completeness	98.4	99.2	97.8
No. of data/restr/ param	46968 / 1343 / 0	13491 / 975 / 449	14550 / 1029 / 337
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0922	0.0393	0.0420
<i>wR</i> ₂ [all data]	0.2894	0.1042	0.1065
<i>GoF</i>	1.029	1.038	1.027
Largest diff. pk and hole [eÅ ⁻³]	3.278, -1.848	0.571, -0.691	0.772, -0.607

Table 6.4: Crystallographic data for **32**, **33** and **38**.

	32	33	38
CCDC	804184	804185	804186
Formula	C ₇₇ H ₆₈ BF ₂₄ P ₂ Rh	C ₇₆ H ₇₂ BF ₂₄ O ₂ P ₂ Rh	C _{72.66} H _{72.31} BCl ₉ O _{1.89} P ₂ RhS
<i>M</i>	1624.97	1649.00	1502.52
Crystal System	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1
<i>T</i> [K]	150(2)	150(2)	150(2)
<i>a</i> [Å]	12.81100(10)	19.8241(2)	12.8020(16)
<i>b</i> [Å]	14.0064(2)	20.2882(2)	18.794(2)
<i>c</i> [Å]	21.8657(3)	21.4016(2)	31.915(4)
α [deg]	77.7118(5)	90	99.370(2)
β [deg]	75.5303(5)	111.5098(4)	93.1700(10)
γ [deg]	87.1919(6)	90	104.344(2)
<i>V</i> [Å ³]	3711.97(8)	1043.25(7)	7303.3(16)
<i>Z</i>	2	4	4 (<i>Z'</i> = 2)
Density [gcm ⁻³]	1.454	1.368	1.366
μ (mm ⁻¹)	0.376	0.351	0.679
θ range [deg]	5.10 $\leq \theta \leq$ 26.37°	5.12 $\leq \theta \leq$ 26.37°	1.102 $\leq \theta \leq$ 31.754°
Refl ^{ns} collected	26104 [<i>R</i> _{int} = 0.0232]	29717 [<i>R</i> _{int} = 0.0255]	46720 [<i>R</i> _{int} = 0.112]
Completeness	99.1 %	99.2 %	85.6 %
No. of data/restr/ param	15025 / 516 / 1066	16254 / 867 / 1104	23810 / 156 / 1605
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0465	0.0510	0.0621
<i>wR</i> ₂ [all data]	0.1239	0.1452	0.1198
<i>GoF</i>	1.022	1.090	1.000
Largest diff. pk and hole [eÅ ⁻³]	0.889, -0.744	1.072, -1.026	1.20, -1.63

Table 6.5: Crystallographic data for **43**, **44** and **47**.

	43	44	47
CCDC	882543	882544	882542
Formula	C ₁₁₉ H ₁₂₂ B ₂₂ F ₁₂ O ₇ P ₄ Rh ₂ S ₂	C ₅₆ H ₅₆ B ₁₂ Cl ₄ F ₆ O ₂ P ₂ RhS	C ₄₅ H ₅₂ B ₁₁ O ₂ P ₂ RhS
<i>M</i>	2523.81	1343.44	940.69
Crystal System	Monoclinic	Triclinic	Triclinic
Space group	<i>C2/c</i>	<i>P</i> -1	<i>P</i> -1
<i>T</i> [K]	150(2)	150(2)	150(2)
<i>a</i> [Å]	39.9424(2)	14.3130(2)	10.0815(1)
<i>b</i> [Å]	15.1952(1)	15.7419(2)	12.1604(1)
<i>c</i> [Å]	26.7210(2)	16.9697(3)	19.4771(2)
α [deg]	90	104.2065(7)	83.6939(4)
β [deg]	130.9851(4)	113.9716(6)	87.4709(4)
γ [deg]	90	105.7973(7)	78.2330(4)
<i>V</i> [Å ³]	12242.52(14)	3073.92(8)	2322.89(4)
<i>Z</i>	4	2	2
Density [gcm ⁻³]	1.369	1.451	1.345
μ (mm ⁻¹)	0.429	0.598	0.519
θ range [deg]	5.10 $\leq \theta \leq$ 27.88	5.10 $\leq \theta \leq$ 26.77	5.15 $\leq \theta \leq$ 27.88
Refl ^{ns} collected	28085 [<i>R</i> _{int} = 0.0392]	21838 [<i>R</i> _{int} = 0.0290]	17970 [<i>R</i> _{int} = 0.0210]
Completeness	99.3%	99.1%	99.3%
No. of data/restr/ param	14498 / 243 / 815	12450 / 292 / 853	10991 / 16 / 583
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0392	0.0424	0.0294
<i>wR</i> ₂ [all data]	0.1015	0.1102	0.0720
<i>GoF</i>	1.021	1.042	1.047
Largest diff. pk and hole [eÅ ⁻³]	0.687, -0.624	0.772, -0.809	0.518, -0.478

Table 6.6: Crystallographic data for **48** and [Rh(κ^3 (POP)-DPEphos-*o*-Me)(Cl)(κ^1 (S)- σ^1 (C)-COC₆H₄SCH₃)] [*closo*-CB₁₁H₁₂].

	48	[Rh(DPEphos- <i>o</i> -Me)(Cl)(COC ₆ H ₄ SMe)] ⁺
CCDC	-	-
Formula	C ₄₈ H ₄₇ B ₁₁ ClO ₂ P ₂ RhS	C ₄₉ H ₅₅ B ₁₁ ClO ₂ P ₂ RhS
<i>M</i>	1007.13	1239.01
Crystal System	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>
<i>T</i> [K]	293(2)	150(2)
<i>a</i> [Å]	10.64110(10)	18.5330(2)
<i>b</i> [Å]	14.3876(2)	17.6684(2)
<i>c</i> [Å]	17.2406(3)	18.7309(2)
α [deg]	88.6550(10)	90
β [deg]	74.7360(10)	111.5274(4)
γ [deg]	82.5700(10)	90
<i>V</i> [Å ³]	2524.89(6)	5705.57(11)
<i>Z</i>	2	4
Density [gcm ⁻³]	1.325	1.442
μ (mm ⁻¹)	0.534	0.713
θ range [deg]	5.12 $\leq \theta \leq$ 27.52	5.11 $\leq \theta \leq$ 27.48
Refl ^{ns} collected	18783 [<i>R</i> _{int} = 0.0275]	25546 [<i>R</i> _{int} = 0.0392]
Completeness	97.8%	99.3%
No. of data/restr/ param	11370 / 564 / 0	12986 / 698 / 63
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.1529	0.1162
<i>wR</i> ₂ [all data]	0.1611	0.1310
<i>GoF</i>	1.168	1.021
Largest diff. pk and hole [eÅ ⁻³]	2.870, -0.806	0.863, -1.183

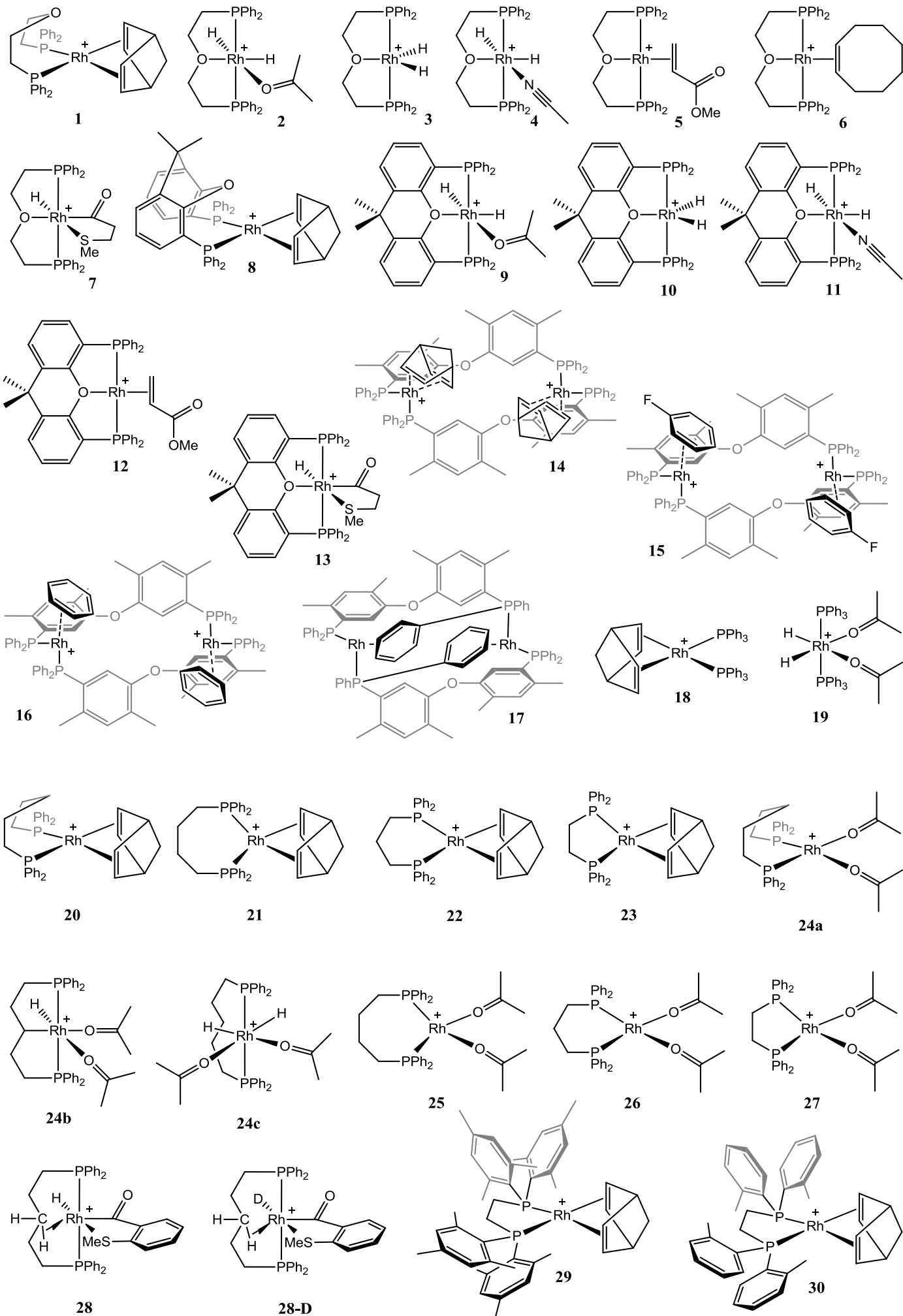
6.2 Publications

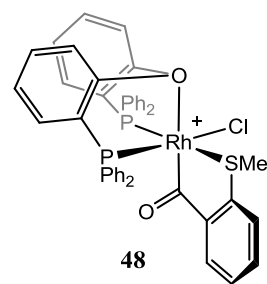
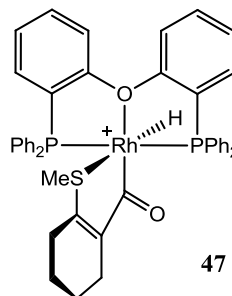
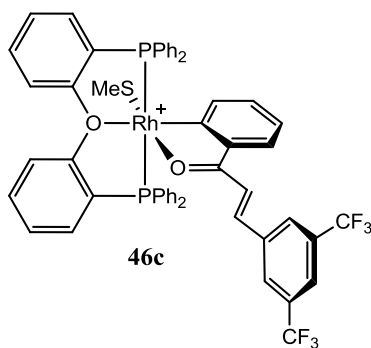
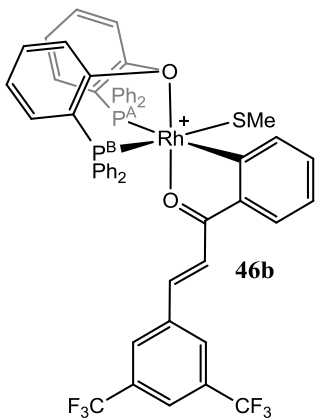
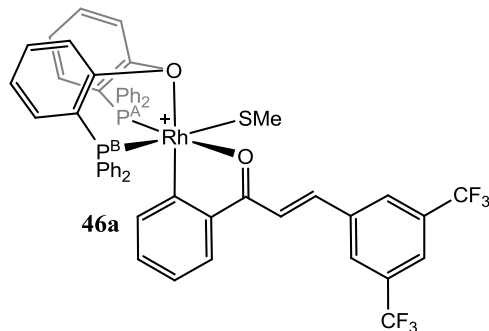
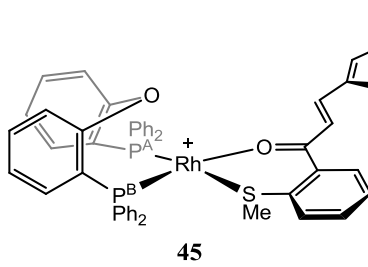
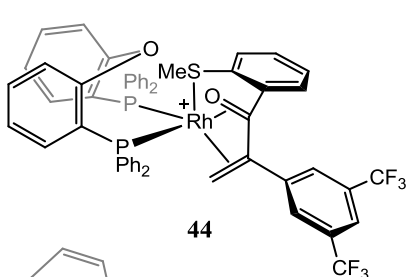
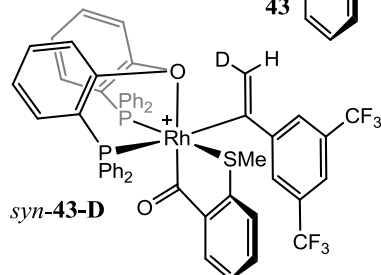
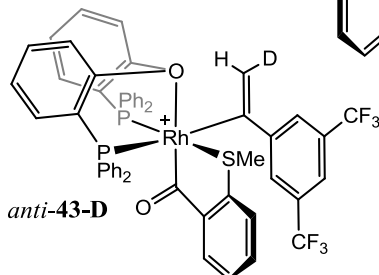
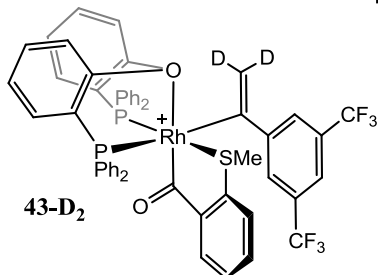
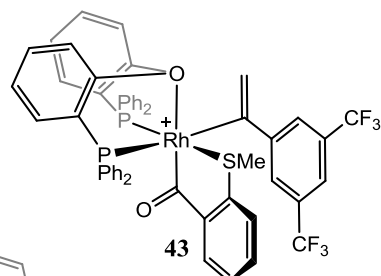
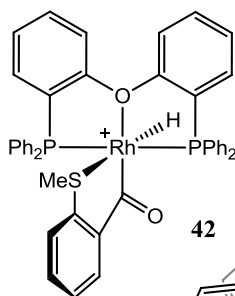
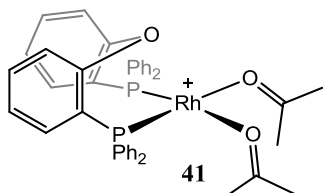
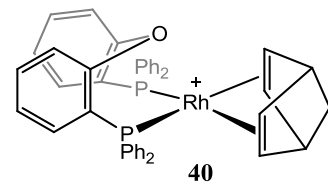
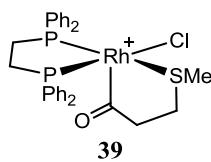
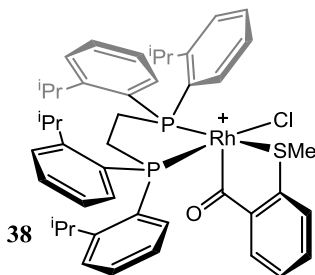
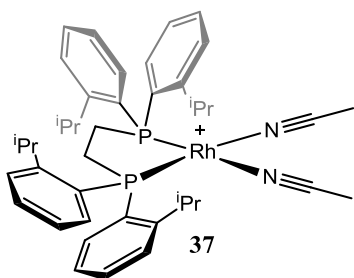
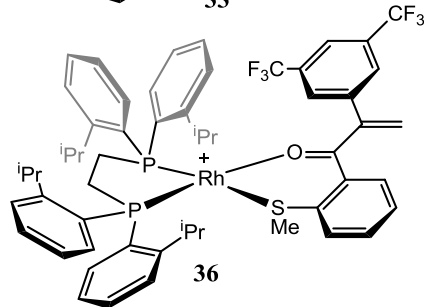
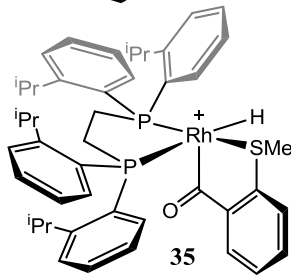
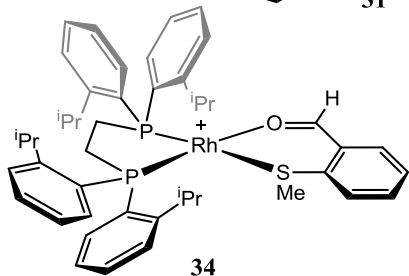
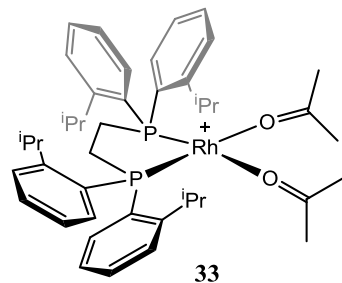
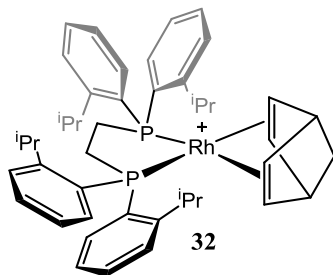
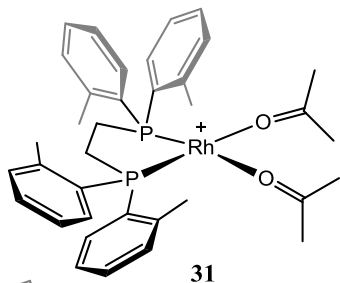
Pawley, R. J.; Huertos, M. A.; Lloyd-Jones, G.; Weller, A. S.; Willis, M. C.: Intermolecular Alkyne Hydroacylation. Mechanistic Insight from the Isolation of the Vinyl Intermediate that Precedes Reductive Elimination. *Organometallics*, **2012**, *31*, 5650-5659. doi: 10.1021/om300647n

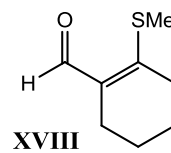
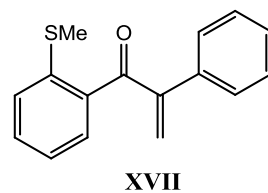
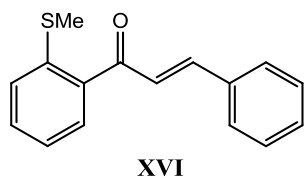
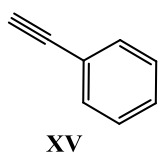
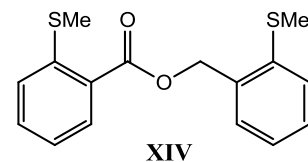
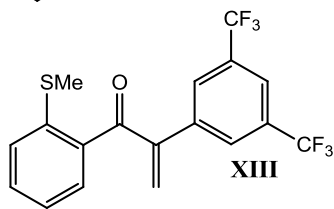
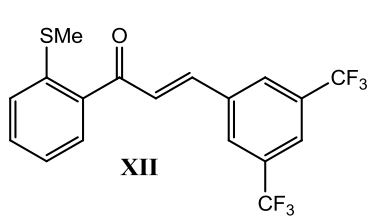
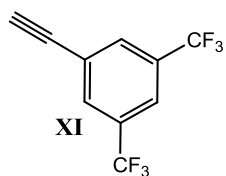
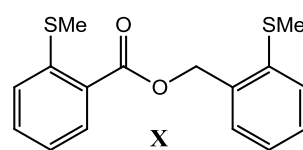
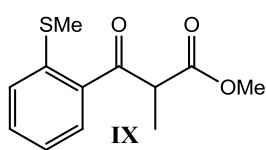
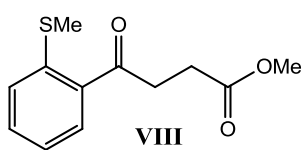
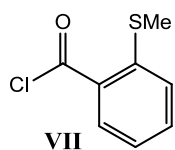
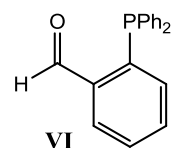
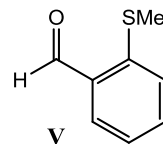
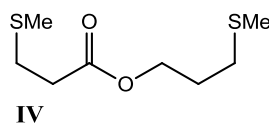
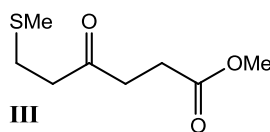
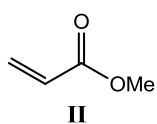
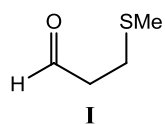
Pike, S. D.; Pawley, R. J.; Chaplin, A. B.; Thompson, A. L.; Hooper, J. A.; Willis, M. C. and Weller, A. S.: Exploring (Ph₂PCH₂CH₂)₂E Ligand Space (E = O, S, PPh) in RhI Alkene Complexes as Potential Hydroacylation Catalysts. *Eur. J. Inorg. Chem.*, **2011**, *36*, 5558–5565. doi: 10.1002/ejic.201100958

González-Rodríguez, C.; Pawley, R. J.; Chaplin, A. B.; Thompson, A. L.; Weller, A. S. and Willis, M. C.: Rhodium-Catalyzed Branched-Selective Alkyne Hydroacylation: A Ligand-Controlled Regioselectivity Switch. *Angew. Chem. Int. Ed.*, **2011**, *50*, 5134–5138. doi: 10.1002/anie.201100956

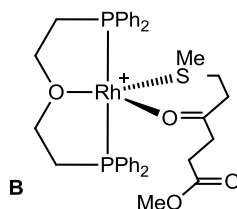
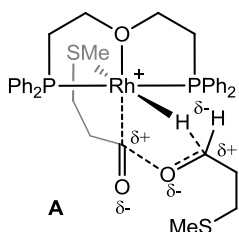
Pawley, R. J.; Moxham, G. L.; Dallanegra, R.; Chaplin, A. B.; Brayshaw, S. K.; Weller, A. S.; Willis, M. C.: Controlling Selectivity in Intermolecular Alkene or Aldehyde Hydroacylation Reactions Catalyzed by {Rh(L₂)}⁺ Fragments. *Organometallics*, **2010**, *29*, 1717-1728. doi: 10.1021/om9011104



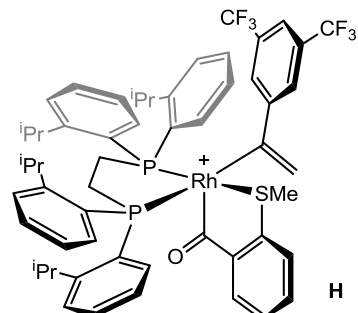
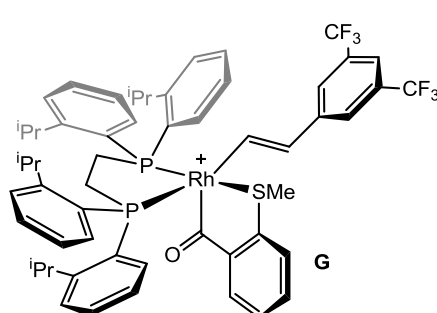
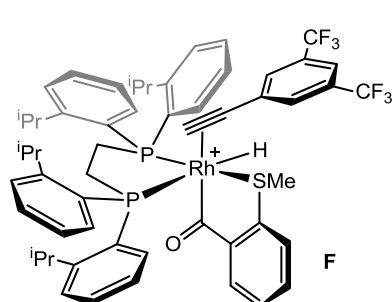
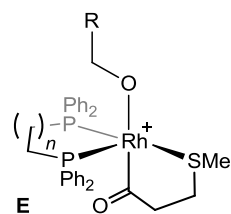
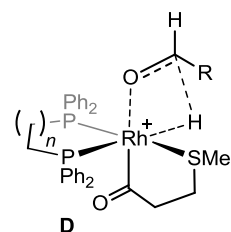
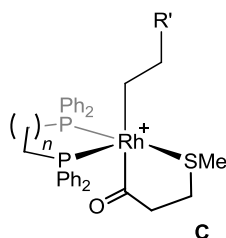
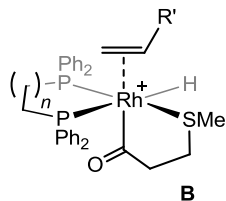
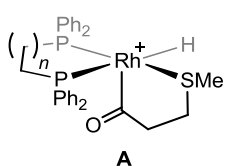




Chapter 2



Chapter 3



Chapter 4

