

Reactivity of a Ruthenium *Bis*(Dinitrogen) Complex

By

Samantha Lau

July 2018

Department of Chemistry

Imperial College London

A thesis submitted for Doctorate of Philosophy

Declaration of Originality

The work discussed in this thesis was conducted in the Department of Chemistry, Imperial College London, between October 2014 and April 2018. Unless stated otherwise, all the work is entirely my own and has not been submitted for a previous degree at this, or any other university.

Copyright Declaration

The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives licence. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes and that they do not alter, transform or build upon it. For any reuse or redistribution, researchers must make clear to others the licence terms of this work.

Abstract

This thesis investigated the reactivity of the ruthenium *bis*(dinitrogen) complex $[\text{Ru}(\text{H})_2(\text{N}_2)_2(\text{PCy}_3)_2]$ (**1**), an analogue of the ruthenium *bis*(dihydrogen) complex $[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$. It was demonstrated that **1** was able to effect the $sp^2\text{C-X}$ ($\text{X} = \text{H}, \text{O}$) bond cleavage of acetophenone substrates to generate 5-membered organometallic intermediates. The by-products from the C–O cleavage reactions were identified as alcohols which also react with **1** at a faster or equal rate to the substrates. The mechanism of these C–X cleavage reactions were probed experimentally and computationally to show that the C–H bond cleavage pathway was operating through a σ -complex assisted metathesis pathway whereas the C–O cleavage pathway was operating through a Ru(II)/Ru(IV) redox mechanism.

In addition, the reactivity of **1** with main group hydrides (aluminium, zinc and magnesium) was presented with the formation of a series of new ruthenium main group heterobimetallic hydride complexes, **M•Ru** ($\text{M} = \text{Al}, \text{Zn}, \text{Mg}$). These heterobimetallic hydride complexes contain either dinitrogen or dihydrogen ligated at the ruthenium centre depending on the partial pressure of N_2 and H_2 in the atmosphere. It was shown that the main group fragment can subtly tune the degree of dinitrogen activation in these **M•Ru-N₂** complexes, $\text{Mg} > \text{Zn} > \text{Al}$. This trend was rationalised by probing the bonding and frontier molecular orbitals of these complexes.

Furthermore, ^{27}Al solid state NMR spectroscopy was implemented to analyse the ruthenium aluminium heterobimetallic hydride complexes and it was determined that there was no linear correlation between the isotropic chemical shift obtained in the ^{27}Al solid state NMR spectra and the oxidation state of the complex.

For my family, my friends

And

Wing Lee

Acknowledgements

You hear the horror stories of people doing PhDs and having a horrid time. Well, this was not one of them. In fact, I couldn't have asked for a better group of people to share my journey with. At the helm of this group has been the most supportive and professional supervisor anyone could wish for. Mark, thank you for being a great mentor. I owe you a lifetime of gratitude and one scoop of mint choc-chip ice cream. Working and growing in your group has been an absolute privilege.

To the rest of the members of Crimmin group, past and present: Adi, David, Olga, Michael, Alex, Wenyi, Andy, BWS Clare, Tom, B-Dawg BryBry, Greg C, Martí, Nick, Ryan, Richard, Baby Bird Greg B and of course Ferial, thanks for the beers, the many office games and of course just humouring my antics. Guys, I'll see you at the 10th anniversary of Crimmyolympics – though preferably sooner. In the meantime, please accept my thanks by being immortalised in my thesis through the medium of photoshop.

Now the bonds you make during your PhD is something unique, stronger than any C–O bonds for sure, a shared experience that only your fellow PhD siblings can understand. With that in mind, to the Goblins, a special thanks for being such great dogs. I'm so grateful and lucky to have had you guys by my side from beginning to end.

Furthermore, it is no understatement to say my thesis could not be complete without the help of Pete Haycock, Dick Sheppard and Andrew White, thank you for running my samples even if they were not always up to your standards. I hope your instruments never fail you and that you will have access to daylight in your new offices in White City. In addition, thank you Ian and Steve for your guidance, whiskeys and grams and grams of RuCl₃. Also, a special shout out to The Model Answers for ensuring I still have a social life outside of academia.

To my parents, I don't know if you'll ever read this but thank you for everything. Mum, Dad, I hope I've made you proud even if I am not the type doctor you anticipated me to be. To my sister Katie, you are my yolk. Thanks for reminding me that it is okay to just do nothing and take a breather in life. You have been the trailblazer in the family and probably allowed me and Ken to take paths we have.

Finally, if there is one person who has truly experienced my PhD with me 24 hours a day, 7 days a week for 4 years, it is you Niall. Thank you. Sorry. And I love you.

Now please give me my J.Young NMR tube drinking vessel, I'm parched.

CONTENT

Declaration of Originality	1
Copyright Declaration	1
Thesis Abstract	2
Acknowledgements	4
List of Figures, Schemes and Tables	9
List of Abbreviations	15
Publications	16

1 CHAPTER ONE – RUTHENIUM BIS(DIHYDROGEN) COMPLEX $[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$ AND ITS DERIVATIVES

1.1	INTRODUCTION	17
1.2	CHEMISTRY OF $[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$	19
1.2.1	Hydrogenation	19
1.2.2	Small Molecules (CO, CO ₂ , CS ₂ , N ₂ and Halocarbons)	22
1.2.3	Alcohols	25
1.2.4	X–H activation (X = C, N, O)	26
1.2.5	σ -complexes with E–H bond (E = B, Si and Ge)	30
1.3	RESULTS AND DISCUSSIONS	50
1.3.1	Synthesis and reactivity of $[\text{Ru}(\text{H})_2(\text{N}_2)_2(\text{PCy}_3)_2]$ (1)	50
1.4	CONCLUSION	54
1.5	REFERENCES	55

2 CHAPTER TWO – $sp^2\text{C–O}$ BOND ACTIVATION BY AN ISOLABLE RUTHENIUM(II) *BIS*(DINITROGEN) COMPLEX: THEORY AND EXPERIMENT

2.1	INTRODUCTION	58
2.1.1	Biomass viability	58

2.2	C–O ACTIVATION	59
2.2.1	Nickel	59
2.2.2	Ruthenium	73
2.2.3	Iridium	81
2.3	RESULTS AND DISCUSSIONS	83
2.3.1	C–H activation	84
2.3.2	C–O activation	85
2.3.3	By-Product	86
2.3.4	Mechanistic and DFT Studies	89
2.3.5	Expansion of scope	100
2.3.6	Functionalisation	106
2.4	CONCLUSION	109
2.5	FUTURE WORK	109
2.6	REFERENCES	111
3	CHAPTER THREE – FORMATION OF A SERIES OF M•Ru (M = Al, Zn, Mg) HETEROBIMETALLIC HYDRIDE COMPLEXES	
3.1	INTRODUCTION	115
3.1.1	Al•Ru heterobimetallic complexes	115
3.1.2	Zn•Ru heterobimetallic complexes	123
3.1.3	Mg•Ru heterobimetallic complexes	129
3.2	RESULTS AND DISCUSSIONS	130
3.2.1	Synthesis and characterisation	130
3.2.2	M•Ru-N ₂	135
3.2.3	Tuneable N ₂ activation	140
3.2.4	Reactivity with CO ₂ and HBpin	144
3.3	CONCLUSION	146
3.4	FUTURE WORK	147
3.5	REFERENCES	148

4 CHAPTER FOUR – REACTIONS OF β -DIKETIMINATE STABILISED ALUMINIUM DIHYDRIDE COMPLEXES WITH RUTHENIUM(II) *BIS*(DINITROGEN) COMPLEX

4.1	INTRODUCTION	150
4.1.1	Tetrameric Aluminium(I) Compounds	150
4.1.2	Molecular Aluminium(I) Compounds	154
4.2	RESULTS AND DISCUSSIONS	156
4.2.1	Synthesis and characterisation	156
4.2.2	^{27}Al MAS NMR spectroscopy	169
4.3	CONCLUSION	174
4.4	FUTURE WORK	174
4.5	REFERENCES	176

5 CHAPTER FIVE – SUPPORTING INFORMATION

5.1	GENERAL	178
5.2	CHAPTER ONE: EXPERIMENTAL	179
5.2.1	Materials	179
5.2.2	Synthesis	179
5.2.3	Intermediate 1- H_2/N_2	180
5.3	CHAPTER TWO: EXPERIMENTAL	183
5.3.1	Materials	183
5.3.2	Synthesis	183
5.3.3	General Procedure for Reduction of Arylketone to Arylethanol	185
5.3.4	Ru-Mediated C–H Bond Activation	187
5.3.5	Ru-Mediated C–O Bond Activation	191
5.3.6	Identification of By-Products from C–O Bond Activation	198
5.3.7	Competition and Inhibition Reactions	204
5.3.8	Directing group	207
5.4	CHAPTER THREE: EXPERIMENTAL	216
5.4.1	Materials	216

5.4.2	Synthesis of Heterobimetallics	216
5.4.3	Substitution reaction	220
5.4.4	Variable Temperature NMR data	228
5.4.5	Kinetic Experiments	232
5.4.6	D ₂ Labelling Experiments	233
5.4.7	DFT and QTAIM	235
5.5	CHAPTER FOUR: EXPERIMENTAL	239
5.5.1	Materials	239
5.5.2	Synthesis of Al•Ru heterobimetallic hydride complexes	239
5.5.3	Variable Temperature NMR Data	244
5.5.4	T ₁ Data	249
6	APPENDIX	
6.1	MULTINUCLEAR NMR SPECTRA	254
6.2	X-RAY DATA	279

List of Figures, Schemes and Tables

Figure 1.1. (Left) Kubas' dihydrogen complex. (Right) Ruthenium bis(dihydrogen) complex, **1-2H₂**

Figure 1.2. (Top) Orbitals involved in dihydrogen bonding to ruthenium centre. (Bottom) Two extreme modes of coordination of dihydrogen

Figure 1.3. Ruthenium bis(dihydrogen) complex (left) [Ru(H)(η^2 -H₂)₂(Tp*)] and (right) [Ru(H)(η^2 -H₂)(THT)(Tp*)].

Figure 1.4. Proposed catalytic cycle of Murai-type coupling reaction

Figure 1.5. Order of the calculated most favourable geometry of model complexes **1.70** and **1.71**

Figure 1.6. X-ray crystal structure of **1**

Figure 1.7. X-ray structure of **Ru•Ru**, hydrogen not located from the Fourier transform map

Figure 1.8, Proposed β -methyl migration mechanism

Figure 2.1 Breakdown of Biomass

Figure 2.2. Generalised Ni(0)/Ni(II) redox mechanism for C–O bond cleavage

Figure 2.3. Phosphine ligand used by Wang et al.

Figure 2.4. Simplified reaction profile of C–O cleavage of aryl carboxylates. Gibbs free energy in kcal mol⁻¹

Figure 2.5. C–O bond breaking of anisole with "Ni(0)-ate" complex (**CP2**). Gibbs free energy in kcal mol⁻¹

Figure 2.6. Proposed catalytic cycle of reduction of aryl methyl ether with Ni(I) species

Figure 2.7 Transition state of C–O cleavage step by "Ni(0)-silyl-ate" species stabilised by K⁺ cation

Figure 2.8. Free energy profile of hydrogenolysis of biary ether. Gibbs free energy in kcal mol⁻¹

Figure 2.9 Free energy profile the formation of the active anionic species **INT2** and subsequent cleavage of C_{Ar}–O bond. Gibbs free energy in kcal mol⁻¹

Figure 2.10. X-ray structure of product from C–O activation of 2,2-dimethyl-1-(2-p-tolylphenyl)propan-1-one

Figure 2.11. Calculated highest TS and selected stationary points for C–H (red) and C–O (blue) functionalisation. Gibbs free energies in kcal mol⁻¹

Figure 2.12. Lowest calculated energy reaction profile to generate reactive ruthenium species for the Murai coupling reaction of acetophenone with ethene. Trans PMe₃ omitted for clarity. Gibbs free energies in kcal mol⁻¹

Figure 2.13. Idealised catalytic cycle on the functionalisation of C–X (X = H, O) bond in acetophenone substrates mediated by **1**

Figure 2.14. Crystal structures of **1**, products of C–X activation **4a–c** (X = H and O), and side products **6b** and **7a**

Figure 2.15. Comparison of the highest TS to generate reactive Ru intermediate and C–O bond activation. P = PCy₃

Figure 2.16. Structures of the intermediates in both C–H and C–O bond activation pathways. P = PCy₃

Figure 2.17. Calculated pathways for C–H (red) and C–O (blue) activation. Gibbs free energies in kcal mol⁻¹; liberated N₂ not shown.

Figure 2.18. (Top) NBO, NPA charges of **Int-4**, **TS-4** and **Int-5** and (Bottom) Electron density contour plot overlaid calculated structures from QTAIM; bond critical points between atoms (green dots),

Figure 2.19. cis-trans isomerisation of PCy₃. P = PCy₃

Figure 2.20. NCI plots of (a) **Int-7** (C–O) and (b) **Int-2** (C–H). (c) Molecular models of **TS-2** and **TS-5** with selected bond lengths (Å).

Figure 2.21. (a) Selected NBO second-order perturbation analysis data on **Int-3**. (b) NBO analysis showing the difference in NPA charges between **Int-2** and **Int-3**

Figure 2.22. (a) Selected NBO second-order perturbation analysis data on **Int-8**. (b) NBO analysis showing the difference in NPA charges between **Int-7/Int-8**

Figure 2.23. Steric argument for the chemoselectivity of C–H versus C–O bond activation of 1-(2-methoxyphenyl)-2,2-dimethylpropan-1-one

Figure 2.24. X-ray structure of **12** including selected bond lengths (Å) and angles (°). Hydride was not located on Fourier transform map.

Figure 2.25. Proposed catalytic cycle of functionalisation of C–X (X = H, O) of acetophenone substrates

Figure 2.26. Speculated products from functionalisation of C–X bond

Figure 3.1 Motifs of the bridging and terminal aluminium hydrides in heterobimetallic complexes (M = transition metal)

Figure 3.2 (Top) Framework of the ruthenium aluminohydride complexes. (Bottom) Synthesis of the cage structures

Figure 3.3 X-ray crystal structures of [Ru(Zn(η⁵-C₅Me₅)₄)(ZnMe)₆] (left) and [Ru(Zn(η⁵-C₅Me₅)₄)(ZnMe)₄(H)₂] (right). Hydrogens omitted for clarity

Figure 3.4 Optimised structures of **M•Ru-H₂** complexes from DFT calculations

Figure 3.5 ¹H-NMR spectra stack plot of the addition of CO to a sample containing a mixture of **Al•Ru-H₂** and **Al•Ru-N₂**

Figure 3.6 (a) VT ¹H NMR of **Zn•Ru-N₂** showing just the methine proton of isopropyl groups. (b) Hindered rotation about N–C_{Ar} bond of β-diketiminato ligand at low temperature

Figure 3.7 Crystal structures of **M•Ru-N₂** (M = Al, Zn, Mg)

Figure 3.8 Calculated bond lengths in **M•Ru-N₂** along with selected NPA charges and WBI

Figure 3.9 Proximity effect of the main group metal through the bridging hydrides on the ruthenium centre

Figure 3.10 CBC and half-arrow notation of heterobimetallic complexes

Figure 3.11 (a) Dewar-Chatt-Duncanson Model for N₂ binding and (b) Tuneable N₂ binding to heterobimetallic complexes

Figure 3.12 (a) Selected fMOs of $\text{cis-}[\text{Ru}(\text{H})_3(\text{PMe}_3)_2]^-$ of relevance for N_2 binding, (b) Selected fMOs and energies of the model heterobimetallic complexes

Figure 3.13 Energies of selected fMOs of model heterobimetallic complex.

Figure 4.1 Aluminium(I) tetramers that have been characterised by X-ray crystallography

Figure 4.2 VT NMR spectra of $^{\text{Mes}}\text{Al}\cdot\text{Ru}$. Only Ru–H region shown in ^1H NMR spectrum for clarity

Figure 4.3 Proposed dissociative mechanism for the exchange of ligands around ruthenium in $^{\text{Mes}}\text{Al}\cdot\text{Ru}$ complex

Figure 4.4 Crystal structure of $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$ with selected bond lengths (Å) and bond angles (°). Hydrogens omitted for clarity

Figure 4.5 Optimised structure of $^{\text{Mes}}\text{Al}\cdot\text{Ru}$ from DFT calculations

Figure 4.6 Calculated bond lengths of $^{\text{Mes}}\text{Al}\cdot\text{Ru}$ (left) and analysis by NBO (middle) and QTAIM (right) calculations

Figure 4.7 Comparison of the CBC and half-arrow notation of the ruthenium aluminium heterobimetallic complexes

Figure 4.8 SCF energy values from gas phase DFT calculations of $^{\text{Mes}}\text{BDIAL}(\text{H})_2$, **1**, $^{\text{Mes}}\text{Al}\cdot\text{Ru}$ and $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$ with different number of hydrides

Figure 4.9 Optimised structures of $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$ containing 4H and 6H respectively by DFT.

Figure 4.10. (Left) Calculated structure of $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$ containing 8H by DFT, not optimised. (Right) Line drawing of $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$ containing 8H

Figure 4.11 Crystal structure of $^{\text{Dipp}}\text{Al}\cdot\text{Ru}$ with selected bond lengths (Å) and bond angles (°). Hydrogens omitted for clarity

Figure 4.12 Calculated bond lengths of $^{\text{Dipp}}\text{Al}\cdot\text{Ru}$ (left) and analysis by NBO (middle) and QTAIM (right) calculations

Figure 4.13 Crystal structure of **1**•**NacNac** with selected bond lengths (Å) and bond angles (°)

Figure 4.14 Aluminium containing complexes studies with solid state ^{27}Al NMR spectroscopy

Figure 4.15 Solid state ^{27}Al MAS NMR spectrum of $^{\text{Dipp}}\text{BDIAL}(\text{I})$ complex (black line) overlaid with pNMRsim calculations from DFT parameters (red line)

Figure 4.16 Solid state ^{27}Al NMR spectroscopy δ_{iso} chemical shifts of aluminium containing molecules

Figure 4.17 Solid state ^{27}Al NMR spectroscopy C_Q values of aluminium containing molecules

Scheme 1.1 Hydrogenation of alkenes with concomitant C–H activation of PCy_3

Scheme 1.2 Ligand substitution to generate complex **1.5** and hydrogenation of alkene and concomitant demethylation to generate complex **1.6** and **1.7**

Scheme 1.3 Ruthenium π -arene complexes

Scheme 1.4 Reaction of **1-2H₂** with thiophenes both stoichiometrically and catalytically

Scheme 1.5. Reaction of **1-2H₂** with CO , CO_2 and a mixture of CO/CO_2

- Scheme 1.6. Reaction of **1-2H₂** with CS₂
- Scheme 1.7. Reaction of **1-2H₂** with N₂ to form ruthenium bis(dinitrogen) complex **1**
- Scheme 1.8. Reaction of **1-2H₂** with halocarbons
- Scheme 1.9. Formation of **5-H₂**
- Scheme 1.10. Reaction of **1-2H₂** with phenol
- Scheme 1.11. C–H activation of acetophenone substrates by **1-2H₂**
- Scheme 1.12. Murai-type coupling reaction
- Scheme 1.13. Reaction of **1-2H₂** with phenylpyridine
- Scheme 1.14. Reaction of **1-2H₂** with heteroaromatic substrates
- Scheme 1.15. Reaction of **1-2H₂** with HBpin
- Scheme 1.16. Formation of bis σ-(B–H) ruthenium complex
- Scheme 1.17. Formation of monoalkyl bis σ-(B–H) ruthenium complex
- Scheme 1.18. Formation of bis σ-(B–H) aminoborane ruthenium complex
- Scheme 1.19. (Top) Reduction of CO₂. (Bottom) Stoichiometric experiment with complex **1.17** and **1.46**.
- Scheme 1.20. Reaction of **1-2H₂** with phosphinomethyl(amino)borane
- Scheme 1.21. Reaction of **1-2H₂** with (o-phosphinophenyl)(amino)borane
- Scheme 1.22. Formation of bis(agostic)phosphinobenzyl(amino)borane ruthenium complexes
- Scheme 1.23. Formation of σ-(Si–H) ruthenium complex with HSiPh₃
- Scheme 1.24. Reaction of **1-2H₂** with bis(silane) compounds
- Scheme 1.25. Formation of bis σ-(Si–H) ruthenium complexes
- Scheme 1.26. Formation of σ(Si–H) and η²-(C=C) ruthenium complex
- Scheme 1.27. Formation of [PCy₃)₂(H)₂Ru₂(SiH₄)Ru(H)₂(PCy₃)₂] (**1.62**)
- Scheme 1.28. Redistribution reaction of **1.62** with (MeO)₃SiH
- Scheme 1.29. Reaction of **1-2H₂** with 1,1,3,3-tetramethylsilazane
- Scheme 1.30. Reaction of **1-2H₂** with 2-pyridinetetramethylsilazane
- Scheme 1.31. Reaction of [Ru(η⁴-1,5-COD)(η⁴-1,3,5-COT)] with 2-pyridinetetramethyldisilazane
- Scheme 1.32. Reaction **1-2H₂** with phosphinobenzylsilane
- Scheme 1.33. Reaction of [Ru(η⁴-1,5-COD)(η⁴-1,3,5-COT)] with phosphinobenzylsilane
- Scheme 1.34. Reaction of **1-2H₂** with HGePh₃
- Scheme 1.35. Reaction of **1-2H₂** with Ph₂GeH₂
- Scheme 1.36. Formation of a ruthenium digermoxane complex, **1.74**
- Scheme 1.37. Formation of **1**
- Scheme 1.38. Formation of **1** from sequential substitution of H₂ with N₂ in **1-2H₂**
- Scheme 1.39. Formation of **Ru•Ru** from **1**
- Scheme 1.40. Formation of **5-N₂** from reaction of **1** with EtOH
- Scheme 2.1 Shi et al.⁴: sp³ versus sp³ C–O activation

Scheme 2.2. C–O cleavage of aryl carboxylate esters

Scheme 2.3. Oxidative addition of PhX (X = OAc, Cl, Br, I) via stepwise electron transfer

Scheme 2.4. (Top) C–O cleavage of aryl ethers with [Ni(COD)₂] / PCy₃. (Bottom) Deuterium labelling experiment

Scheme 2.5. Formation of undesired Ni species in attempt to isolate C_{Ar}–Ni–OMe intermediate

Scheme 2.6. Formation of Ni(I) species

Scheme 2.7. Ipso-silylation of aryl methyl ethers

Scheme 2.8.(a) C–O activation of biaryl ethers, alkyl aryl ethers and benzyl ethers, (b) Relative reactivity of ethers towards hydrogenolysis of C–O bonds

Scheme 2.9. (Top) Reductive cleavage of aryl alkyl ethers. (Bottom) Deuterium labelling experiment

Scheme 2.10. C–O cleavage of acetophenone substrates via a 5-membered intermediate

Scheme 2.11. Products from C–H and C–O activation of 2,2-dimethyl-1-(2-p-tolylphenyl)propan-1-one

Scheme 2.12. Sequential C–C bond formation

Scheme 2.13. Chelation assisted sp³C–O activation. Ligands around Ru omitted for clarity

Scheme 2.14. Amide directed C–O activation

Scheme 2.15. (Top) Ester directed C–O functionalisation. (Bottom) reactivity order of isomeric naphthoates

Scheme 2.16. Model C–X bond (X = H, O) functionalisation reaction examined by DFT

Scheme 2.17. [Ir(Tp(Me₂))Ph₂] mediated sp³C–O bond cleavage via a carbene intermediate.

Scheme 2.18 Iridium pincer complex mediated sp³C–O bond cleavage via a carbene intermediate.

Scheme 2.19. sp²C–H and sp²C–O activation of acetophenone substrates.

Scheme 2.20. Intermolecular competition between sp²C–H and sp²C–O activation

Scheme 2.21. By-product from reaction of **1** with **3a**

Scheme 2.22. By-product from reaction of **1** with **3b**

Scheme 2.23. Plausible reaction pathways to obtain reactive Ru intermediate

Scheme 2.24. C–H activation of 1-(2-methoxyphenyl)-2,2-dimethyl-1-propanone

Scheme 2.25. Speculated products from reaction of **1** with **9a**

Scheme 2.26. Speculated products from reaction of **1** with **9b**

Scheme 2.27. C–H activation of benzofuran with **1**

Scheme 2.28. Reaction of **1** with 1-(2-methoxyphenyl)ethan-1-ol

Scheme 2.29. Speculated product formation of **13** from reaction of solketal with **1**

Scheme 3.1 Synthesis of dimeric aluminohydride complexes of Ru(II)

Scheme 3.2 Formation of first isolated ruthenium tetrahydridoaluminate complex with (Al₂H₈)²⁻ unit

Scheme 3.3 Synthesis of novel monomeric aluminohydride complexes of Ru(II)

Scheme 3.4 Formation of [(η⁵-C₅Me₅)Ru₂(μ-Ph₂PCH₂PPh₂)(μ-AlH₅)]

Scheme 3.5 Formation of [{η⁵-C₅Me₅)Ru}₃(μ-H)₃(μ₃-AlEt)]

Scheme 3.6 C–H activation of methyl groups in [AlCp*]₄

Scheme 3.7 (Top) Reaction of $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_2(\mu\text{-H})_4]$ with $[\text{AlCp}^*]_4$. (Bottom) Reaction of $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_3(\mu\text{-H})_3(\mu_3\text{-H})_2]$ with $[\text{AlCp}^*]_4$ to give $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_3(\mu\text{-H})_5(\mu_3\text{Al}(\eta^1\text{-C}_5\text{Me}_5))]$

Scheme 3.8 Formation of guanidinato stabilised Al–Ru heterobimetallic complex

Scheme 3.9 Formation of $[(\text{DmpS})\text{Ru}(\text{PR}_3)(^i\text{Bu}_2\text{AlH})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (R = Et or Cy)

Scheme 3.10 Formation of $[\text{RuZn}(\mu\text{-2-PhPC}_5\text{H}_4\text{N})_2(\text{CO})_3\text{Cl}_2]\cdot\text{MeOH}$

Scheme 3.11 Formation of novel zinc ruthenocene complex

Scheme 3.12 Formation of $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_3(\mu\text{-H})_3(\mu_3\text{-ZnR})(\mu_3\text{-H})]$ (R = Me, Et)

Scheme 3.13 Crossover experiment using $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_2(\mu\text{-H})_3(\mu\text{-ZnEt})]$ and $[\{\eta^5\text{-C}_5\text{Me}_4\text{EtRu}\}_2(\mu\text{-H})_3(\mu\text{-ZnEt})]$

Scheme 3.14 Formation of $[\text{Ru}(\text{PCy}_3)_2(\text{ZnMe})_2(\mu\text{-H})_4]$

Scheme 3.15 Formation of $[\text{Zn}\{\text{Ru}(\mu\text{-H})_3(\text{PR}_3)_3\}_2]$ (R = Ph or 4- $\text{C}_6\text{H}_5\text{Me}$)

Scheme 3.16 Formation and reactivity of zinc ruthenium heterobimetallic complexes

Scheme 3.17 Formation of $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_3(\mu\text{-H})_3(\mu_3\text{-Mg}^i\text{Pr})(\mu_3\text{-H})]$

Scheme 3.18 Preparation of dihydrogen and dinitrogen complexes of a series of heterobimetallic hydrides

Scheme 3.19 Reaction of $\text{M}\cdot\text{Ru}$ (M = Zn, Mg) hydride complexes with HBpin and CO_2

Scheme 3.20 Reaction of $\text{M}\cdot\text{Ru}$ (M = Zn, Mg) hydride complexes with $^{13}\text{CO}_2$

Scheme 4.1 Equilibrium between tetrameric and monomeric form of " AlCp^* "

Scheme 4.2 Equilibrium between tetrameric and monomeric form of " $(\text{C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Al}$ "

Scheme 4.3 Synthesis of $^{\text{Dipp}}\text{BDIAL}(\text{I})$

Scheme 4.4 Synthesis of analogue of $^{\text{Dipp}}\text{BDIAL}(\text{I})$

Scheme 4.5 Synthesis of an anionic aluminium(I) nucleophile, $[\text{K}\{\text{Al}(\text{NON})\}]_2$

Scheme 4.6 Preparation of $^{\text{Ar}}\text{Al}\cdot\text{Ru}$ heterobimetallic hydride complexes (Ar = Mes, 2,6-Xylyl)

Scheme 4.7 Preparation of $^{\text{Dipp}}\text{Al}\cdot\text{Ru}$ heterobimetallic hydride complex

Scheme 4.8 Reactivity of $^{\text{Dipp}}\text{Al}\cdot\text{Ru}$ with H_2

Scheme 4.9 Identification of $\mathbf{1}\cdot\text{NacNac}$ as a by-product in reaction of $\mathbf{1}$ with $^{3,5\text{-Xylyl}}\text{BDIAL}(\text{H})_2$

Table 2.1 Bond Lengths (Å) and Angles (°) in $\mathbf{1}$ and $\mathbf{4a-c}$

Table 3.1 Selected bond lengths (Å) and bond angles (°) from optimised DFT models of the dihydrogen heterobimetallic complexes. ^aSum of single bond radii (Ru + M)¹¹

Table 3.2 Experimental and computation data on N_2 binding to $\text{M}\cdot\text{Ru-N}_2$

Table 4.1 Experimental and Calculated ^{27}Al NMR spectra chemical shifts of Al(I) compounds

Table 4.2. Comparison of measured and calculated bond lengths and angles of $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$

List of Abbreviations

α	Alpha
Ar	Aryl
β	Beta
BDI	β -diketiminate, κ^2 -(ArNC(Me)) ₂ CH
br	Broad
C ₆ D ₆	Deuterated Benzene
CDCl ₃	Deuterated Chloroform
COD	1,5-Cyclooctadiene
Cp	Cyclopentadienyl, η^5 -C ₅ H ₅
Cp*	Permethylcyclopentadienyl, η^5 -C ₅ Me ₅
Cy	Cyclohexyl
Cyp	Cyclopentyl
δ	Chemical Shift
°	Degrees
D	Deuterium, ² H
d	Doublet
DFT	Density functional theory
Dipp	1,6-Diisopropylphenyl
ϵ	Epsilon
E	Element
<i>esd</i>	Estimated standard deviation
<i>fsr</i>	Formal shortness ratio
g	Grams
η	Hapticity
h	Hour
{ ¹ H}	¹ H Decoupled
HMBC	Heteronuclear Multiple Bond Correlation
HSQC	Heteronuclear Single Quantum Correlation
INEPT	Insensitive Nuclei Enhanced Polarization Transfer
INS	Inelastic Neutron Scattering
INT	Intermediate
IR	Infrared
ⁱ Pr	Isopropyl
J	Spin-spin coupling constant
κ	Denticity
∇	Lapacian
μ	Bridging
m	Multiplet
M	Main group metal
MAS	Magic Angle Spinning
Me	Methyl
Mes	Mesityl
μ L	Microlitre
mg	Milligram
mmol	Millimole
mol	Mole
NBO	Natural Bond Order

NCI	Non-Covalent Interactions
NHC	N-Heterocyclic carbene
NMR	Nuclear Magnetic Resonance
<i>o</i>	Ortho
<i>p</i>	Para
Ph	Phenyl
ppm	Parts per million
q	quartet
QTAIM	Quantum Theory of Atoms In Molecules
ρ	Rho
σ	Sigma
s	Singlet
t	Triplet
T ₁	Spin-Lattice relaxation time
TS	Transition State
WBI	Wiberg Bond Index

Publications

This thesis has resulted in the following publications:

Mild sp²Carbon-Oxygen Bond Activation by an Isolable Ruthenium(II) bis(Dinitrogen) Complex: Experiment and Theory

Samantha Lau, Bryan Ward, Xueer Zhou, Andrew J. P. White, Ian J. Casely, Stuart A. Macgregor, Mark R. Crimmin.

Organometallics, **2017**, 36, 3654–3663

Tunable Binding of Dinitrogen to a Series of Heterobimetallic Hydride Complexes

Samantha Lau, Andrew J. P. White, Ian J. Casely, Mark R. Crimmin

Organometallics, **2018**, DOI: 10.1021/acs.organomet.8b00340

1 CHAPTER ONE – RUTHENIUM BIS(DIHYDROGEN) COMPLEX $[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$ AND ITS DERIVATIVES

1.1 INTRODUCTION

The ruthenium *bis*(dihydrogen) complex $[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$ (**1-2H₂**) was first synthesised in 1982 however this complex was initially incorrectly assigned as a hexahydride complex $[\text{RuH}_6(\text{PCy}_3)_2]$.¹ This assignment was later rectified as a *bis*(dihydrogen) complex in light of the discovery of the first isolated dihydrogen complex $[\text{W}(\eta^2\text{-H}_2)(\text{CO})_3(\text{P}^i\text{Pr}_3)_2]$ (Figure 1.1) by Kubas *et al.*^{2,3} A combination of different spectroscopic techniques (IR, INS, ¹H NMR and T₁), DFT calculations and X-ray diffraction has unambiguously confirmed the assignment of the ruthenium complex as a *bis*(dihydrogen) complex whereby the two hydrides were arranged *cis* to each other (Figure 1.1).⁴⁻⁶

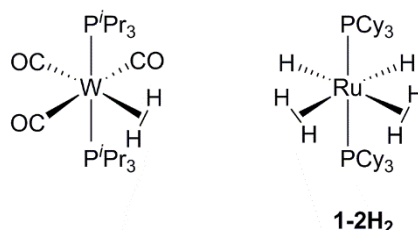


Figure 1.1. (Left) Kubas' dihydrogen complex. (Right) Ruthenium *bis*(dihydrogen) complex, **1-2H₂**

Coordination of the dihydrogen ligand to the ruthenium centre within $[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$ in a η^2 -fashion can be described by analogy to the Dewar-Chatt-Duncanson model of alkene coordination to a metal centre.^{7,8} The donation from the σ -orbital of the H₂ ligand into an empty *d*-orbital of the ruthenium is complemented by the back-donation of a filled *d*(π)-orbital into the anti-bonding σ^* -orbital of the H₂ ligand. The successful formation of dihydrogen ligated as a σ -bond is therefore dependent on the balance between the donation and back-donation ability of the metal centre. This balance, in turn, is determined by the geometry and nature of the other ligands surrounding the ruthenium centre (Figure 1.2).

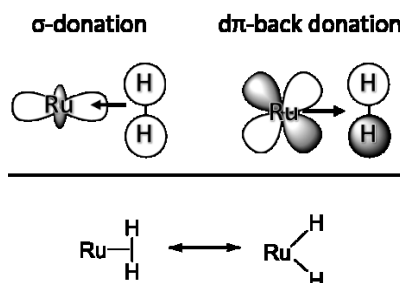


Figure 1.2. (Top) Orbitals involved in dihydrogen bonding to ruthenium centre. (Bottom) Two extreme modes of coordination of dihydrogen

If the ruthenium is surrounded by more electron donating ligands then the back donation of the filled $d(\pi)$ -orbital of the nucleophilic metal centre into the empty σ^* -orbital of the dihydrogen interaction will dominate causing elongation and weakening of the H–H bond. This dihydrogen in turn will become more electrophilic. Conversely if the ruthenium is surrounded by more electron withdrawing ligands then the filled σ -orbital donation into the empty d -orbital of the electrophilic metal centre interaction will dominate. The dihydrogen ligand here will be more nucleophilic in nature.

There has been a handful of publications on changing the tricyclohexylphosphine ligands in **1-2H₂** with other phosphine ligands and observing how this affects the dihydrogen binding on ruthenium and its reactivity.^{9–13} Similar synthesis procedure to form $[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$ was replicated using PPh_3 and also P^iPr_3 to generate $[\text{Ru}(\text{H})(\text{X})(\eta^2\text{-H}_2)_2(\text{L})_2]$ (where $\text{X} = \text{H}$ or I and $\text{L} = \text{PPh}_3$ or P^iPr_3) however these complexes were incredibly unstable and were only spectroscopically characterised *in-situ* before decomposing and dimerising into ruthenium dinuclear complexes (*vide infra*).^{4,14,15} In 2005, Sabo-Etienne's group synthesised the analogous $[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCyp}_3)_2]$ complex (PCyp_3 = tricyclopentylphosphine) and were able to get a neutron structure of this *bis*(dihydrogen) complex, amongst other spectroscopic characterisation techniques, to unambiguously confirm the presence of two dihydrogen ligands ligated in an η^2 -fashion to the ruthenium centre.¹⁶

Two additional ruthenium dihydrogen complexes have also been isolated by Sabo-Etienne *et al.*,¹⁷ $[\text{Ru}(\text{H})(\eta^2\text{-H}_2)_2(\text{Tp}^*)]$ and $[\text{Ru}(\text{H})(\eta^2\text{-H}_2)(\text{THT})(\text{Tp}^*)]$ (Tp^* = hydridotris(3,5-dimethylpyrazolyl)borate and THT = tetrahydrothiophene). IR stretches of the dihydrogen bonds are traditionally difficult to observe in transition metal complexes as the stretches are normally found within the aromatic, alkenyl and alkyl region of IR spectrum however the H–H stretches of these two complexes were observed and characterised by IR spectroscopy ($[\text{Ru}(\text{H})(\eta^2\text{-H}_2)_2(\text{Tp}^*)]$ $\nu_{\text{H-H}} = 2361 \text{ cm}^{-1}$, $[\text{Ru}(\text{H})(\eta^2\text{-H}_2)(\text{THT})(\text{Tp}^*)]$ $\nu_{\text{H-H}} = 2250 \text{ cm}^{-1}$ where upon deuteration these two stretches shifted to $\nu_{\text{D-D}} = 1705$ and 1620 cm^{-1} respectively. For comparison, the Ru–H stretching frequency was found at $\nu_{\text{Ru-H}} = 1950 \text{ cm}^{-1}$ for both hydridotris(pyrazolyl) borate dihydrogen ruthenium complexes which also shifted to lower wavenumber upon deuteration $\nu_{\text{Ru-D}} = 1530 \text{ cm}^{-1}$.

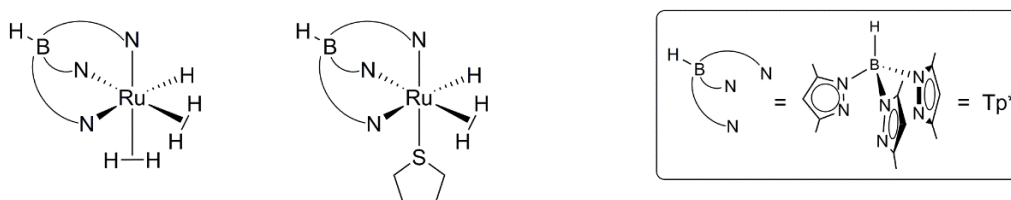


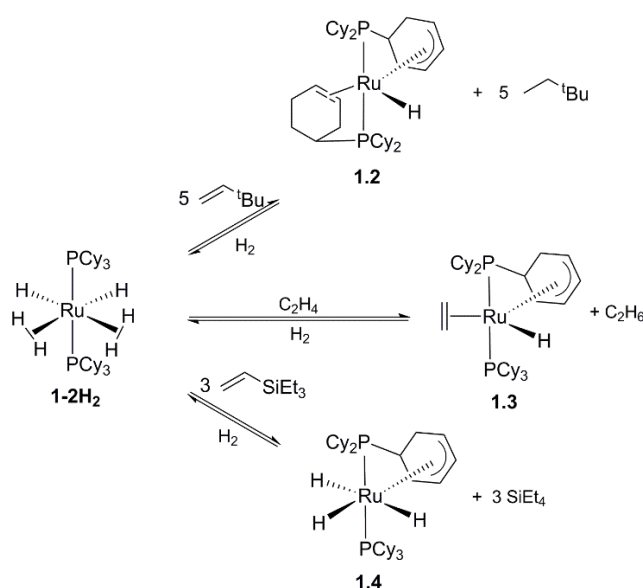
Figure 1.3. Ruthenium *bis*(dihydrogen) complex (left) $[\text{Ru}(\text{H})(\eta^2\text{-H}_2)_2(\text{Tp}^*)]$ and (right) $[\text{Ru}(\text{H})(\eta^2\text{-H}_2)(\text{THT})(\text{Tp}^*)]$.

1.2 CHEMISTRY OF $[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$

1.2.1 Hydrogenation

The chemistry of $[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$ has been widely explored by Chaudret's group and further expanded by Sabo-Etienne's group respectively.¹⁸ The interest in this ruthenium complex was originally attributed to its high hydrogen content (containing 6 hydrogen atoms per complex) and therefore the potential for this complex to participate in hydrogenation chemistry.^{19,20}

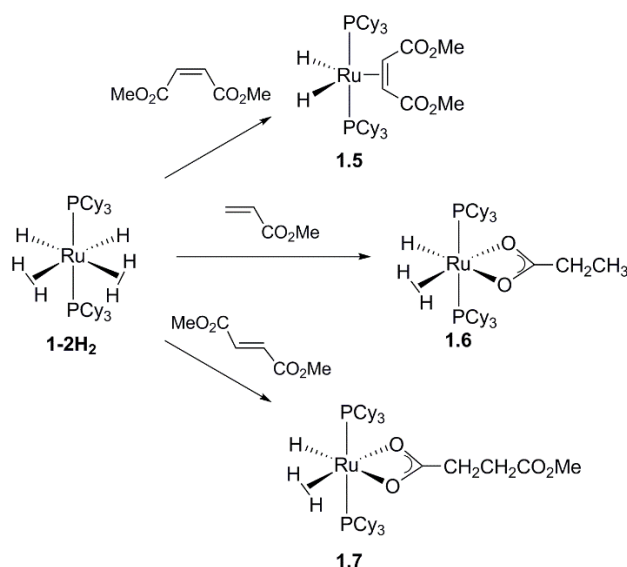
$[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$ effects the hydrogenation of alkenes (Scheme 1.1).²⁰ The reaction of **1-2H₂** with 5 equivalents of *tert*-butylethylene resulted in hydrogenation of the alkene and concomitant intramolecular C–H activation of the cyclohexyl ring moiety on both of the PCy₃ ligands – a totally of 10 hydrogen atoms transferred from a single ruthenium complex to generate complex **1.2** (Scheme 1.1). The level of dehydrogenation of the ruthenium complex was controlled by the equivalents of alkene in the system. In addition, the reactions of **1-2H₂** with *tert*-butylethylene, ethene and triethylvinylsilane were reversible and bubbling dihydrogen through the solution of the cyclometallated product returns the starting ruthenium complex (**1-2H₂**) indicating the reversible C–H activation of the PCy₃ ligand.



Scheme 1.1 Hydrogenation of alkenes with concomitant C–H activation of PCy₃

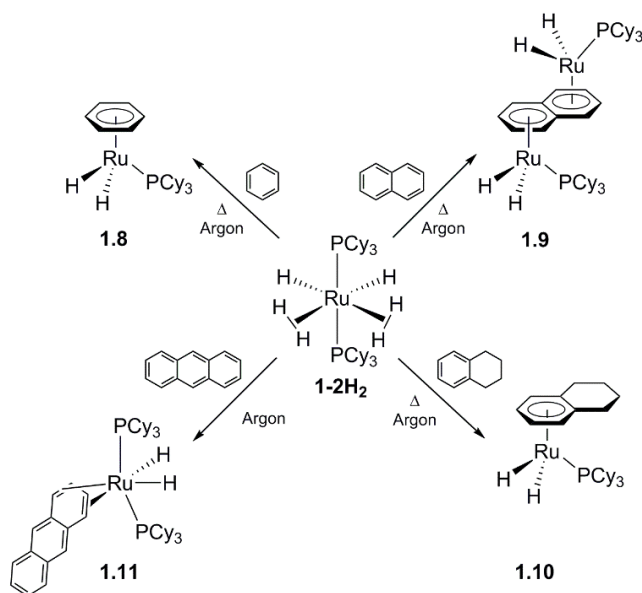
Reaction of **1-2H₂** with alkene bearing ester substituents resulted in either ligand substitution to form η^2 -alkene complex **1.5** or hydrogenation of the alkene moiety with concomitant demethylation of the methyl ester group resulting in the formation of complex **1.6** and **1.7**. It was anticipated that methane was formed as the by-product in this unprecedented demethylation reactions of a methyl ester. These reactions highlighted the nucleophilic behaviour of the dihydrogen ligands.

Unambiguous confirmation of some of these complexes was not successful due to their instability and therefore clean isolation and verification by X-ray or neutron diffraction was not possible in all cases except complex **1.6**. Nevertheless, a combination of other spectroscopic techniques and further reactivity with the postulated complexes provided compelling evidence for the formulations of these complexes.



*Scheme 1.2 Ligand substitution to generate complex **1.5** and hydrogenation of alkene and concomitant demethylation to generate complex **1.6** and **1.7***

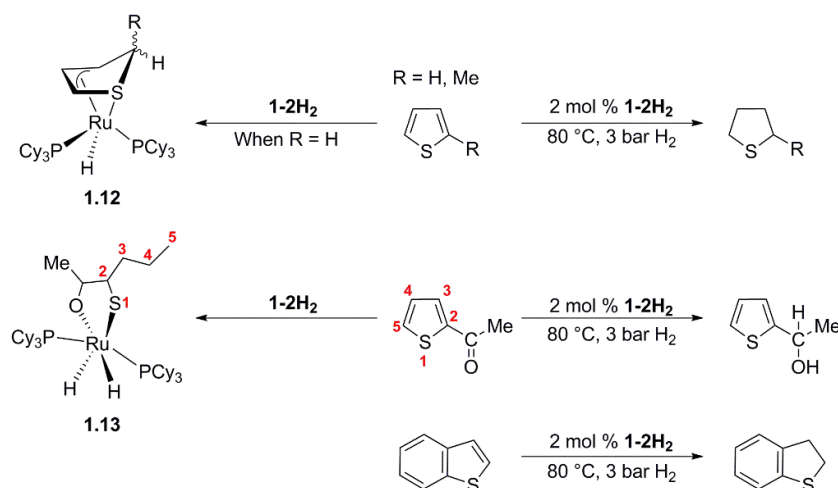
The reaction of **1-2H₂** with benzene, naphthalene and anthracene under 3 bar of H₂ at 80 °C resulted in the formation of cyclohexane, tetralin and a mixture of 4H-anthracene and 8H-anthracene respectively.²¹ In the absence of dihydrogen **1-2H₂** reacted with these arenes to generate new ruthenium π -complexes (**1.8** – **1.11**) which were also found as minor components in the hydrogenation chemistry reactions (Scheme 1.3). These complexes were characterised by multinuclear NMR spectroscopy however no X-ray crystallographic data were obtained. Further investigation into the hydrogenation reactions of these arenes suggested only complex **1.11** showed catalytic competence in the semi-hydrogenation of anthracene into 4H-anthracene and 8H-anthracene as the major product and minor product respectively.²² In addition, the formation of complex **1.8** was observed initially from refluxing **1-2H₂** in C₆D₆ resulting in the formation of a minor product characterised by a new signal in the ¹H NMR spectrum at $\delta_{\text{H}} = -10.15$ ppm (d, $J_{\text{HP}} = 42.3$ Hz) for Ru–H environment. Formation of complex **1.8** was further substantiated by the observation of free PCy₃ in ³¹P NMR spectrum as well as a new resonance for the arene complex observed at $\delta_{\text{P}} = 78.3$ ppm. The formation of these ruthenium arene complexes indicated the finite stability of the ruthenium *bis*-(dihydrogen) complex in aromatic solvents.



Scheme 1.3 Ruthenium π -arene complexes

Beyond the reactivity of **1-2H₂** with alkenes and arenes, the reaction of thiophenes with **1-2H₂** was investigated to observe if C–S bond cleavage occurred (Scheme 1.4).²³ Instead, the reaction of 1 equivalent of **1-2H₂** with 1 equivalent of thiophene resulted in the formation of a piano-stool complex **1.12**. Complex **1.12** demonstrated a resonance at $\delta_{\text{H}} = -20.90$ ppm (dd, $J_{\text{HP}} = 28$ and 35 Hz) in the ¹H NMR spectrum which had equal intensity with 5 other signals in the proton NMR spectrum assigned to the thioallyl ligand. For example, only one other η^4 -thioallyl complex had been previously reported, $[\text{ReH}_2(\eta^4\text{-SC}_4\text{H}_5)(\text{PPh}_3)_2]$.²⁴ However the reaction of **1-2H₂** with 2-acetylthiophene led to hydrogenolysis of the C–S bond to generate complex **1.13**. Complex **1.13** was isolated and characterised by multinuclear NMR spectroscopy and X-ray crystallography to confirm its structure.

In comparison, under catalytic conditions, the reaction of **1-2H₂** (2 mol %) with thiophene and 2-methylthiophene under 3 bar H₂ at 80 °C resulted in the formation of tetrahydrothiophene and 2-methyltetrahydrothiophene respectively (Scheme 1.4). However, the same reaction conditions employed with 2-acetylthiophene as the substrate gave 1-(2-thienyl)ethanol selectively and no hydrogenation of the aromatic ring was observed. Complex **1.13** was also shown to be catalytically competent at the hydrogenation of 2-acetylthiophene into the alcohol. In addition, the catalytic reaction of **1-2H₂** with benzothiophene as the substrate yielded 2,3-dihydrobenzothiophene as the product and no further hydrogenation of the aromatic ring was observed. A stoichiometric reaction between **1-2H₂** and benzothiophene was not reported although it would be interesting to see if any bond activation chemistry occurred instead of hydrogenation of the unsaturated bond of benzothiophene based on the stoichiometric reactions with 2-acetylthiophene.



Scheme 1.4 Reaction of **1-2H₂** with thiophenes both stoichiometrically and catalytically

Complex **1-2H₂** was also competent at the hydrogenation of benzonitrile to benzylamine (20 °C, 14 bar H₂ resulted in 96 % conversion over 50 h).²⁵ The hydrogenation of benzonitrile with **1-2H₂** was superseded by the analogue [Ru(H)₂(η^2 -H₂)₂(PCy₃)₂] whereby similar conversions were achieved at a much shorter time frame of 24 h.²⁶ The use of **1-2H₂** as a catalyst precursor for the nitrile hydrogenation was also demonstrated in a series of patents by Beatty and Paciello employed by Du Pont.²⁷

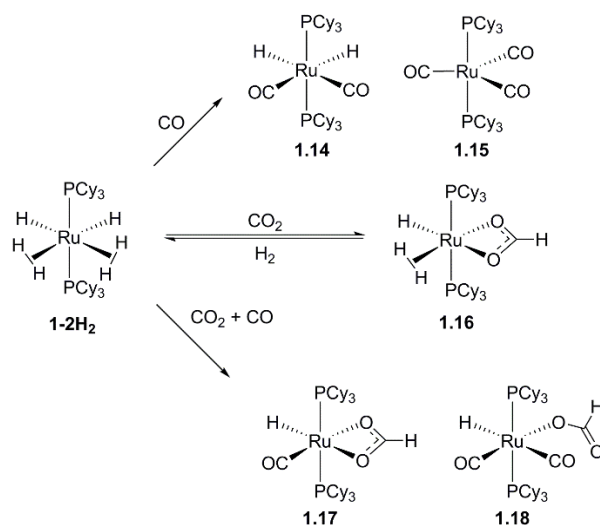
1.2.2 Small Molecules (CO, CO₂, CS₂, N₂ and Halocarbons)

The lability of the dihydrogen ligands of [Ru(H)₂(η^2 -H₂)₂(PCy₃)₂] has provided a fertile avenue for exploratory chemistry into forming new complexes through substitution of the nucleophilic dihydrogen with small molecules (Scheme 1.5).

Bubbling CO through a suspension of **1-2H₂** in pentane for 30 mins resulted in formation of yellow pale solid characterised as [Ru(H)₂(CO)₂(PCy₃)₂] (complex **1.14**).²⁸ IR spectroscopy stretches were obtained $\nu_{\text{C=O}}$ = 2004 and 1994 cm⁻¹ and multinuclear NMR data were consistent with *cis*-disposed ruthenium dicarbonyl complex. In the ¹H NMR spectrum, complex **1.14** demonstrated a single resonance for the Ru–H environment, δ_{H} = –7.90 ppm (t, J_{HP} = 23 Hz) with a corresponding singlet in the ³¹P{¹H} NMR spectrum at δ_{P} = 68.8 ppm. Prolonged exposure to CO resulted in full conversion to the trigonal bipyramidal [Ru(CO)₃(PCy₃)₂] complex **1.15**.^{29,30}

The reaction of **1-2H₂** with CO₂ resulted in insertion of the CO₂ into the Ru–H bond to generate a κ^2 -formate complex (Scheme 1.5, complex **1.16**).³¹ A single resonance was observed for both the Ru–H and η^2 -ligated H₂ environments in the ¹H NMR spectrum at δ_{H} = –14.19 ppm (t, J_{HP} = 13.8 Hz) which did not decoalesce upon cooling to 193 K. T₁(min) value of 35 ms (243 K, 250 MHz) was measured for this hydride resonance, indicative of a non-classical hydride interaction and presence of dihydrogen

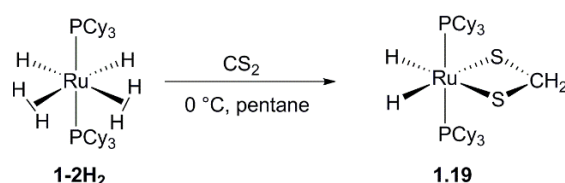
ligand in this complex.³² Further to these characterisation data, complex **1.16** also demonstrated diagnostic IR spectroscopy stretches at $\nu_{\text{C=O}} = 1566 \text{ cm}^{-1}$ and $\nu_{\text{Ru-H}} = 2050 \text{ cm}^{-1}$. Subjecting complex **1.16** to an atmosphere of H_2 returned **1-2H₂** back.



Scheme 1.5. Reaction of **1-2H₂** with CO, CO₂ and a mixture of CO/CO₂

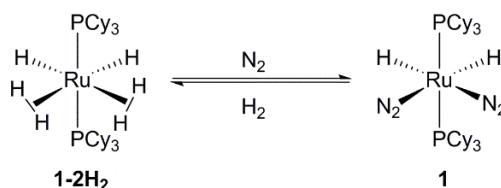
Exposing **1-2H₂** to a mixed atmosphere of CO/CO₂ resulted in the formation of two new ruthenium complexes (Scheme 1.5, complex **1.17** and **1.18**).³³ Complex **1.17** was characterised by two diagnostic IR spectroscopy stretches observed at $\nu_{\text{C=O}} = 1900 \text{ cm}^{-1}$ for the single carbonyl environment and $\nu_{\text{C=O}} = 1559 \text{ cm}^{-1}$ for the κ^2 -carboxylate ligand. In comparison, complex **1.18** was characterised by three diagnostic IR spectroscopy stretches found at $\nu_{\text{C=O}} = 2024$ and 1947 cm^{-1} for the two carbonyl ligands and $\nu_{\text{C=O}} = 1621 \text{ cm}^{-1}$ for the κ^1 -carboxylate ligand. Formation of these two new complexes was verified by multinuclear NMR spectroscopy and from their isolation and characterisation by X-ray crystallography.

Bubbling CS₂ gas through a suspension of **1-2H₂** at 0 °C in pentane resulted in the formation of a Ru(IV) complex **1.19** (Scheme 1.6).³¹ Complex **1.19** demonstrated a resonance in the ¹H NMR spectrum for the Ru–H environment found at $\delta_{\text{H}} = -10.85 \text{ ppm}$ (t, $J_{\text{HP}} = 32.9 \text{ Hz}$) and a downfield resonance at $\delta_{\text{H}} = 6.17 \text{ ppm}$ for the methylene protons on the sulphur atom. The T₁(min) measured for the Ru–H signal was measured as 134 ms (243 K, 250 MHz) which indicated classical hydride behaviour.³² The double insertion of CS₂ was ascribed to the affinity between ruthenium and sulphur and why this reaction was non-reversible in the presence of H₂ in comparison to the reactivity of **1-2H₂** with CO₂ (*vide supra*).



Scheme 1.6. Reaction of **1-2H₂** with CS₂

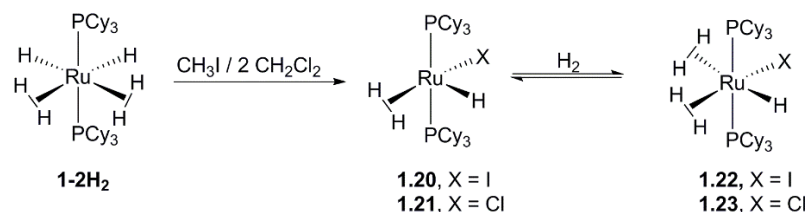
Bubbling N₂ through a suspension of **1-2H₂** in pentane gave a new pale yellow solid characterised as the ruthenium *bis*(dinitrogen) complex [Ru(H)₂(N₂)₂(PCy₃)₂] (**1**) (Scheme 1.7).³¹ Complex **1** demonstrated a triplet in the ¹H NMR spectrum at δ_H = −12.83 ppm (²J_{HP} = 22 Hz) for Ru–H environment however no phosphorus NMR spectrum resonance was reported for **1**. IR spectrum absorptions in pentane were obtained for the dinitrogen stretches ν_{N≡N} = 2163 and 2126 cm^{−1}. This ruthenium *bis*(dinitrogen) complex was originally deemed too reactive to isolate and was observed to decompose slowly under an atmosphere of argon or upon exposure to a vacuum however bubbling dihydrogen gas through a solution of **1** reformed the original ruthenium *bis*(dihydrogen) complex. No further reactivity was reported on complex **1**.



Scheme 1.7. Reaction of **1-2H₂** with N₂ to form ruthenium *bis*(dinitrogen) complex **1**

The reaction of **1-2H₂** with either one equivalent of CH₃I or two equivalents of CH₂Cl₂ formed 16 valence electron ruthenium complexes **1.20** and **1.21** respectively (Scheme 1.8).^{28,34} Complex **1.20** was characterised by X-ray crystallography with the Ru–H bond length measured as 1.51(5) Å and the Ru–H₂ bond lengths were measured as 1.60(5) and 1.59(4) Å, it is worth noting these bond lengths were within the *esd*. In comparison, the H–H bond length was determined as 1.03 (7) Å. Complex **1.20** demonstrated a broad peak at δ_H = −16.30 ppm in ¹H NMR spectrum for the Ru–H environment and a short T₁(min) was measured for this resonance (30 ms, 243 K, 250 MHz) indicative of non-classical hydride behaviour.³² When complex **1.20** was placed under an atmosphere of H₂ a new resonance was observed in ¹H NMR spectrum at δ_H = −12.00 ppm which upon cooling to 203 K decoalesced into two broad signals at δ_H = −7.90 and −16.90 ppm. The new signals in the ¹H NMR spectra was assigned to complex **1.22** whereby a second dihydrogen ligand complexed onto the ruthenium at the vacant site to form a new 18 valence electron ruthenium complex (Scheme 1.8). An analogous reaction with complex **1.21** and H₂ to form complex **1.23** was also reported. An equilibrium mixture existed between the 16

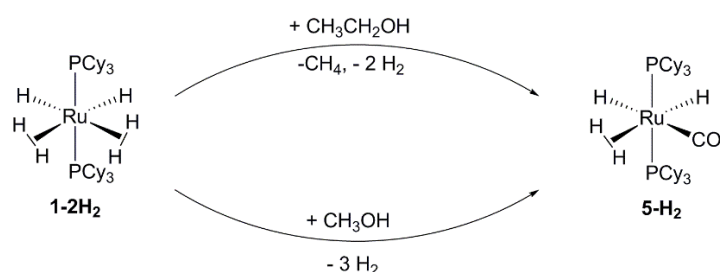
and 18 valence electron ruthenium complexes and increasing the pressure of H_2 pushed the equilibrium towards the 18 valence electron ruthenium complexes **1.22** and **1.23**. It was noted that, surprisingly, the 16 valence electron configuration was more favourable at standard conditions than the 18 valence electron configuration of these ruthenium complexes.



Scheme 1.8. Reaction of **1-2H₂** with halocarbons

1.2.3 Alcohols

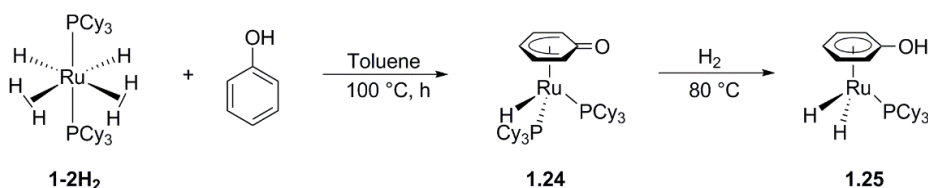
The reaction of 1 equivalent of **1-2H₂** with 1 equivalent of ethanol at 50 °C in toluene generated a new mono-carbonyl species **5-H₂** (Scheme 1.9).³³ Complex **5-H₂** demonstrated a broad resonance at $\delta_{\text{H}} = -7.00$ ppm in ^1H NMR spectrum for the Ru–H environments and a resonance at $\delta_{\text{P}} = 71.9$ ppm in $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The indicative carbonyl resonance was found at $\delta_{\text{C}} = 204$ ppm (t, $J_{\text{HC}} = 3.7$ Hz) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. Repeating the reaction using methanol as the substrate also generated the same ruthenium mono-carbonyl species **5-H₂**. No further discussion on the mechanism of the formation of **5-H₂** was reported.



Scheme 1.9 Formation of **5-H₂**

Aside from ethanol and methanol, **1-2H₂** showed reactivity with phenol to form $[\text{RuH}(\eta^5\text{-C}_6\text{H}_5\text{O})(\text{PCy}_3)_2]$, complex **1.24** (Scheme 1.10). In the ^1H NMR spectrum a resonance was observed at $\delta_{\text{H}} = 12.80$ ppm (t, $J_{\text{HP}} = 38.2$ Hz) for the Ru–H environment. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this complex displayed a single resonance at $\delta = 53.6$ ppm and an indicative C=O moiety was observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at $\delta = 166$ ppm and assigned to the phenoxo group of complex **1.24**. Only multinuclear NMR and IR spectroscopy data were collected for this complex however the postulated structure of this piano-stool complex was similar to a complex characterised by Wilkinson *et al.* from the reaction of $[\text{Ru}(\text{H})_2(\text{PPh}_3)_4]$ with phenol.^{31,35} Subjecting **1.24** to an atmosphere of H_2 resulted in the heterolytic cleavage of H_2 and concomitant loss of PCy_3 to give a new complex with the

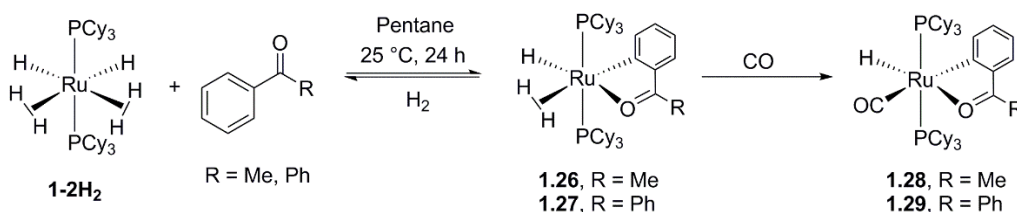
proposed structure $[\text{Ru}(\text{H})_2(\eta^6\text{-C}_6\text{H}_5\text{OH})(\text{PCy}_3)]$ (Scheme 1.10 – complex **1.25**). Complex **1.25** demonstrated a resonance in ^1H NMR spectrum at $\delta = -0.57$ ppm (d, $J_{\text{HP}} = 42.6$ Hz) assigned to the Ru–H environment. The indicative C–OH environment in $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum was not observed as it was most likely found under the solvent peaks. Isolation of complex **1.25** proved difficult with contamination from complex **1.24** pervasive during work-up. Nevertheless, formation of complex **1.24** was very similar to the reaction of **1-2H₂** with benzene to generate complex **1.8** (Scheme 1.3) with similar characteristics of the η^6 -coordination of the arene ring in both complexes observed by multinuclear NMR spectroscopy.



Scheme 1.10. Reaction of **1-2H₂** with phenol

1.2.4 X–H activation (X = C, N, O)

The ability for **1-2H₂** to undergo C–H activation chemistry was not confined to the intramolecular C–H activation of positions of the PCy_3 ligands (*vide supra*) but included acetophenone substrates. Chaudret *et al.* reported the reaction of **1-2H₂** with acetophenone to generate 5-membered cyclometallated intermediates *via* the *ortho*-C–H activation of the substrate (Scheme 1.11 – **1.26**).³⁶ Complex **1.26** demonstrated a broad resonance in the ^1H NMR spectrum at $\delta_{\text{H}} = -9.01$ ppm for the terminal Ru–H and Ru–H₂ environments which decoalesced into 2 signals upon cooling to 193 K at $\delta_{\text{H}} = -5.60$ and -14.90 ppm, in addition the $T_1(\text{min})$ were measured to give 31 ms and 85 ms respectively. The $T_1(\text{min})$ values were indicative of non-classical hydride behaviour and agreeing with the assignment of a dihydrogen ligand still ligated on the metal centre in complex **1.26**.³² Complex **1.26** was also characterised by a single resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum $\delta_{\text{P}} = 48.0$ ppm. An analogous reaction of **1-2H₂** with benzophenone was also performed to give complex **1.27**.

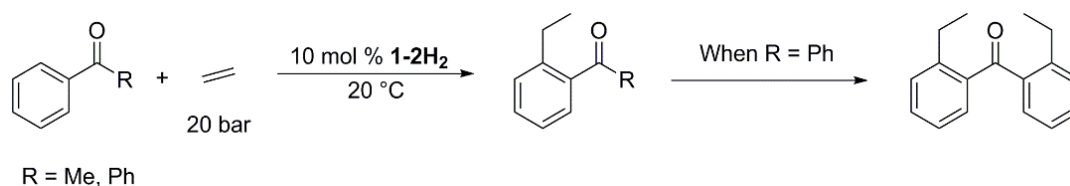


Scheme 1.11. C–H activation of acetophenone substrates by **1-2H₂**

Exposing complex **1.26** and **1.27** to an atmosphere of CO generated **1.28** and **1.29** respectively from the substitution of the dihydrogen ligand with CO (Scheme 1.11).³⁶ Complex **1.28** demonstrated

a triplet in ^1H NMR spectrum at $\delta_{\text{H}} = -16.03$ ppm ($J_{\text{HP}} = 23.4$ Hz) for the Ru–H environment and an indicative resonance in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at $\delta_{\text{C}} = 208$ and 207 ppm for the carbonyl and Ru–C environments. Similar characterisation data were found for complex **1.29**.

Chaudret *et al.* commented that the formation of the 5-membered cyclometallated intermediate from C–H activation of acetophenones were “reminiscent of intermediates proposed by Murai for the insertion of olefins into aromatic C–H bonds” (Scheme 1.11).^{36,37} Following this observation Chaudret and co-workers reacted the 5-membered cyclometallated complexes **1.26** and **1.27** with 20 bar ethylene which resulted in the formation of a new organic product and generation of a new C–C bond (Scheme 1.12). When acetophenone was used, the major product was the mono-coupled product from one C–C bond making process but when benzophenone was used the double-coupled product was the major product *via* two *ortho*-C–H functionalisation of benzophenone (Scheme 1.12). This Murai-type coupling reaction was also catalytic at room temperature. The original catalyst system reported by Murai required the reaction to be performed at elevated temperatures >130 °C.^{38–40} It was noted that when trying to perform the same reaction but using the carbonyl analogue of the 5-membered cyclometallated intermediate (**1.28** and **1.29**) no coupling was observed which suggested that CO may act as an inhibitor for this reaction.



Scheme 1.12. Murai-type coupling reaction

In 2001, Leitner *et al.* replicated the Murai-type coupling reaction with **1-2H₂** and expanded the different acetophenone substrates used in these reactions.⁴¹ Leitner and co-workers found electron withdrawing substituents *para* to the ketone group of the acetophenone substrate helped to improve yields but also favoured the double C–H activation product. This trend in reactivity was opposite to what was observed by Murai *et al.* suggesting two different mechanism were in operation when using **1-2H₂** or $[\text{Ru}(\text{H})_2(\text{CO})(\text{PCy}_3)_3]$ as the catalyst precursor (and triethoxyvinylsilane as the coupling partner).⁴¹ Aside from this investigation into substituent effects, Leitner *et al.* found that these reactions were limited due to a catalyst deactivation pathway however the identity of these deactivation products were not deciphered.

In 2003, Chaudret *et al.* investigated further into the deactivation pathways of these Murai-type coupling reactions of acetophenone substrates mediated by **1-2H₂**. Chaudret and co-workers investigated how varying the temperature, solvent, catalyst/ketone ratio and substituent effects *para* to

the ketone group affected the outcome of the reaction. Unsurprisingly, increasing the temperature increased the initial rate of reactions but this was negated by the increase in decomposition product formed at elevated temperatures. Aliphatic hydrocarbon solvents were better for overall conversion even though there were minor solubility issues associated with **1-2H₂** however the use of aromatic hydrocarbon solvents were known to form π -arene complexes with ruthenium over time (Scheme 1.3) and coordinating solvents like THF were found to slow down the initial rate of reaction and also reduce selectivity between the mono and double *ortho*-C-H functionalised product. Chaudret *et al.* also observed the same trend as Leitner *et al.*⁴¹ with greater yields of C-C coupled products when electron withdrawing substituents were found *para* to the ketone group of the acetophenone substrate. Chaudret *et al.* mentioned that the observed order of reactivity for these substituents was $H \approx CH_3 > Cl > CH_3O$ and therefore electronic effects may not be the simple explanation for the trend proposed by both Leitner's group and themselves. The slow rate of reaction for *p*-CH₃O substituted acetophenone was most likely due to competitive coordination between the *p*-CH₃O substituent and the ketone directing group within the same substrate with the ruthenium centre. The catalyst/substrate ratio showed that there was an optimum ratio for good conversion (1/10) and that more substrate actually inhibited the reaction (ratio 1/100 gave trace product formation), in addition higher yields of the deactivation product was observed with greater concentration of substrate. The deactivation product was identified as the doubly complexed substrate on ruthenium $[Ru(C_6H_4C(O)CH_3)_2(PCy_3)_2]$, **1.30** (Figure 1.4). This product exhibited a phosphorous resonance at $\delta_P = 21.2$ ppm and the only resonances observed in ¹H NMR spectrum were found in the aromatic region and at $\delta_H = 2.53$ ppm attributed to the methyl groups. Bubbling dihydrogen through a solution of **1.30** returned a mixture of **1-2H₂**, the 5-membered cyclometallated intermediate and the starting acetophenone substrate.

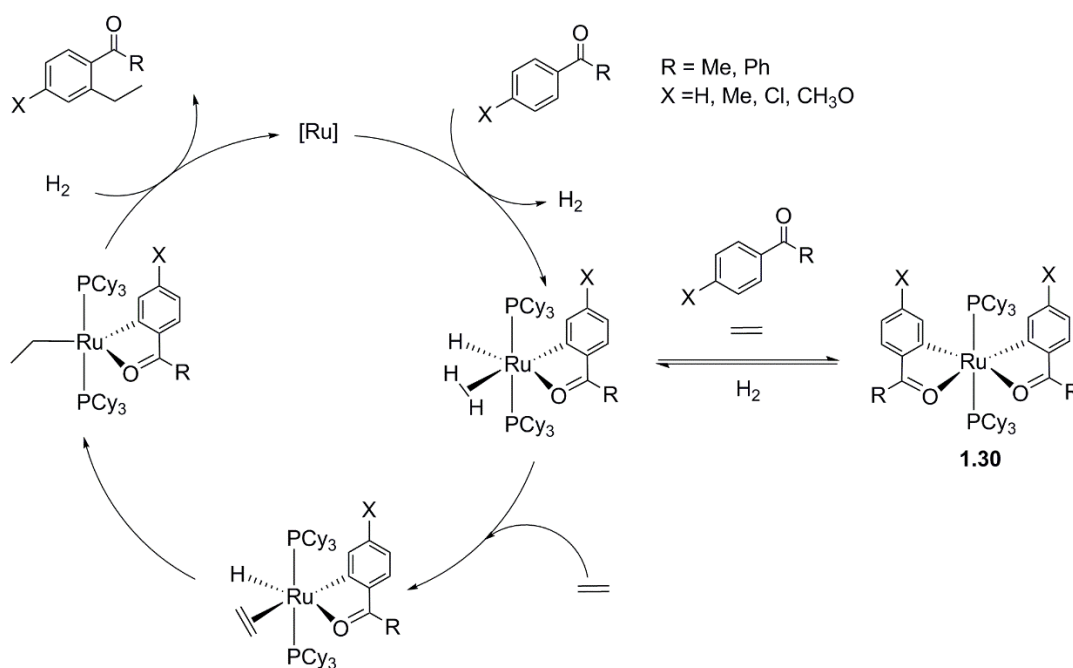
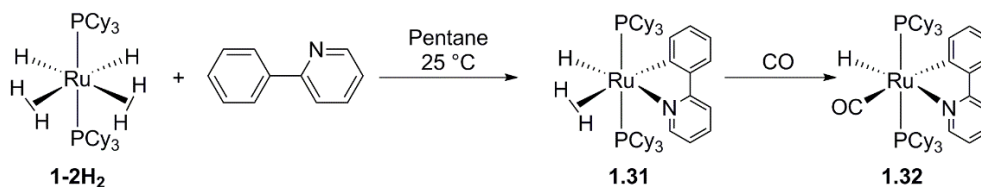


Figure 1.4. Proposed catalytic cycle of Murai-type coupling reaction

Similar C–H activation of aromatic substrates bearing a chelating group was demonstrated by the reaction of **1-2H₂** with phenylpyridine, where the N-atom of pyridine acted as the chelating group, to generate complex **1.31** (Scheme 1.13). Complex **1.31** demonstrated one broad resonance in the hydride region of the ¹H NMR spectrum at $\delta_{\text{H}} = -8.44$ ppm which decoalesced into 2 broad signals at 183 K, $\delta_{\text{H}} = -6.90$ (Ru–H₂; $T_1(\text{min}) = 105$ ms) and -13.00 ppm (Ru–H; $T_1(\text{min}) = 267$ ms). The higher than expected $T_1(\text{min})$ value for the Ru–H₂ resonance indicated that the dihydrogen and hydride were still in chemical exchange which resulted in the T_1 averaging value observed for both signals *i.e.* the dihydrogen resonance was misleadingly long and the hydride signal was misleadingly short. Again, exposing complex **1.31** to an atmosphere of CO resulted in the exchange of the dihydrogen with CO to generate complex **1.32** and corroborated with the assignment of **1.31** containing a dihydrogen ligand.



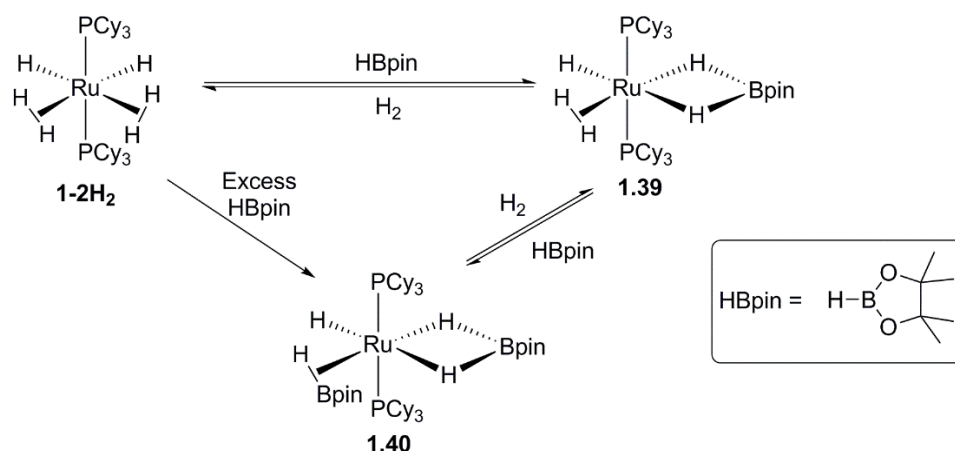
Scheme 1.13. Reaction of **1-2H₂** with phenylpyridine

As well as C–H activation, **1-2H₂** was capable of activating both N–H and O–H bonds of heteroaromatic substrates (Scheme 1.14).⁴² The reaction of **1-2H₂** with either quinoline or pyridine bearing either hydroxy or amino substituents resulted in formation of 4 new ruthenium complexes **1.33**

In addition to hydrogenation, other chemical process such as hydrosilylation^{43,44} and hydroboration¹⁹ are postulated to also go through similar η^2 -fashion complexation of the E–H bond (E = B, Si). These σ -complexes are often invoked as intermediates in hydrofunctionalisation catalysis, however their isolation is often more challenging than the dihydrogen analogues.

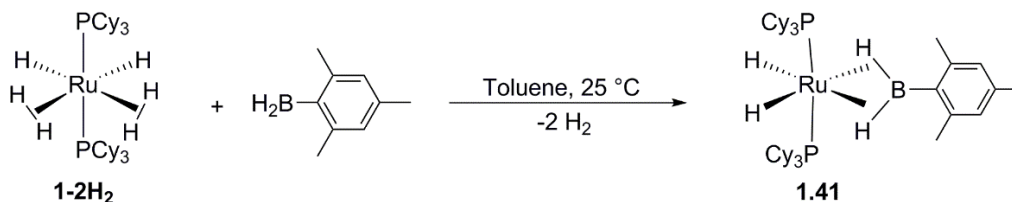
1.1.1.1 E = Boron

In 2002, Chaudret *et al.* reported the reaction of **1-2H₂** with pinacolborane (HBpin) (Scheme 1.15). The reaction of 1 equivalent of **1-2H₂** with 1 equivalent of HBpin resulted in formation of a ruthenium dihydridoborate complex (**1.39**) however the reaction of **1-2H₂** with an excess of HBpin resulted in another dihydridoborate complex which also contained a σ -(B–H) bond (**1.40**).⁴⁵ Formation of **1.40** was confirmed by X-ray crystallography. Comparison of the bond lengths helped to justify the assignment of the complex as a σ -complex. Ru–B bond length for the σ -borane moiety in **1.40** was determined to be 2.157(5) Å which was shorter than the Ru–B bond length for the dihydridoborate moiety of the complex (2.188(5) Å) but both bond lengths were longer than the sum of the single bond radii of Ru and B (2.04 Å).⁴⁶ At 233 K in the ¹H NMR spectrum three resonances were observed in the upfield region in a 2:1:1 ratio for the hydrides, $\delta_{\text{H}} = -11.40$ ppm (br s) for the two bridging hydrides, $\delta_{\text{H}} = -8.03$ ppm (t, $J_{\text{HP}} = 25$ Hz) for the terminal hydride and $\delta_{\text{H}} = -7.13$ ppm for the σ -bonded B–H proton. Formulation of the structure to include a dihydrogen ligand was dismissed due to the long T₁ minimum values determined for all three signals as ~100 ms (300 MHz). In comparison, at 233 K complex **1.39** demonstrated a single resonance for all 5 hydrides in the ¹H NMR spectrum at $\delta_{\text{H}} = -8.83$ ppm with the T₁(min) value determined as 40 ms (300 MHz). The possibility that complex **1.39** contained a dihydride and σ -(B–H) bond, instead of a dihydrogen and dihydridoborate motif, was also valid but based on the current data the ability to distinguish between the two structures was not possible. The competency of complex **1.40** to catalyse the hydroboration of alkenes was demonstrated and thereby justifying these σ -complexes as potential intermediates in hydrofunctionalisation reactions.⁴⁷



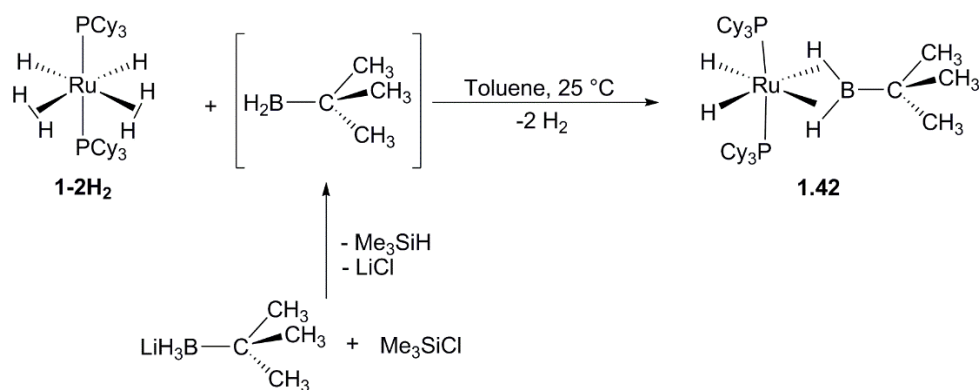
Scheme 1.15. Reaction of **1-2H₂** with HBpin

The isolation of the first *bis* σ -(B–H) ligand bound to Ru centre, was reported in 2007 by Sabo- Etienne *et al.*⁴⁸ The reaction of **1-2H₂** with H₂BMes (Mes = 2, 4, 6-trimethylbenzene) in toluene at 25 °C was facile and work-up gave a yellow powder which was characterised by multinuclear NMR spectroscopy and X-ray crystallography to confirm the formation of complex **1.41** (Scheme 1.16). Two resonances in the ¹H NMR spectrum were observed at 296 K at $\delta_{\text{H}} = -5.90$ and -11.05 ppm and long T₁(min) values measured for these resonances dismissed the presence of a η^2 -H–H ligand in the complex. The ¹¹B{¹H} NMR spectrum showed a single broad signal at $\delta = 58$ ppm which was within the characteristic region of a three-coordinated boron atom. The X-ray crystal of the structure allowed for bond lengths to be determined with a very short Ru–B bond distance of 1.938(4) Å found for this structure – much shorter than the Ru–B bond lengths of the dihydridoborate complex **1.39**. The Ru–H bond lengths from the σ -(B–H) moiety were determined to be 1.24(3) and 1.29(3) Å which were close to the computational calculated parent borane B–H bond length (1.197 Å). Computational analysis was performed in tandem to confirm the locations of the hydrides but also to rationalise the favourable interactions of the σ -(B–H) interactions. NBO calculations showed that while the σ -donation of the σ -(H–H) and σ -(B–H) orbitals to ruthenium were similar, the π -back-donation from the Ru d(π)-orbital to the σ^* -(H–H) was significantly less in comparison to the π -back-donation into the vacant p-orbital at boron (LP*(B)). This increase in population into the vacant p-orbital helped to stabilise the complex and was thought to be an effect of the Lewis acidic nature of the boron.



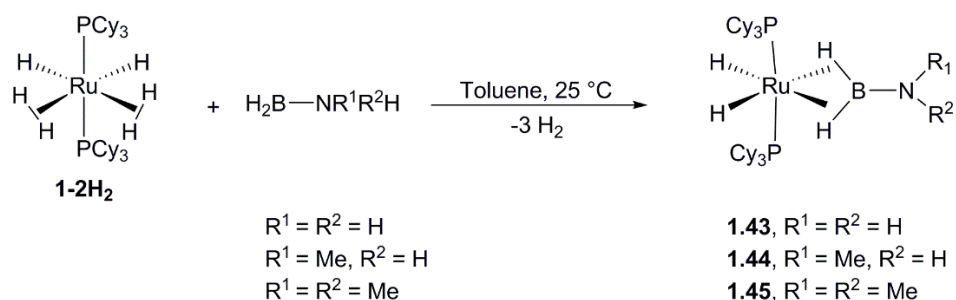
Scheme 1.16. Formation of *bis* σ -(B–H) ruthenium complex

An analogous complex but using *tert*-butylborane (generated *in-situ* from reaction of ^tBuBH₃Li and Me₃SiCl) instead of H₂BMes gave the first example and isolation of a monoalkyl *bis* σ -(B–H) complex, **1.42** (Scheme 1.17).⁴⁹ Multinuclear NMR data and X-ray crystallography data were collected to confirm the assignment of complex **1.42**. The Ru–B bond length was determined as 1.934(2) Å which fell within the range determined for complex **1.41** (Scheme 1.16).



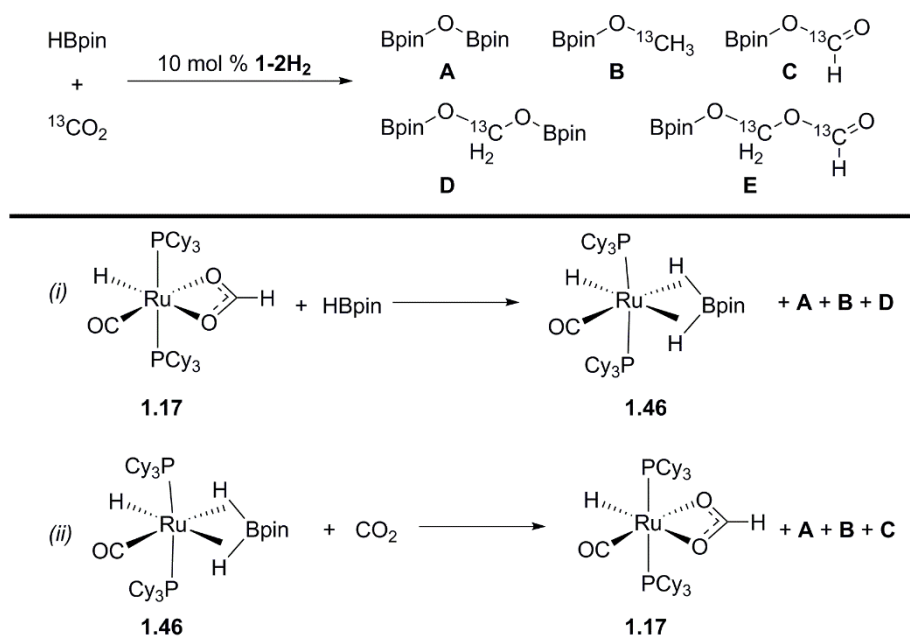
Scheme 1.17. Formation of monoalkyl bis σ -(B–H) ruthenium complex

Dehydrocoupling of amine-boranes are important reactions in borane chemistry. Ammonia-boranes can act as a potential hydrogen storage material; however the elementary steps of dehydrogenation are not well understood. These steps can be interrogated by studying the model reactions of related amine-boranes with transition metals which are postulated to go through σ -complex intermediates.⁵⁰ In 2010, Sabo-Etienne *et al.* isolated three similar *bis* σ -(B–H) aminoborane complexes.⁵¹ The reaction of **1.2H₂** and the amine-boranes proceeded at 25 °C and work-up of the reactions gave satisfactory yields of the products which were characterised by multinuclear NMR and X-ray diffraction spectroscopy (Scheme 1.18). The structures of **1.43** – **1.45** were very similar to the reported *bis* σ -(B–H) ruthenium complexes **1.41** and **1.42** (Scheme 1.16 and Scheme 1.17). Two resonances were observed in ¹H NMR spectrum for complex **1.43** at $\delta_{\text{H}} = -6.80$ ppm for the two σ -(B–H) hydrides (br s) and $\delta_{\text{H}} = -11.85$ ppm (t, $J_{\text{HP}} = 24.8$ Hz) for the two terminal hydrides. A 1D TOCSY ¹H{¹¹B} experiment in which the resonance at $\delta_{\text{H}} = -6.80$ ppm was selectively irradiated led to signal enhancement of a resonance at $\delta_{\text{H}} = 2.34$ ppm assigned to the NH₂ protons. In addition, X-ray data showed the B–N bond distance was shortened (1.396(3) Å) compared to the parent ammonia-borane (1.58(2) Å). In parallel, the B–H bond distances (1.25(2) and 1.22(3) Å) in the complex were elongated when against the parent ammonia-borane (1.15(3) and 1.18(3) Å). This analysis supported the formation of **1.43** and the trapping of the ammonia-borane as a *bis* σ -(B–H) aminoborane complex. A further study into the nature of the bonding within these complexes was published. The work concluded that the back-donation from the metal d(π)-orbital to the vacant atomic orbital of boron helped to stabilise these complexes.⁵² The importance of the vacant σ^* -(Ru–H) orbital *trans* to the σ -(B–H) orbital was also highlighted, however, as aiding this σ -(B–H) orbital donation into the empty d-orbital of the metal.



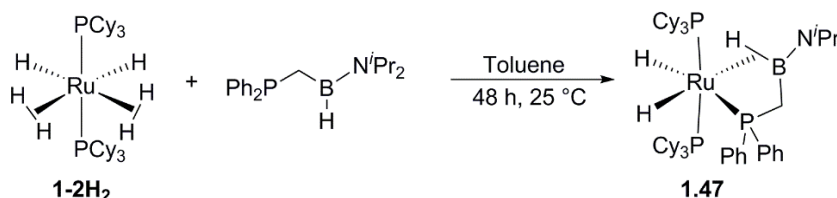
Scheme 1.18. Formation of bis σ -(B-H) aminoborane ruthenium complex

The investigation of CO₂ reduction with HBpin mediated by **1-2H₂** by Sabo-Etienne *et al.* led them to look into the active species involved in these reactions (Scheme 1.15 – Top).^{33,53} At the end of the catalytic runs of the reaction, four ruthenium species were identified by multinuclear NMR spectroscopy as complexes **1.14**, **1.16**, **1.17** and **1.18** in addition to a fifth species identified as [RuH{(μ²-H)₂Bpin}(CO)(PCy₃)₂] (**1.46**). Complex **1.46** was also independently synthesised from the reaction of HBpin with [Ru(H)₂(η²-H₂)(CO)(PCy₃)₂] (**5-H₂**) in pentane at 25 °C. Complex **1.46** demonstrated 3 resonances at 298 K in the ¹H NMR spectrum at δ_H = –6.88, –8.67, and –10.04 ppm, all observed as broad singlets due to the fast chemical exchange process of all the Ru–H protons. Both complexes **1.17** and **1.46** were also found to be catalytically competent in the reduction of CO₂ with HBpin (Scheme 1.19 – Bottom).



Scheme 1.19. (Top) Reduction of CO₂. (Bottom) Stoichiometric experiment with complex **1.17** and **1.46**.

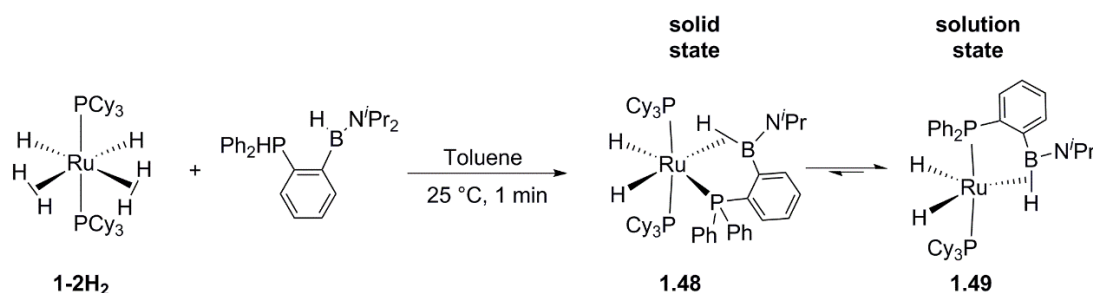
The scope of coordination of organoboranes to **1-2H₂** was extended to phosphino(amino)borane ligands resulting in a number of new complexes with agostic B–H interactions with the ruthenium centre.^{54–56} Synthesis of the specialised bidentate phosphinomethyl(amino)borane ligand allowed for isolation of the first δ -agostic ruthenium complex containing an η^2 -B–H bond, **1.47** (Scheme 1.20).⁵⁴ This ruthenium complex was fully characterised by multinuclear 1-D and 2-D NMR spectroscopy and X-ray crystallography. ¹H NMR spectrum of **1.47** demonstrated 3 peaks for the Ru–H environments in 1:1:1 ratio at $\delta_{\text{H}} = -7.29$ (br s), -11.52 (tdd, $J_{\text{HP}} = 70.6$ and 30.9 Hz, $J_{\text{HH}} = 8.5$ Hz) and -18.38 ppm (br, $J_{\text{HP}} = 25.1$ and 9.8 Hz, $J_{\text{HH}} = 8.5$ Hz) with the signal at $\delta_{\text{H}} = -7.29$ ppm sharpening after boron decoupling. The bond length of the agostic Ru–H bond was determined as $1.92(7)$ Å, which was longer than normal Ru– σ -(B–H) bonds mentioned thus far (*vide supra*). The Ru---B distance was determined as 2.7574 Å which was greater than the sum of single bond radii of Ru and B⁴⁶, and the bond angle of B–C–P was determined to be $103.2(4)^\circ$, all this data pointed towards an agostic B–H interaction. DFT calculations were performed to confirm the geometry of the isomer isolated by X-ray crystallography and was confirmed as the favoured geometry with the two phosphines *trans* to each other. NBO calculations corroborated with the description of the complex as d⁶ Ru(II) centre whereby the most significant interaction of the agostic B–H bond was between the Ru and H atoms. Differing to previous NBO calculations for these sigma ruthenium borane complexes, the investigation notes that no significant stabilisation energy from the back-donation of the filled d-orbital of Ru into the B (LP*) orbital was observed but rather donation from the lone pair of the nitrogen to the B (LP*) orbital was the main stabilisation – which was also present in the free ligand.



Scheme 1.20. Reaction of **1-2H₂** with phosphinomethyl(amino)borane

Changing the spacer of the phosphino(amino)borane ligand from CH₂ to C₆H₄ and repeating the reaction gave rise to complexes **1.48** in the solid state and **1.49** in the solution.⁵⁵ This suggested that the dissociation of the PCy₃ in solution state was favoured to generate the 16 electron ruthenium species **1.49** and therefore simply changing the linker of these phosphino(amino)borane ligands can indirectly tune the degree of B–H activation. The solution state ¹H NMR spectrum for complex **1.49** demonstrated three resonances for the Ru–H environments at $\delta = -6.41$ (br, $J_{\text{PH}} = 5.0$ Hz), -12.67 (ddd, $J_{\text{PH}} = 22.5$ and 20.0 Hz, $J_{\text{HH}} = 5.0$ Hz) and -25.69 (br) ppm with the peak at $\delta = -6.41$ ppm sharpening upon boron decoupling. Single crystals of **1.48** were isolated for X-ray crystallography and B–H bond distance of $1.79(3)$ Å and Ru---B distance of $2.503(3)$ Å were determined which again pointed towards the

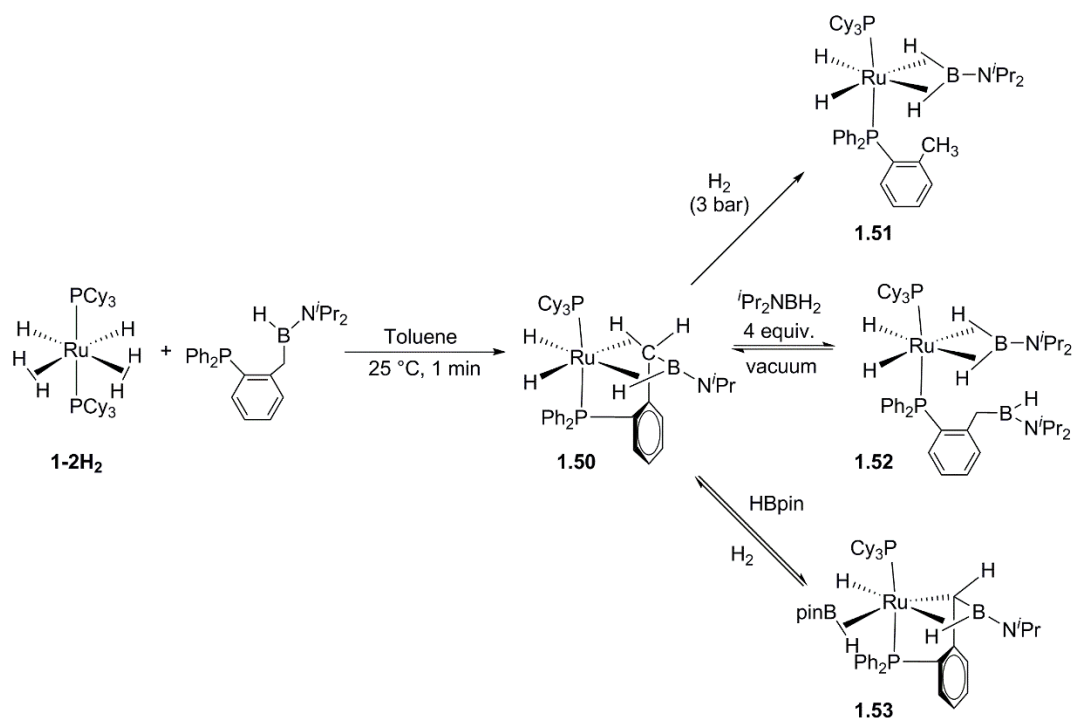
formation of an agostic B–H interaction. Importantly, solid state NMR spectroscopy was used to scrutinise complex **1.48** to corroborate the information ascertained *via* solution NMR spectroscopic data as complex **1.48** was found as a minor component in solution.



Scheme 1.21. Reaction of **1-2H₂** with (*o*-phosphinophenyl)(amino)borane

The reaction of the phosphino(amino)borane ligand *o*-Ph₂PC₆H₄CH₂BH(*i*Pr)₂ with **1-2H₂** generated a new complex bearing both agostic C–H and B–H bonds, **1.50** (Scheme 1.22).⁵⁶ This complex was characterised by multinuclear 1-D and 2-D NMR spectroscopy and also X-ray crystallography to confirm its structure. At 25 °C the Ru–H peak in ¹H NMR spectrum was not assigned due to broadening of the signal into the baseline of the spectrum but at 183 K four broad peaks were observed at $\delta_{\text{H}} = -1.00, -6.71, -8.58$ and -13.22 ppm with the peak at $\delta = -6.71$ ppm sharpening upon boron decoupling. The peak at $\delta_{\text{H}} = -1.00$ ppm at 213 K was resolved into a doublet with coupling constant measured as $J_{\text{HH}} = 15.0$ Hz which indicated this resonance was the agostic C–H environment. In addition, a sample in which the benzylic carbon was enriched in ¹³C was synthesised in order to confirm the assignments by ¹³C NMR spectroscopy. From the X-ray crystallographic data, the B–H bond length was determined to be 1.24(3) Å, significantly shorter than the previous two agostic B–H complexes **1.47** and **1.48**, but still within the range of an agostic B–H bond. The Ru---B interaction was measured to be 2.173(3) Å which again was shorter than the length determined for complex **1.47** and **1.48**. Further reactivity of complex **1.50** was investigated.

The reaction of complex **1.50** with HBpin (resulting in cleavage of the agostic C–H bond), with excess ⁱPrNBH₂ (resulting in ligand exchange to form new *bis* σ -(B–H) bonds) and with 3 bar H₂ (resulting in B–C cleavage and reduction) yielded complexes **1.51**, **1.52** and **1.53** respectively (Scheme 1.22). The observed reactivity of complex **1.50** with HBpin, ⁱPrNBH₂ and H₂ corroborated that weak agostic B–H and C–H interactions were present in complex **1.50**. DFT calculations were performed on complex **1.50** to confirm the X-ray crystallography assignment and geometry. In addition, NBO calculations revealed the stabilising interactions within complex **1.50** was found from donation of the filled σ -(B–H) and σ -(C–H) orbitals into the empty d-orbital of ruthenium but also that the back-donation could come from a number of filled d-orbitals of ruthenium into both the σ^* -(B–H) and σ^* -(C–H) orbitals *and* the B (LP*) as seen in previous σ -borane complexes (*vide supra*).

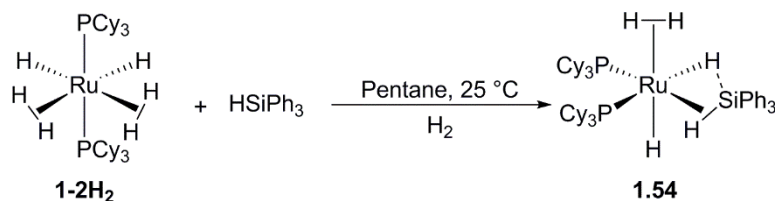


Scheme 1.22. Formation of bis(agostic)phosphinobenzyl(amino)borane ruthenium complexes

1.1.1.2 E = Silicon

The coordination of σ -(Si-H) bonds to ruthenium complexes related to **1-2H₂** has been well explored by Chaudret and Sabo-Etienne. In 1994, they published the reaction of **1-2H₂** with HSiPh₃ to form complex **1.54** (Scheme 1.23).⁵⁷ A single broad peak was detected for all five hydrides in the ¹H NMR spectrum, even at low temperature (173 K). The X-ray crystal structure was obtained and published in a follow-up paper.⁵⁸ These data confirmed the assignment of the complex as a σ -silane complex with the dihydrogen ligand possessing an unstretched bond determined as 0.82(2) Å. The original assignment of the structure had *trans* PCy₃ groups, however the X-ray data showed the *cis*-disposed PCy₃ ligands where P-Ru-P bond angle was 109.71(5) °. The bending of the phosphine ligands into this *cis* geometry was attributed to the bulky phenyl groups on the silicon. The σ -(Si-H) bond length was measured to be (1.54(4) Å), in addition the corresponding Si---H_{eq} bond length was measured as (1.83(3) Å). This Si---H_{eq} bond length was within the limit of a σ -(Si-H) bond (being 2 Å) and hence this complex was characterised as containing a *bis* σ -(Si-H) moiety. It was postulated that this favourable interaction helped to stabilise the *cis*-PCy₃ geometry of the complex. DFT calculations were performed to interrogate the nature of the Si---H interaction within complex **1.54** and two Si---H interactions from the two terminal hydrides were located helping to stabilise the complex by 1.9 kcal mol⁻¹. The secondary interactions between silicon and hydrogen atoms (SISHA) were found to be important in the exchange process of the hydrogens in these ruthenium σ -silane complexes.^{59,60} The silane ligand in complex **1.54** was proposed to be weakly bound based on the spectroscopic data. The

experimental reactivity was consistent with this hypothesis and when complex **1.54** was placed under an atmosphere of H₂ or N₂ the silane was eliminated to reform **1-2H₂** and **1** respectively.



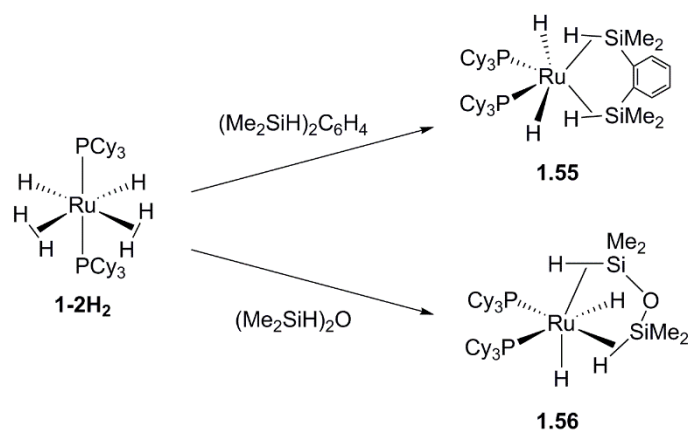
Scheme 1.23. Formation of σ -(Si-H) ruthenium complex with HSiPh₃

Prior to isolation of the complex **1.54**, Chaudret *et al.* were able to obtain crystal structures of two similar complexes from the reaction of **1-2H₂** with *bis*(silane) compounds to generate complexes **1.55** and **1.56** (Scheme 1.24).⁶¹ In this investigation, the use of a *bis*(silane) helped to force the phosphine ligands to adopt the *cis* conformation once the silane was ligated to the ruthenium centre. In addition to the X-ray crystallography data, the two new *bis* σ -(Si-H) ruthenium complexes were characterised by elemental analysis, multinuclear NMR and IR spectroscopy.

For complex **1.55** two resonances in the ¹H NMR spectrum at 296 K were observed for the 4 hydrides at $\delta_{\text{H}} = -7.74$ (t, $J_{\text{HP}} = 13$ Hz) and -12.03 ppm (m) for the σ -(Si-H) and Ru-H protons respectively. A resonance at $\delta_{\text{Si}} = 4.8$ ppm (d, $J_{\text{HSi}} = 63$ Hz) was observed in ²⁹Si{³¹P} INEPT ¹H spectrum at 288 K. The ¹J_{Si-H} coupling was within the known range of values for σ -(Si-H) bonds (20 – 140 Hz)^{62–67}. In addition, only one resonance was observed at 296 K in ³¹P{¹H} NMR spectrum at $\delta_{\text{P}} = 51.0$ ppm and with no further decoalescence of this resonance at lower temperatures. The multinuclear NMR data would agree with assignment of **1.55** as being a highly symmetric complex (Scheme 1.25). Further to the NMR spectroscopy data, the lengthening of the Si-H bonds (1.88(3) and 1.83(3) Å) coupled with the IR resonance at 1778 cm⁻¹ for Ru- σ -(Si-H) all pointed towards the formation of a *bis*(σ -silane) complex.

For complex **1.56** (Scheme 1.24) only one broad resonance was observed in the ¹H NMR spectrum at 296 K at $\delta_{\text{H}} = -9.40$ ppm which decoalesced into two resonances of the same intensity upon cooling to 253 K at $\delta_{\text{H}} = -8.50$ and -9.90 ppm. A second decoalescence process was observed at 178 K to reveal 4 broad peaks of equal intensity at $\delta = -8.10$, -8.50 , -9.40 and -10.20 ppm. The ²⁹Si{³¹P} INEPT ¹H spectrum of **1.56** displayed a single resonance at $\delta_{\text{Si}} = -5.7$ ppm (d, $J_{\text{HSi}} = 22$ Hz) with the J-coupling at the lower end of the spectrum for σ -Si-H bonds complex and lower than the J-coupling value measured for complex **1.55**. In the ³¹P{¹H} NMR spectrum at 25 °C, complex **1.56** displayed one signal at $\delta_{\text{P}} = 49.9$ ppm which decoalesced into two peaks $\delta_{\text{P}} = 53.2$ and 52.7 ppm at 173 K. This indicated that there were two chemically and magnetically inequivalent PCy₃ ligands in complex **1.56**.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of both complexes **1.55** and **1.56** suggested that two different isomers of these *bis* σ -(Si-H) complexes existed depending on the linker group of the *bis*(silane) compound. Further comparison of the spectroscopic data between complex **1.55** and **1.56** (**1.56**, $\nu_{\text{Ru}-\sigma(\text{SiH})} = 1699\text{ cm}^{-1}$) indicated a weaker coordination of the silane in **1.56** relative to **1.55**. This weaker coordination of the siloxane in **1.56** was further demonstrated by the reactions of **1.56** with H_2 , CO or $^t\text{BuNC}$ displacing the siloxane to generate the corresponding ruthenium complexes: **1-2H₂**, $[\text{Ru}(\text{H})_2(\text{CO})_2(\text{PCy}_3)_2]$ or $[\text{Ru}(\text{H})_2(^t\text{BuCN})_2(\text{PCy}_3)_2]$ respectively whereas no further reactivity was reported for complex **1.55**.

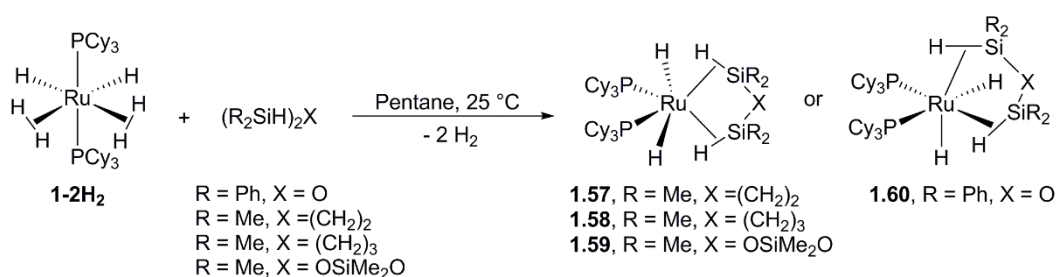


Scheme 1.24. Reaction of **1-2H₂** with *bis*(silane) compounds

A follow-up paper was published in which a number of additional *bis* σ -(Si-H) complexes were prepared, isolated and characterised.⁶⁸ This series showed similar structural motifs with familiar bonding metrics and spectroscopic data (Scheme 1.25). Comparison between the linker groups allowed for investigation of this variable on the structure and bonding at ruthenium. When the linker group was only one atom long *i.e.* X = O (complex **1.56** and **1.60**) DFT calculations pointed towards a geometry with a low symmetry due to the constraints imposed by the shorter linker backbone of the *bis*(silane) and therefore rationalised the two signals observed in $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 173 K for complex **1.56**. This constraint also explained the greater reactivity shown by complexes **1.56** and **1.60** in comparison to **1.55** and **1.57 – 1.59** due to the weaker σ -silane bonds in **1.56** and **1.60** from this unfavourable geometry. DFT calculations were performed on both isomers of the ruthenium *bis*(silane) complexes to confirm that the favoured geometries did not change from the geometries obtained from the solid state data.

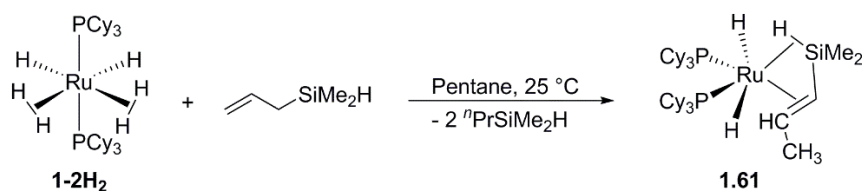
Interest into which factors affect the degree of activation of the σ -(Si-H) bond led to an investigation on how changing the steric of the phosphine ligands from PCy₃ to PPh₃ altered the structure and bonding of these *bis* σ -(Si-H) complexes. This change resulted in minimal deviation from

the geometries of the complexes and minimal changes to the J-coupling values of the Si–H bond. Furthermore, changing the electronic properties of the phosphine from PPh₃ to Ppyl₃ (pyl = tripyrrolylphosphine), which has the same cone angle as PPh₃ but is a stronger π -acceptor,⁶⁹ also resulted in minimal changes to geometries and the J-coupling values. The motivation behind this research was to find any linear correlation between the degree of activation of the Si–H bond and the measurable structural properties of the complex. The various data collected from the analysis of these complexes (J_{HSi} values, $\nu_{\text{Ru-H}}$ stretches, Si–H and Ru–H bond distances and Ru– σ -(Si–H) bond angles) however led to the conclusion that there was no correlation to be drawn – which in itself was an important conclusion.



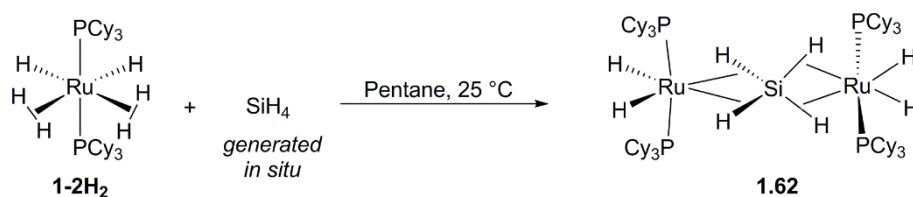
Scheme 1.25 Formation of bis σ -(Si–H) ruthenium complexes

Besides isolation of silane σ -complexes having some combination of σ -(Si–H) and η^2 -(H–H) bond motifs, Chaudret *et al.* have also isolated a ruthenium complex with both σ -(Si–H) and η^2 -(C=C) coordination modes.⁷⁰ Previous studies have already shown the reactivity of **1-2H₂** towards alkenes and arenes (*vide supra*) and the ability to form η^2 -bonding modes with these unsaturated bonds. Extending this reactivity, the reaction of **1-2H₂** with allyldimethylsilane in pentane resulted in formation of complex **1.61** (Scheme 1.26).⁷⁰ The reaction was monitored by ¹H NMR spectroscopy which showed the formation of ⁿPrSiMe₂H as a by-product from the transfer hydrogenation of the substrate along with concomitant isomerisation of allyldimethylsilane to dimethyl(prop-1-enyl)silane, as confirmed by the X-ray crystal structure of **1.61**. Again, the double binding site of the same substrate forced the *cis*-PCy₃ geometry of the complex. Complex **1.61** demonstrated three signals in the upfield region in the ¹H NMR spectrum at 296 K at $\delta_{\text{H}} = -8.77, -9.46$ and -12.46 ppm for the σ -(Si–H) and the two Ru–H environments respectively. In the ³¹P{¹H} NMR spectrum at 253 K, two resonances were observed at $\delta_{\text{P}} = 69.1$ and 63.7 ppm for the two chemically and magnetically inequivalent phosphine environments. ²⁹Si{³¹P} INEPT ¹H NMR spectrum displayed a resonance at $\delta_{\text{Si}} = -11.3$ ppm (d, $J_{\text{HSi}} = 105$ Hz) with the coupling constant falling within the range of σ -(Si–H) bonds (*vide supra*). The Si–H bond length in **1.62** was determined as 1.59(8) Å which was slightly longer than the free silane complex, and in conjunction with the IR resonance at 1945 cm⁻¹ for Ru– σ -(Si–H), pointed towards a weakly coordinated σ -silane complex. This weak coordination was exemplified by the reaction of **1.61** with H₂, CO or C₂H₄ forming **1-2H₂**, [Ru(H)₂(CO)₂(PCy₃)₂] or **1.3** respectively.



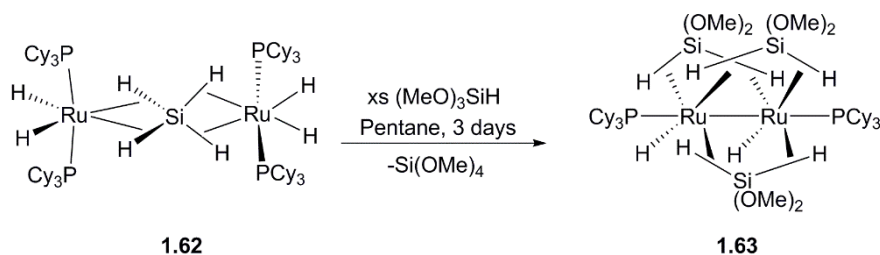
Scheme 1.26. Formation of $\sigma(\text{Si-H})$ and $\eta^2\text{-(C=C)}$ ruthenium complex

The reaction of **1-2H₂** with SiH₄, the simplest of silanes, led to the unexpected formation of a new complex (**1.62**) that was described as SiH₄ trapped by two ruthenium units (Scheme 1.27).⁷¹ Due to the hazardous pyrophoric nature of SiH₄, this silane was generated *in-situ* from the redistribution of PhMeSiH₂ catalysed by the **1-2H₂**. The formation of complex **1.54**, Ph₂MeSiH and PhMe₂Si were also observed in this redistribution reaction. The redistribution of alkoxyhydrosilane is known to be catalysed by titanium, zirconium and hafnium complexes.^{72–74} Complex **1.62** demonstrated a pseudo triplet in the ¹H NMR spectrum at $\delta_{\text{H}} = -7.89$ ppm, with satellites observed due to silicon coupling ($J_{\text{HSi}} = 36$ Hz). Cooling the sample, the triplet decoalesced into two broad signals at $\delta_{\text{H}} = -6.00$ and -8.60 ppm for the Si–H and Ru–H environments respectively. The ²⁹Si{¹H} NMR spectrum showed a highly downfield signal at $\delta_{\text{Si}} = 290.2$ ppm with the corresponding ²⁹Si INEPT spectrum showing a nonet, in line with coupling to eight hydrogens at 25 °C, all in chemical exchange and in agreement with the assignment of the structure. The analogous [(P^{*i*}Pr)₃]₂(H)₂Ru₂(SiH₄)Ru(H)₂(P^{*i*}Pr)₂] complex was isolated and characterised by multinuclear NMR spectroscopy and X-ray crystallography. The short Ru–Si bond distance (2.1875(4) Å)⁷⁵ and downfield ²⁹Si resonance of [(P^{*i*}Pr)₃]₂(H)₂Ru₂(SiH₄)Ru(H)₂(P^{*i*}Pr)₂] complex indicated a silylene type bonding. DFT was performed to further probe the bonding in both these complexes. NBO analysis indicated that the Ru–Si bonds were highly polar with a bond order smaller than 1. Instead, the molecular orbital analysis would suggest the SiH₄ moiety was interacting with the two ruthenium units through $\sigma(\text{Si-H})$ orbital donation into an empty d-orbital of ruthenium with the concomitant d-orbital back-donation into the vacant $\sigma^*(\text{Si-H})$ orbital from the *other* ruthenium centre. The DFT calculation suggested these interactions were the cause for the short Ru–Si bond distance and no silylene character was actually present within the bonding. Ultimately a new mode of bonding of a silane was discovered in this investigation.



Scheme 1.27. Formation of $[\text{PCy}_3]_2(\text{H})_2\text{Ru}_2(\text{SiH}_4)\text{Ru}(\text{H})_2(\text{PCy}_3)_2$ (**1.62**)

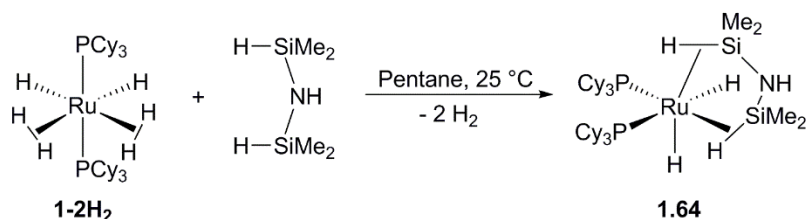
A follow-up paper was published in 2003.⁷⁶ The new bonding mode of the silane in **1.62** was investigated in more detail and further reactivity of this complex explored. The reaction of **1.62** with CO, ^tBuNC and CH₂Cl₂ gave [Ru(H)₂(CO)₂(PCy₃)₂], [Ru(H)₂(^tBuNC)₂(PCy₃)₂]⁶⁸ and [RuH(η^2 -H₂)(Cl)(PCy₃)₂] respectively. In these reactions the fate of the silane was unclear as no free silane was detected by ¹H NMR spectroscopy ($\delta_{\text{H}} = 3.20$ ppm). Chaudret, Sabo-Etienne and co-workers suggested that this highly reactive species was adsorbed onto the glassware surface. It was interesting to note that the reaction of **1.62** with H₂ did not return **1-2H₂**, an indication the silane was strongly bound and will only be displaced by strong π -accepting ligands. Further to these reactions, addition of (MeO)₃SiH to a pentane solution of **1.62** yielded a new product from redistribution of ligands, complex **1.63** (Scheme 1.28). Multinuclear NMR spectroscopy and ultimately X-ray crystallography helped to reveal the identity of this new complex containing six σ -(Si-H) bonds with the usual characteristics associated with σ -silane complexes. DFT calculations performed on this structure helped to locate the hydrides as the crystal data quality did not allow the hydrides to be located from the Fourier transform map. NBO analysis indicated that the bonding description of this structure suggested each Ru centre was ligated by three σ -(Si-H) bonds, a hydride and a phosphine however it was stated that this was only a static picture of the bonding description when the reality involved multiple interactions between all the Ru, Si and H atoms.⁷⁶



Scheme 1.28. Redistribution reaction of **1.62** with (MeO)₃SiH

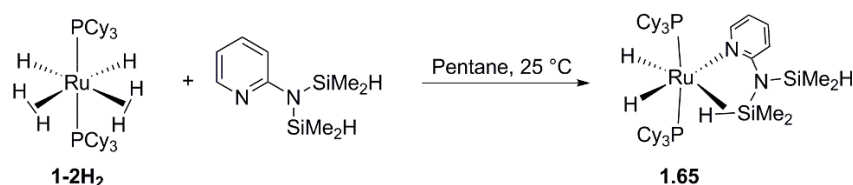
The reactivity of **1-2H₂** with silazane compounds was investigated.⁷⁷ It is of note that disilazane compounds are starting materials for ceramics in organic synthesis^{78,79} and hold the potential for further functionalisation steps to occur at the nitrogen. The first ruthenium disilazane complex was synthesised in 2005 from the reaction of **1-2H₂** with 1,1,3,3-tetramethyldisilazane to form **1.64** (Scheme 1.29). Coordination of the silazane to the ruthenium centre occurred through two σ -(Si-H) bonds and not the nitrogen lone pair. Complex **1.64** was characterised by multinuclear NMR spectroscopy and single crystal X-ray diffraction. The *cis* disposition of the PCy₃ ligands was observed once again due to the dual σ -(Si-H) coordination and the short linker space group of the disilazane ligand. In the ¹H NMR spectrum at 298 K, one broad resonance was observed at $\delta_{\text{H}} = -9.80$ ppm integrating into four hydrogens for the Ru-H environments. This signal decoalesced at 273 K to give two resonances at $\delta_{\text{H}} = -8.72$ (br s) and -10.39 (t, $J_{\text{HP}} = 40$ Hz) ppm respectively which underwent a further decoalescence process at

213 K to give four broad resonances at $\delta_{\text{H}} = -8.36, -8.62, -9.93$ and -10.76 ppm. In $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 298 K, one resonance was observed at $\delta_{\text{P}} = 53.5$ ppm which decoalesced at 213 K into two signals at $\delta_{\text{P}} = 52.3$ and 50.5 ppm – similar to the constrained geometry observed for the ruthenium *bis*(siloxane) complexes **1.56** and **1.60**. The Si–H bond lengths were determined as 1.91(5) and 1.93(5). The Ru–Si bond lengths were determined as 2.395(2) and 2.434(2) Å which were within the upper range of reported σ -silane complexes. The short distance between the silicon atom and terminal Ru–H suggested SISHA were present and helped to stabilise the complex.



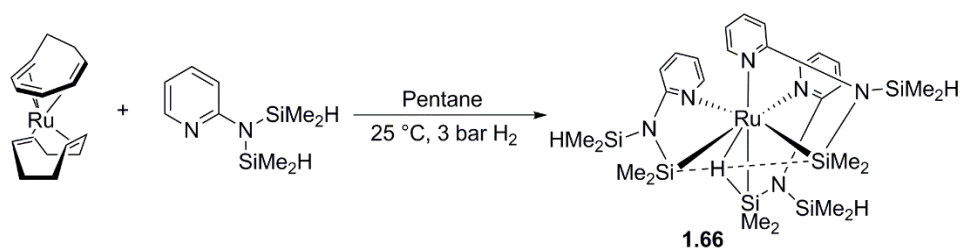
Scheme 1.29. Reaction of **1-2H₂** with 1,1,3,3-tetramethylsilazane

Reacting 2-pyridinetetramethylsilazane with **1-2H₂** led to a new complex with potential coordination of the silazane to the ruthenium centre at three different ligand sites: the nitrogen atom of the pyridine group, the nitrogen atom of the spacer group and also the silane bonds. The product of the reaction was identified as loss of two dihydrogen ligands from **1-2H₂** with complexation of the substrate to form complex **1.65** (Scheme 1.30).⁸⁰ The ^{29}Si – ^1H HMBC NMR spectrum confirmed the presence of two different silicon environments for complex **1.65** at $\delta_{\text{Si}} = -14.50$ ppm for the dangling SiMe_2H group and $\delta_{\text{Si}} = 56.9$ ppm for the σ -(Si–H) bond. Upon cooling the sample **1.65** to 223 K, three resonances were observed in ^1H NMR spectrum at $\delta_{\text{H}} = -3.79$ (t, $J_{\text{HP}} = 27.2$ Hz), -10.70 (m, $J_{\text{HP}} = 9.5$ Hz and $J_{\text{HH}} = 9.5$ Hz) and -13.55 (dt, $J_{\text{HP}} = 21.5$ Hz and $J_{\text{HH}} = 9.5$ Hz) ppm respectively. Ultimately, X-ray diffraction helped to confirm the identity of the ruthenium silazane complex with the σ -silane bond motif and coordination at the nitrogen atom of the pyridine group. Comparison of the Si–H bonds within the molecule provided a clear picture of the stretched σ -(Si–H) bond (1.63(4) Å) *versus* the dangling free Si–H bond (1.44(5) Å). DFT calculations were performed to confirm the geometry obtained by X-ray crystallography. Alternative modes of binding *i.e.* a *bis* σ -(Si–H) or through both nitrogen were investigated computationally, however both bonding scenarios were higher in energy than the configuration from the crystal structure. Vibrations recorded by IR spectroscopy also confirmed the geometry and binding of the complex with a broad band at 1897 cm^{-1} attributed to the mixing of the Ru–H and Ru–Si–H stretches whereas two stretches found at higher wavenumbers 1987 and 2191 cm^{-1} were assigned to the free Si–H stretch.



Scheme 1.30. Reaction of **1-2H₂** with 2-pyridinetetramethylsilazane

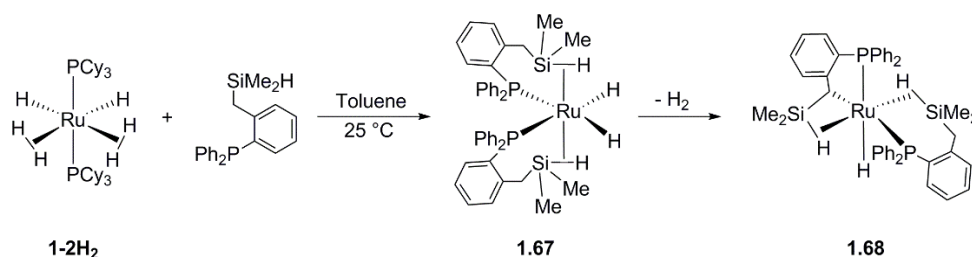
Alternatively, when $[\text{Ru}(\eta^4\text{-1,5-COD})(\eta^6\text{-1,3,5-COT})]$ was reacted with 2-pyridinetetramethylsilazane under an atmosphere of dihydrogen (3 bar) a ruthenium(IV) hydridotrisilyl complex was formed, **1.66** (Scheme 1.31). Reaction with $[\text{Ru}(\eta^4\text{-1,5-COD})(\eta^6\text{-1,3,5-COT})]$, which is the precursor to form **1-2H₂**, was initially undertaken to see if the same ruthenium silazane complex (**1.65**) could be formed in a shorter number of steps. Instead of the target compound, oxidative addition of two Si–H bonds to ruthenium was observed with loss of H₂ to form **1.66**. In the ¹H NMR spectrum complex **1.66** was characterised by one resonance at $\delta_{\text{H}} = -13.63$ ppm with silicon satellites flanking the resonance. ¹H NMR spectroscopic data pointed toward a structure with three pyridines, three SiMe₂H, three SiMe₂ fragments and one Ru–H environment. X-ray and neutron diffraction data were obtained for this ruthenium hydridosilyl complex to confirm the identity of this complex but also importantly the location of the single hydride ligand. The Ru–H bond lengths obtained through both diffraction techniques (1.41(5) Å by X-ray and 1.559(7) Å by neutron) and DFT calculations (1.557) Å were compared with good agreement between all 3 data sets. The presence of SISHA were once again suggested by the short Si---H lengths obtained. Ultimately, the combined spectroscopic and DFT data unambiguously indicated a Ru(IV) complex was formed.



Scheme 1.31. Reaction of $[\text{Ru}(\eta^4\text{-1,5-COD})(\eta^6\text{-1,3,5-COT})]$ with 2-pyridinetetramethylsilazane

The precedent of phosphino(amino)borane ligands synthesised by Sabo-Etienne *et al.* to form agostic B–H interactions with **1-2H₂** (*vide supra*) led the same authors to react phosphinobenzylsilane with **1-2H₂** to investigate if similar coordination modes could be achieved.⁸¹ The reaction of **1-2H₂** and phosphinobenzylsilane generated complex **1.67** from the loss of the two dihydrogen ligand and substitution of the two PCy₃ ligands with concomitant coordination of the phosphinobenzylsilane and the formation of two agostic Si–H interactions (Scheme 1.32). At 298 K, the ¹H NMR spectrum of **1.67**

demonstrated one broad signal at $\delta_{\text{H}} = -7.80$ ppm which decoalesced at 273 K into two broad signals of equal intensity at $\delta_{\text{H}} = -5.20$ and -10.40 ppm for the agostic Si–H and Ru–H environments respectively. Complex **1.67** demonstrated one resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at all temperatures at $\delta_{\text{P}} = 39.2$ ppm that was assigned to the chemically and magnetically equivalent phosphine environments and suggested a highly symmetrical complex. In the ^{29}Si NMR spectrum a single resonance was observed at $\delta_{\text{Si}} = 8.3$ ppm with small J_{HSi} coupling of 28 and 15 Hz for the agostic and terminal hydrides respectively. No X-ray data of complex **1.67** was available however based on the spectroscopic data and similarities with the reactions of **1-2H₂** with bis(silane) compounds (Scheme 1.25), a similar structure was proposed for complex **1.67** (Scheme 1.32). DFT calculations were employed to confirm that the favoured geometry of complex **1.67** involved the phosphines being in the equatorial position and *cis* to each other. Two alternative isomers of this ruthenium agostic Si–H complex were optimised and were both higher in energy by +0.7 and +8.0 kcal mol⁻¹.⁸¹

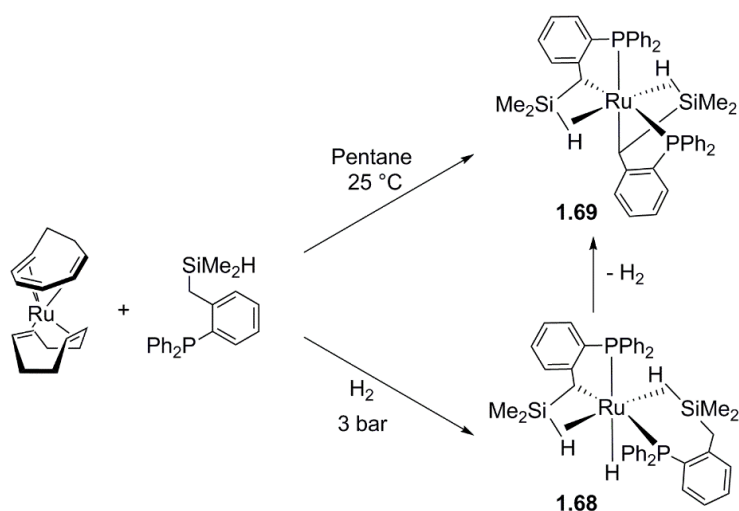


Scheme 1.32. Reaction **1-2H₂** with phosphinobenzylsilane

Repeating the reaction using $[\text{Ru}(\eta^4\text{-1,5-COD})(\eta^6\text{-1,3,5-COT})]$ in place of **1-2H₂** resulted in formation of complex **1.69** through C–H activation of the methylene groups of the phosphinobenzylsilane ligand (Scheme 1.33). Complex **1.69** was characterised by multinuclear NMR spectroscopy and X-ray crystallography. The agostic Si–H bonds were determined to be *ca.* 1.70 Å – typical of σ -(Si–H) bonds. In the ^1H NMR spectrum a resonance at $\delta_{\text{H}} = -9.80$ ppm (t, $J_{\text{HP}} = 9$ Hz) was observed for the equivalent σ -(Si–H) environments with satellites flanking this resonance due to Si coupling ($J_{\text{HSi}} = 67$ Hz). The Ru–CH resonance was found as a broad singlet at $\delta_{\text{H}} = 2.20$ ppm in ^1H NMR spectrum with the corresponding signal for the Ru–C carbon found in $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shielded at $\delta_{\text{C}} = 24.8$ ppm.

Reacting $[\text{Ru}(\eta^4\text{-1,5-COD})(\eta^6\text{-1,3,5-COT})]$ with the phosphinobenzylsilane under dihydrogen (3 bar) formed intermediate **1.68** which was identified *in-situ* by multinuclear NMR spectroscopy with two resonances in the ^{29}Si NMR spectrum at $\delta_{\text{Si}} = 11.0$ and -13.0 ppm for the non-metallated and carbometallated ligands respectively. Intermediate **1.68** displayed two resonances in $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at $\delta_{\text{P}} = 56.5$ (d, $J_{\text{PP}} = 21$ Hz) and 42.7 (d, $J_{\text{PP}} = 21$ Hz) ppm for the non-equivalent phosphine environments. In addition, in the ^1H NMR spectrum three resonances were seen at $\delta_{\text{H}} = -6.00$ ($J_{\text{HSi}} = 76$

Hz), -8.00 ($J_{HP} = 21$ and 27 Hz) and -9.40 ($J_{HP} = 24$ and 54 Hz) ppm. The value of the J_{HSi} coupling was in good agreement that a σ -(Si–H) bond was found within the complex and DFT calculations supported the proposed structure of this intermediate. This intermediate was also observed during the formulation of **1.67** and over time loss of H_2 and C–H activation of one of the methylene groups led to the formation of **1.68** (Scheme 1.32). Intermediate **1.68** was unstable and formation of **1.69** was observed in the reaction mixture after a period of time. Intermediate **1.68** was postulated to undergo a further loss of H_2 from a second C–H activation of the remaining methylene group to form complex **1.69**. This investigation demonstrated that silicon containing ligands can form rare ϵ -agostic Si–H interactions with ruthenium complexes.



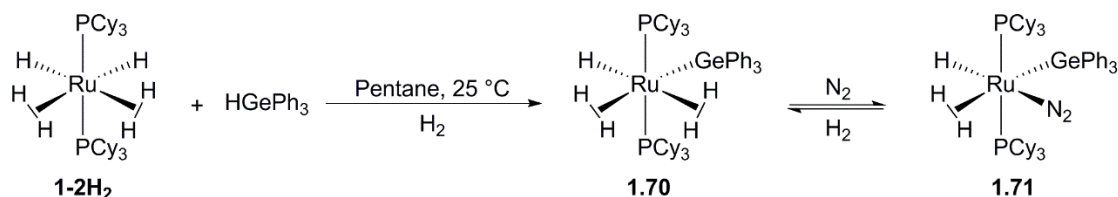
Scheme 1.33. Reaction of $[Ru(\eta^4\text{-}1,5\text{-COD})(\eta^4\text{-}1,3,5\text{-COT})]$ with phosphinobenzylsilane

1.1.1.3 E = Germanium

Reactivity of **1-2H₂** with germanes have been much less studied extensively however the introduction of germanium into compounds is highly desirable due to their applications in electronic and optical devices.⁸² The reaction of **1-2H₂** with $HGePh_3$ resulted in the formation of **1.70** (Scheme 1.34).⁵⁷ At 173 K, complex **1.70** demonstrated a resonance in ^1H NMR spectrum at $\delta_H = -3.50$ and -8.40 ppm for the one σ -(Ge–H) and remaining four hydride signals respectively. In addition, the $T_1(\text{min})$ for the Ru–H resonance was measured as 17 ms at 263 K. No X-ray crystal structure was obtained for complex **1.70** however the geometry of **1.70** was also anticipated to be the same as the silane analogue of this complex (**1.54**, Scheme 1.23) which was originally assigned as a *trans* complex.⁵⁷ However, we now know from the X-ray structure of **1.54** that the solid state data of complex **1.54** showed *cis*-disposed PCy_3 ligands.⁵⁸

Exposing complex **1.70** to an atmosphere of N_2 resulted in the formation of the analogous dinitrogen complex **1.71** from the substitution of one dihydrogen ligand with one dinitrogen ligand.

PCy₃



Scheme 1.34. Reaction of 1-2H₂ with HGePh₃

A follow-up paper was published in 2003 to probe the bonding within complex **1.70**.⁸³ Based on the reaction of **1.70** with N₂, it was investigated whether it was correct to assume a σ -germane complex was formed without unambiguous evidence and only inference of the geometry of complex **1.70** through association with the analogous σ -silane complex **1.54** (Scheme 1.23). DFT methods were used to calculate the most favourable isomer of complex **1.70** and **1.71**, *cis* or *trans* disposition of PCy₃ but also whether complete oxidative addition of the Ge–H bond or whether formation of a σ -(Ge–H) moiety occurred in the reaction. GeH₄ and [Ru(H)₂(η^2 -H₂)(PH₃)₂] were used in the calculation modelling of the reaction (Figure 1.5).

Differing to the σ -silane complex **1.54** the most favourable geometry for the model of complex **1.70** was the *trans*-disposition of the phosphine but also the complete oxidative addition of the Ge–H bond (Figure 1.5). However, the *cis*-isomer with oxidative addition of Ge–H bond was only 2.1 kcal mol⁻¹ higher in energy and the corresponding *cis*-isomer with a σ -(Ge–H) moiety was only 2.0 kcal mol⁻¹ higher in energy. The same outcome was calculated for the model of complex **1.71**, but again, the *cis*-isomer with oxidative addition of Ge–H bond was only 2.0 kcal mol⁻¹ higher in energy and the corresponding *cis*-isomer with a σ -(Ge–H) moiety was only 1.7 kcal mol⁻¹ higher in energy. The *caveat* of this conclusion was that simplified models of the system was used and different substituents on germanium and phosphine could influence which isomer was the more favourable geometry. In addition, based on the experimental data it was not clear if only one dihydrogen ligand was replaced by dinitrogen or whether both were displaced to form a *bis*(dinitrogen) species [Ru(H)(GePh₃)(N₂)₂(PCy₃)₂]. The formation of this complex was not proposed but cannot be dismissed based on the facile exchange between dihydrogen and dinitrogen ligands.

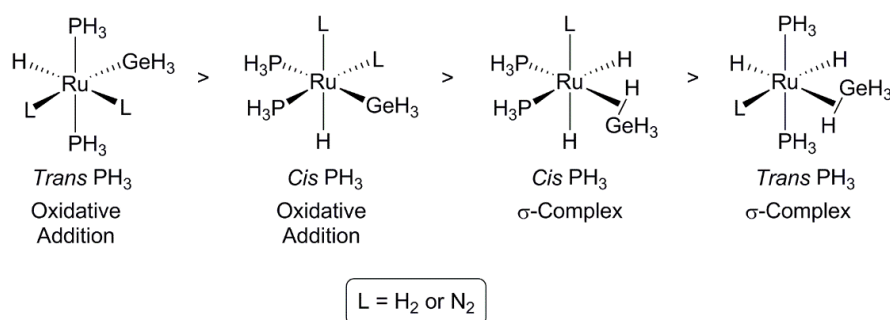
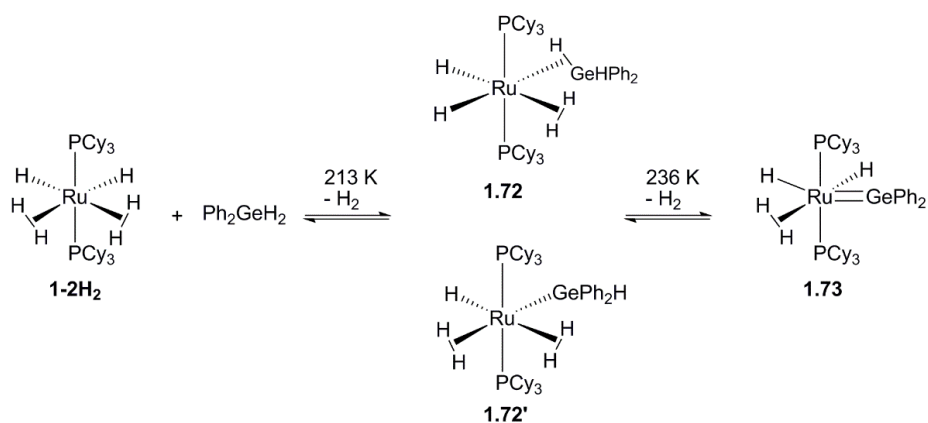


Figure 1.5. Order of the calculated most favourable geometry of model complexes **1.70** and **1.71**

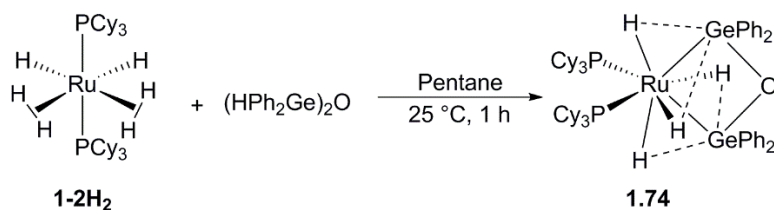
In 2015, Sabo-Etienne *et al.* reported the formation of a ruthenium dihydrogen germylene complex (**1.73**) from the reaction of **1-2H₂** with Ph₂GeH₂ (Scheme 1.35).⁸⁴ At 236 K, complex **1.73** was characterised by ¹H NMR spectroscopy demonstrating a resonance at $\delta_{\text{H}} = -7.67$ (t, $J_{\text{HP}} = 14.0$ Hz) for all the hydrides. No decoalescence of this signal was observed at lower temperatures however a $T_1(\text{min})$ value of 55 ms (253 K, 500 MHz) was measured for this resonance, indicative of non-classical hydride behaviour.³² In ³¹P{¹H} NMR spectrum, only one resonance at $\delta_{\text{P}} = 84.5$ ppm was observed for **1.73**, again no decoalescence of this signal was observed at lower temperatures. The formation of this ruthenium dihydrogen germylene complex was confirmed by X-ray crystallography. The H–H bond length was determined to be 1.06(5) Å and at the upper limit for compressed dihydride complexes.⁸⁵ Long Ge---H length (2.53(2) Å) in combination with small Wiberg index value for this interaction (0.09) ruled out any residual interaction between these two atoms and instead, confidence of the presence of the germylene moiety in complex **1.73**.

Following the reaction of **1-2H₂** with Ph₂GeH₂ by multinuclear NMR spectroscopy at 213 K yielded an intermediate postulated as **1.72** or **1.72'** (Scheme 1.35). This intermediate demonstrated resonances in ¹H NMR spectrum at $\delta_{\text{H}} = 5.28$ (t, $J_{\text{HP}} = 13.0$ Hz) and -7.88 (s) ppm assigned to the Ge–H proton and remaining five hydrides respectively. A resonance at $\delta_{\text{P}} = 67.4$ ppm in ³¹P{¹H} NMR spectrum was observed for this intermediate. Low temperature NMR spectroscopy failed to decoalesce the resonances in the proton and phosphorous NMR spectra however $T_1(\text{min})$ value of 35 ms (213 K, 500 MHz) was measured to support the assignment of the intermediate containing dihydrogen ligand. Heating the reaction mixture saw the formation of peaks corresponding to **1.73** by multinuclear NMR spectroscopy.



Scheme 1.35. Reaction of **1-2H₂** with Ph_2GeH_2

The formation of a ruthenium digermoxane complex (**1.74**) was also reported from the reaction of **1-2H₂** with $(\text{HPh}_2\text{Ge})_2\text{O}$.⁸⁴ Complex **1.74** was characterised by a resonance at $\delta_{\text{H}} = -7.51$ ppm (t, $J_{\text{HP}} = 8.3$ Hz) for all four hydrides at 25 °C in the ^1H NMR spectrum with the corresponding resonance at $\delta_{\text{P}} = 49.6$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The $T_1(\text{min})$ value for the hydride resonance was determined as 322 ms (273 K, 500 MHz) which was indicative of more classical hydride behaviour.³² X-ray crystallographic data of **1.74** confirmed the structure of this complex with similar geometry as the ruthenium siloxane complexes (**1.56**, Scheme 1.24 and **1.60**, Scheme 1.25). In line with the long $T_1(\text{min})$ time for the hydride resonance, long Ge–H bonds were measured at 2.16(3) – 2.50(6) and short Ru–H bond lengths were determined at 1.57(3) – 1.64(4) Å which suggested the assignment of complex **1.74** as a Ru(IV) complex. On the other hand, DFT calculations supported the presence of σ -(Ge–H) interactions in **1.74** with Wiberg bond index values of 0.16 calculated between the Ge and H atoms which suggested complex **1.74** as a Ru(II) complex. This data was reminiscent of the SISHA present in a number of ruthenium silane complexes (*vide supra*) and therefore the assignment of oxidation state of this complex was unhelpful as the true nature of bonding laid somewhere between the two extreme bonding descriptions.



Scheme 1.36. Formation of a ruthenium digermoxane complex, **1.74**

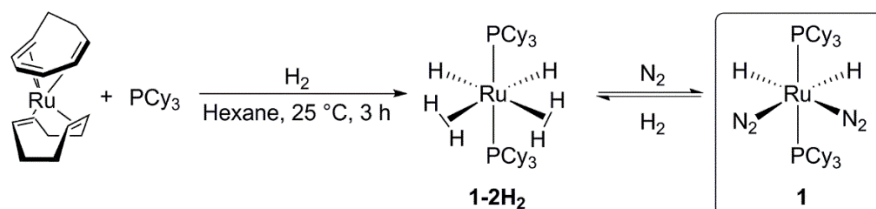
1.3 RESULTS AND DISCUSSIONS

The chemistry of **1-2H₂** has been well explored however the analogous complexes have barely been investigated with the exception of $[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$ due to the greater reactivity demonstrated in reactions (*vide supra*) as a result of the less stable phosphine ligand. The following work presented by this author will look to expand on the existing knowledge into the ruthenium *bis*(dinitrogen) complex, **1**.

1.3.1 Synthesis and reactivity of $[\text{Ru}(\text{H})_2(\text{N}_2)_2(\text{PCy}_3)_2]$ (**1**)

Investigation of the ruthenium *bis*(dinitrogen) complex $[\text{Ru}(\text{H})_2(\text{N}_2)_2(\text{PCy}_3)_2]$ (**1**) was originally hindered by the inability to isolate and store the complex for long periods of time in an argon environment. This has resulted in the reactivity of complex **1**, compared to its *bis*(dihydrogen) analogue, being underexplored.

Slight modification to the original procedure to synthesise **1** as reported by Chaudret *et al.*³¹ was performed. The reduction of $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ with zinc generated $[\text{Ru}(\eta^4\text{-1,5-COD})(\eta^6\text{-1,3,5-COT})]$.⁸⁶ Hydrogen gas was bubbled through a hexane solution of $[\text{Ru}(\eta^4\text{-1,5-COD})(\eta^6\text{-1,3,5-COT})]$ in the presence of 2 equivalents of PCy_3 at 25 °C resulting in the precipitation of **1-2H₂**. Recrystallization of **1-2H₂** in a dinitrogen atmosphere, from hexane, resulted in the gradual conversion of **1-2H₂** to the desired ruthenium *bis*(dinitrogen) complex, **1** as a green/yellow solid (Scheme 1.37). $[\text{Ru}(\text{H})_2(\text{N}_2)_2(\text{PCy}_3)_2]$ was indefinitely stable under a dinitrogen atmosphere at modest temperatures, 25 – 50 °C.



Scheme 1.37. Formation of **1**

The ^1H NMR spectrum of complex **1** was similar to the data reported by Chaudret *et al.*³¹ with a resonance observed at $\delta_{\text{H}} = -12.96$ ppm (br s) for the ruthenium hydride environment and a single resonance observed at $\delta_{\text{P}} = 59.3$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The observed resonances in the IR spectrum were found at $\nu_{\text{Ru-H}} = 1918$ and 1986 cm^{-1} and $\nu_{\text{N}\equiv\text{N}} = 2131$ and 2163 cm^{-1} . Low temperature ^1H NMR spectroscopy failed to sharpen the peaks to observe the coupling between the hydride and phosphines however T_1 measurement was taken (193 K, 400 MHz) with a value of 1.08 s obtained for the hydride resonance and indicative of classical hydride behaviour.³² The combined spectroscopic data would confirm the original assignment of complex **1** as *bis*(dinitrogen) complex with *cis*-disposed

dinitrogen ligands bound in an end on fashion.³¹ The geometry and assignment of complex **1** was unambiguously confirmed with the successful characterisation by X-ray crystallography (Figure 1.6). The Ru–H bond lengths in **1** were determined to be 1.5039(27) and 1.5879(28) Å which were shorter than the Ru–H bond lengths measured for **1-2H₂** (1.708(38) and 1.687(37) Å) except for one of the bond lengths which was within the *esd* error of measurement. The N–N bond lengths of **1** were determined to be 1.104(2) and 1.101(2) Å which was only a subtle lengthening of the N–N bond from free dinitrogen (1.098 Å).⁸⁷ The P–Ru–P bond angle was determined as 154.714(18) ° which was further away from ideal *trans* geometry compared to P–Ru–P bond angle of **1-2H₂** (179.79(11) °).

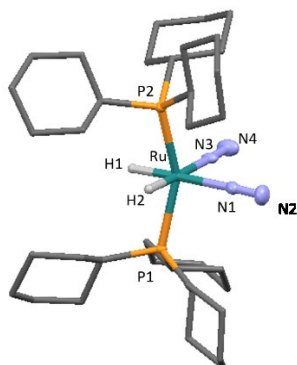
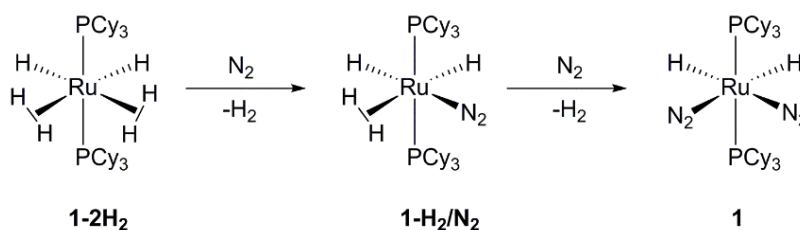


Figure 1.6. X-ray crystal structure of **1**

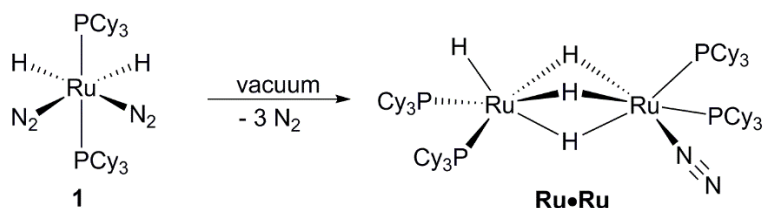
An intermediate was observed by multinuclear NMR spectroscopy while monitoring the conversion of **1-2H₂** into **1**. This intermediate was not isolated however it was postulated as having the structure [Ru(H)₂(η²-H₂)(N₂)(PCy₃)₂] (**1-H₂/N₂**) (Scheme 1.38). Intermediate **1-H₂/N₂** demonstrated a broad signal in the ¹H NMR spectrum at δ_H = –8.48 ppm and a single resonance in the ³¹P{¹H} NMR spectrum at δ_P = 68.8 ppm. This intermediate also had a diffusion co-efficient similar to that of **1-2H₂** and **1** by DOSY NMR studies. The assignment of this intermediate as a mixed dinitrogen/dihydrogen complex was confirmed by mixing a sample of **1-2H₂** with **1** in a 1 : 1 ratio under an argon environment resulting in a sample containing all 3 species. In addition, T₁ measurement was taken (193 K, 400 MHz) with a value of 217 ms obtained for the hydride resonance of **1-H₂/N₂** which was shorter than the T₁ time for **1** (*vide supra*) but longer than the T₁ time for **1-2H₂** (52 ms). This data corroborated with the intermediate **1-H₂/N₂** containing both classical and non-classical hydrides.



Scheme 1.38 Formation of **1** from sequential substitution of H₂ with N₂ in **1-2H₂**

Aside from bubbling H_2 through a solution of **1** to reform **1-2H₂**, the formation a ruthenium dimer (**Ru•Ru**) has been the only reported discussion on the reactivity concerning **1** (Scheme 1.39).³ The formation of **Ru•Ru** was originally reported by Chaudret *et al.* from exposing the dihydrogen analogue of the dimer $[\text{Ru}_2(\text{H})_4(\eta^2\text{-H}_2)(\text{PCy}_3)_4]$ to an atmosphere of N_2 .³ **Ru•Ru** was synthesised directly here from placing a solution of **1** under vacuum to generate a red solution (Scheme 1.39). Slow evaporation of this red solution resulted in formation of crystals of **Ru•Ru** suitable for X-ray diffraction and confirmed the original assignment of **Ru•Ru** complex by Chaudret *et al.* (Figure 1.7).³ An alternative route to obtain **Ru•Ru** was also accessible (5.2 CHAPTER ONE: EXPERIMENTAL).

Ru•Ru was characterised by ^1H NMR spectroscopy demonstrating a single broad resonance at $\delta_{\text{H}} = -12.49$ ppm for the hydride environments and a resonance in $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at $\delta_{\text{P}} = 75.7$ ppm. IR spectrum demonstrated two strong absorbance at $\nu_{\text{Ru-H}\mu} = 1446\text{ cm}^{-1}$ and $\nu_{\text{N}\equiv\text{N}} = 2084\text{ cm}^{-1}$. The absorbance for the terminal hydride was not observed in the spectrum although Chaudret *et al.* originally reported this terminal stretch at 1935 cm^{-1} but did not report the stretch for the bridging hydrides.³ Nevertheless, the remaining spectroscopic data measured here were very similar to the spectroscopic data originally reported by Chaudret *et al.*³



Scheme 1.39 Formation of **Ru•Ru** from **1**

The quality of the data acquired from X-ray diffraction did not allow for the hydrides to be located from the Fourier transform map for **Ru•Ru** (Figure 1.7). Nevertheless, an analogous ruthenium dimer $[\text{Ru}_2(\text{H})_4(\text{N}_2)(\text{PPh}_3)_4]$, was synthesised and fully characterised including X-ray crystallography by Chaudret *et al.*⁴ The hydrides were located in the X-ray structure of $[\text{Ru}_2(\text{H})_4(\text{N}_2)(\text{PPh}_3)_4]$ and therefore, in combination with the spectroscopic data of **Ru•Ru** and comparison of the location of the heavier atoms in $[\text{Ru}_2(\text{H})_4(\text{N}_2)(\text{PPh}_3)_4]$ and **Ru•Ru**, it was likely **Ru•Ru** had the same number of hydrides surrounding the ruthenium and in a similar geometry. The Ru---Ru bond length of **Ru•Ru** was determined to be $2.6254(3)\text{ \AA}$ which was larger than the sum of the single bond radii of two ruthenium.⁴⁶ This suggested that the bridging hydrides were the main interaction between the two ruthenium centres however no computational analysis was performed to corroborate this. The N–N bond length was determined to be $1.120(4)\text{ \AA}$ and in combination with the $\nu_{\text{N}\equiv\text{N}}$ stretch of **Ru•Ru**, suggested an inactivated dinitrogen ligand. In addition, no formation of **1-2H₂** or **1** occurred upon subjecting a

solution of **Ru•Ru** to an atmosphere of H₂ (only formation of the dihydrogen analogue of the dimer) suggesting these ruthenium dimers were incredibly stable.

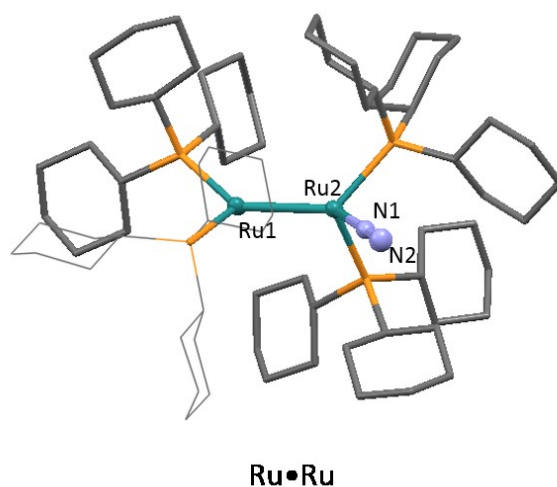
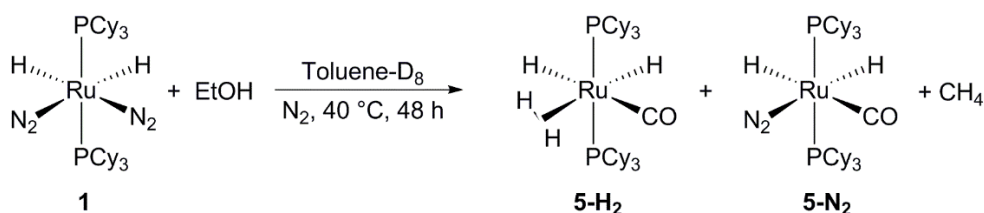


Figure 1.7. X-ray structure of **Ru•Ru**, hydrogen not located from the Fourier transform map

The reactivity of **1** was briefly interrogated. Reacting 1 equivalent of **1** with 1 equivalent of ethanol at 40 °C resulted in the formation of 2 species, **5-H₂** (Scheme 1.9) and **5-N₂** (Scheme 1.40). Complex **5-N₂** was an analogue of **5-H₂** where the dihydrogen ligand was substituted by a dinitrogen ligand. At 233K, complex **5-N₂** was characterised by ¹H NMR spectroscopy and demonstrated two resonances at $\delta_{\text{H}} = -6.68$ ppm (td, $J_{\text{HP}} = 23.4$ and 6.3 Hz) and -13.51 ppm (td, $J_{\text{HP}} = 21.4$ and 6.6 Hz) for the two inequivalent hydrides. At higher temperatures the resonances for the hydrides were lost in the baseline of the spectrum however at 293 K a broad signal was observed in ³¹P{¹H} NMR spectrum at $\delta_{\text{P}} = 63.9$ ppm which sharpened upon cooling to 193 K. The characteristic resonance in the ¹³C{¹H} NMR spectrum for the carbonyl environment was observed at $\delta_{\text{C}} = 205.6$ ppm.



Scheme 1.40. Formation of **5-N₂** from reaction of **1** with EtOH

In addition to the formation of **5-N₂** and **5-H₂**, in the reaction of **1** with ethanol, evolution of methane ($\delta_{\text{H}} = 0.16$ ppm) and dihydrogen ($\delta_{\text{H}} = 4.47$ ppm) were observed *in-situ* by ¹H NMR spectroscopy which was not reported in the original publication on the reaction of **1-2H₂** with ethanol.³³ The mechanism of this reaction was suggested to go through a β -methyl migration route (Figure 1.8) to

form methane with the breaking of C–C bond. β -methyl migration has been postulated as part of the mechanism in olefin polymerisation processes although β -methyl migration/elimination events are much rarer than β -hydride elimination events.^{88–90} The carbonyl moiety from the postulated mechanism (Figure 1.8) can then undergo decarbonylation *via* β -hydride elimination to generate H₂ and CO as postulated for nickel alkoxide species.^{91,92}

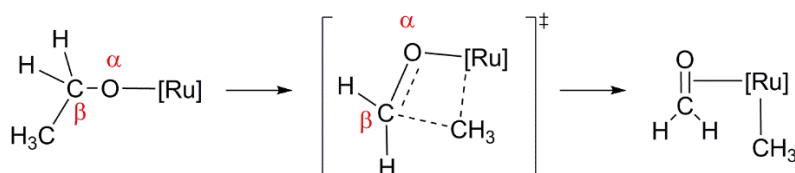


Figure 1.8, Proposed β -methyl migration mechanism

1.4 CONCLUSION

The ruthenium *bis*(dinitrogen) complex (**1**) was synthesised and fully characterised including X-ray crystallographic structure. Under an atmosphere of dinitrogen and modest temperatures, **1** was indefinitely stable allowing for the reactivity of this complex to be investigated.

Initial reactivity of **1** showed similar behaviour with **1-2H₂** with facile exchange between end-on bound dinitrogen and η^2 -bound dihydrogen ligands within similar complexes.

The remainder of this thesis will explore and expand on the known reactivity of the ruthenium *bis*(dinitrogen) complex (**1**) specifically looking into C–X (X = H or O) activation and also reactivity with other main group hydrides, including those of aluminium, zinc and magnesium.

1.5 REFERENCES

- 1 B. Chaudret, G. Commenges and R. Poilblanc, *J. Chem. Soc. - Ser. Chem. Commun.*, 1982, 1388–1390.
- 2 G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini and H. J. Wasserman, *J. Am. Chem. Soc.*, 1984, **106**, 451–452.
- 3 T. Arliguie, B. Chaudret, R. H. Morris and A. Sella, *Inorg. Chem.*, 1988, **27**, 598–599.
- 4 B. Chaudret and R. Poilblanc, *Organometallics*, 1985, **4**, 1722–1726.
- 5 A. F. Borowski, B. Donnadiou, J.-C. Daran, S. Sabo-Etienne and B. Chaudret, *Chem. Commun.*, 2000, 543–544.
- 6 V. Rodriguez, S. Sabo-Etienne, B. Chaudret, J. Thoburn, S. Ulrich, H.-H. Limbach, J. Eckert, J.-C. Barthelat, K. Hussein and C. J. Marsden, *Inorg. Chem.*, 1998, **37**, 3475–3485.
- 7 M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, 1951, **18**, C79.
- 8 J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939–2947.
- 9 M. Kranenburg, P. C. J. Kamer, P. W. N. M. van Leeuwen and B. Chaudret, *Chem. Commun.*, 1997, 373–374.
- 10 K. Abdur-Rashid, D. G. Gusev, A. J. Lough and R. H. Morris, *Organometallics*, 2000, **19**, 1652–1660.
- 11 K. Almeida Leñero, M. Kranenburg, Y. Guari, P. C. J. Kamer, P. W. N. M. van Leeuwen, S. Sabo-Etienne and B. Chaudret, *Inorg. Chem.*, 2003, **42**, 2859–2866.
- 12 R. Gilbert-Wilson, L. D. Field and M. Bhadbhade, *Inorg. Chem.*, 2014, **53**, 12469–12479.
- 13 J. Alós, T. Bolaño, M. A. Esteruelas, M. Oliván, E. Oñate and M. Valencia, *Inorg. Chem.*, 2014, **53**, 1195–1209.
- 14 B. Chaudret, J. Devillers and R. Poilblanc, *Organometallics*, 1985, **4**, 1727–1732.
- 15 T. Burrow, S. Sabo-Etienne and B. Chaudret, *Inorg. Chem.*, 1995, **34**, 2470–2472.
- 16 M. Grellier, L. Vendier, B. Chaudret, A. Albinati, S. Rizzato, S. Mason and S. Sabo-Etienne, *J. Am. Chem. Soc.*, 2005, **127**, 17592–17593.
- 17 B. Moreno, S. Sabo-Etienne, B. Chaudret, A. Rodriguez, F. Jalon and S. Trofimenko, *J. Am. Chem. Soc.*, 1995, **117**, 7441–7451.
- 18 S. Sabo-Etienne and B. Chaudret, *Coord. Chem. Rev.*, 1998, **178–180**, 381–407.
- 19 G. Alcaraz, M. Grellier and S. Sabo-Etienne, *Acc. Chem. Res.*, 2009, **42**, 1640–1649.
- 20 A. F. Borowski, S. Sabo-Etienne, M. L. Christ, B. Donnadiou and B. Chaudret, *Organometallics*, 1996, **15**, 1427–1434.
- 21 A. F. Borowski, S. Sabo-Etienne and B. Chaudret, *J. Mol. Catal. A Chem.*, 2001, **174**, 69–79.
- 22 A. F. Borowski, L. Vendier, S. Sabo-Etienne, E. Rozycka-Sokolowska and A. V. Gaudyn, *Dalt. Trans.*, 2012, **41**, 14117–14125.
- 23 A. F. Borowski, S. Sabo-Etienne, B. Donnadiou and B. Chaudret, *Organometallics*, 2003, **22**, 4803–4809.
- 24 G. P. Rosini and W. D. Jones, *J. Am. Chem. Soc.*, 1992, **114**, 10767–10775.
- 25 T. Li, I. Bergner, F. N. Haque, M. Z. De Iuliis, D. Song and R. H. Morris, *Organometallics*, 2007, **26**, 5940–5949.
- 26 R. Reguillo, M. Grellier, N. Vautravers, L. Vendier and S. Sabo-Etienne, *J. Am. Chem. Soc.*, 2010, **132**, 7854–7855.
- 27 R. P. Beatty and R. A. Paciello, *WO Pat.*, 1996, 96/23802-804.
- 28 M. L. Christ, S. Sabo-Etienne and B. Chaudret, *Organometallics*, 1994, **13**, 3800–3804.
- 29 L. Song and W. C. Trogler, *J. Am. Chem. Soc.*, 1992, **114**, 3355–3361.
- 30 J. P. Dunne, D. Blazina, S. Aiken, H. A. Carteret, S. B. Duckett, J. A. Jones, R. Poli and A. C. Whitwood, *Dalt. Trans.*, 2004, 3616–3628.
- 31 M. L. Christ, S. Sabo-Etienne, G. Chung and B. Chaudret, *Inorg. Chem.*, 1994, **33**, 5316–5319.
- 32 D. G. Hamilton and R. H. Crabtree, *J. Am. Chem. Soc.*, 1988, **110**, 4126–4133.
- 33 S. Bontemps, L. Vendier and S. Sabo-Etienne, *Angew. Chemie Int. Ed.*, 2012, **51**, 1671–1674.
- 34 B. Chaudret, G. Chung, O. Eisenstein, S. A. Jackson, F. J. Lahoz and J. A. Lopez, *J. Am. Chem. Soc.*, 1991, **113**, 2314–2316.
- 35 D. J. Cole-Hamilton, R. J. Young and G. Wilkinson, *J. Chem. Soc., Dalt. Trans.*, 1976, 1995–2001.

- 36 Y. Guari, S. Sabo-Etienne and B. Chaudret, *J. Am. Chem. Soc.*, 1998, **120**, 4228–4229.
- 37 S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda and N. Chatani, *Nature*, 1993, **366**, 529–531.
- 38 F. Kakiuchi, Y. Tanaka, T. Sato, N. Chatani and S. Murai, *Chem. Lett.*, 1995, **24**, 679–680.
- 39 F. Kakiuchi, Y. Yamamoto, N. Chatani and S. Murai, *Chem. Lett.*, 1995, **24**, 681–682.
- 40 F. Kakiuchi, M. Yamauchi, N. Chatani and S. Murai, *Chem. Lett.*, 1996, **25**, 111–112.
- 41 S. Busch and W. Leitner, *Adv. Synth. Catal.*, 2001, **343**, 192–195.
- 42 Y. Guari, S. Sabo-etienne and B. Chaudret, *Organometallics*, 1996, **15**, 3471–3473.
- 43 F. Delpech, J. Mansas, H. Leuser, S. Sabo-Etienne and B. Chaudret, *Organometallics*, 2000, **19**, 5750–5757.
- 44 S. Lachaize, S. Sabo-Etienne, B. Donnadieu and B. Chaudret, *Chem. Commun. (Camb.)*, 2003, **24**, 214–215.
- 45 V. Montiel-Palma, M. Lumbierres, B. Donnadieu, S. Sabo-Etienne and B. Chaudret, *J. Am. Chem. Soc.*, 2002, **124**, 5624–5625.
- 46 L. Pauling, *J. Am. Chem. Soc.*, 1947, **69**, 542–553.
- 47 A. Caballero and S. Sabo-Etienne, *Organometallics*, 2007, **26**, 1191–1195.
- 48 G. Alcaraz, E. Clot, U. Helmstedt, L. Vendier and S. Sabo-Etienne, *J. Am. Chem. Soc.*, 2007, **129**, 8704–8705.
- 49 Y. Gloaguen, G. Alcaraz, L. Vendier and S. Sabo-Etienne, *J. Organomet. Chem.*, 2009, **694**, 2839–2841.
- 50 C. W. Hamilton, R. T. Baker, A. Staubitz and I. Manners, *Chem. Soc. Rev.*, 2009, **38**, 279–293.
- 51 G. Alcaraz, L. Vendier, E. Clot and S. Sabo-Etienne, *Angew. Chemie Int. Ed.*, 2010, **49**, 918–920.
- 52 G. Alcaraz, A. B. Chaplin, C. J. Stevens, E. Clot, L. Vendier, A. S. Weller and S. Sabo-Etienne, *Organometallics*, 2010, **29**, 5591–5595.
- 53 S. Bontemps and S. Sabo-Etienne, *Angew. Chemie Int. Ed.*, 2013, **52**, 10253–10255.
- 54 Y. Gloaguen, G. Alcaraz, A.-F. Pécharman, E. Clot, L. Vendier and S. Sabo-Etienne, *Angew. Chemie*, 2009, **121**, 3008–3012.
- 55 Y. Gloaguen, G. Alcaraz, A. S. Petit, E. Clot, Y. Coppel, L. Vendier and S. Sabo-Etienne, *J. Am. Chem. Soc.*, 2011, **133**, 17232–17238.
- 56 A. Cassen, Y. Gloaguen, L. Vendier, C. Duhayon, A. Poblador-Bahamonde, C. Raynaud, E. Clot, G. Alcaraz and S. Sabo-Etienne, *Angew. Chemie Int. Ed.*, 2014, **53**, 7569–7573.
- 57 S. Sabo-Etienne, M. Muñoz-Hernández, G. Chung and B. Chaudret, *New J. Chem.*, 1994, **18**, 175–177.
- 58 K. Hussein, C. J. Marsden, J.-C. Barthelat, V. Rodriguez, S. Conejero, S. Sabo-Etienne, B. Donnadieu and B. Chaudret, *Chem. Commun.*, 1999, 1315–1316.
- 59 I. Atheaux, F. Delpech, B. Donnadieu, S. Sabo-Etienne, B. Chaudret, K. Hussein, J.-C. Barthelat, T. Braun, S. B. Duckett and R. N. Perutz, *Organometallics*, 2002, **21**, 5347–5357.
- 60 S. Lachaize and S. Sabo-Etienne, *Eur. J. Inorg. Chem.*, 2006, **2006**, 2115–2127.
- 61 F. Delpech, S. Sabo-Etienne, B. Chaudret and J.-C. Daran, *J. Am. Chem. Soc.*, 1997, **119**, 3167–3168.
- 62 U. Schubert and H. Gilges, *Organometallics*, 1996, **15**, 2373–2375.
- 63 F. R. Lemke, *J. Am. Chem. Soc.*, 1994, **116**, 11183–11184.
- 64 X.-L. Luo, G. J. Kubas, C. J. Burns, J. C. Bryan and C. J. Unkefer, *J. Am. Chem. Soc.*, 1995, **117**, 1159–1160.
- 65 R. S. Simons and C. A. Tessier, *Organometallics*, 1996, **15**, 2604–2610.
- 66 J. Yin, J. Klosin, K. A. Abboud and W. M. Jones, *J. Am. Chem. Soc.*, 1995, **117**, 3298–3299.
- 67 U. Schubert, *Adv. Organomet. Chem.*, 1990, **30**, 151–187.
- 68 F. Delpech, S. Sabo-Etienne, J.-C. Daran, B. Chaudret, K. Hussein, C. J. Marsden and J.-C. Barthelat, *J. Am. Chem. Soc.*, 1999, **121**, 6668–6682.
- 69 K. G. Moloy, J. L. Peterser and K. G. Moloy, *J. Am. Chem. Soc.*, 1995, **117**, 7696–7710.
- 70 F. Delpech, S. Sabo-Etienne, B. Donnadieu and B. Chaudret, *Organometallics*, 1998, **17**, 4926–4928.
- 71 I. Atheaux, B. Donnadieu, V. Rodriguez, S. Sabo-Etienne, B. Chaudret, K. Hussein and J.-C. Barthelat, *J. Am. Chem. Soc.*, 2000, **122**, 5664–5665.

- 72 L. Hao, A.-M. Lebuis, J. F. Harrod, L. Hao and E. Samuel, *Chem. Commun.*, 1997, 2193–2194.
73 S. Xin, C. Aitken, J. F. Harrod, Y. Mu and E. Samuel, *Can. J. Chem.*, 1990, **68**, 471–476.
74 H. G. Woo, R. H. Heyn and T. D. Tilley, *J. Am. Chem. Soc.*, 1992, **114**, 5698–5707.
75 J. Y. Corey and J. Braddock-Wilking, *Chem. Rev.*, 1999, **99**, 175–292.
76 R. Ben Said, K. Hussein, J.-C. Barthelat, I. Atheaux, S. Sabo-Etienne, M. Grellier, B. Donnadieu and B. Chaudret, *Dalt. Trans.*, 2003, 4139–4146.
77 T. Ayed, J.-C. Barthelat, B. Tangour, C. Pradère, B. Donnadieu, M. Grellier and S. Sabo-Etienne, *Organometallics*, 2005, **24**, 3824–3826.
78 A. M. Wróbel, I. Błaszczak, A. Walkiewicz-Pietrzykowska, A. Tracz, J. E. Klemberg-Sapieha, T. Aoki and Y. Hatanaka, *J. Mater. Chem.*, 2003, **13**, 731–737.
79 T. Rasul and D. Y. Son, *J. Organomet. Chem.*, 2002, **655**, 115–119.
80 M. Grellier, T. Ayed, J. C. Barthelat, A. Albinati, S. Mason, L. Vendier, Y. Coppel and S. Sabo-Etienne, *J. Am. Chem. Soc.*, 2009, **131**, 7633–7640.
81 V. Montiel-Palma, M. A. Muñoz-Hernández, T. Ayed, J.-C. Barthelat, M. Grellier, L. Vendier and S. Sabo-Etienne, *Chem. Commun. (Camb.)*, 2007, 3963–3965.
82 R. C. Fischer and P. P. Power, *Chem. Rev.*, 2010, **110**, 3877–3923.
83 R. Ben Said, K. Hussein, B. Tangour, S. Sabo-Etienne and J.-C. Barthelat, *New J. Chem.*, 2003, **27**, 1385–1391.
84 K. A. Smart, E. Mothes-Martin, L. Vendier, R. N. Perutz, M. Grellier and S. Sabo-Etienne, *Organometallics*, 2015, **34**, 4158–4163.
85 G. J. Kubas, *Proc. Natl. Acad. Sci.*, 2007, **104**, 6901–6907.
86 P. Pertici, G. Vitulli, M. Paci and L. Porri, *J. Chem. Soc. Dalt. Trans.*, 1980, 1961–1964.
87 G. Herzberg and K. P. Huber, *Molecular Spectra and Molecular Structure*, Van Nostrand Reinhold Company, New York, 1979.
88 K. McNeill, R. A. Andersen and R. G. Bergman, *J. Am. Chem. Soc.*, 1995, **117**, 3625–3626.
89 M. E. O'Reilly, S. Dutta and A. S. Veige, *Chem. Rev.*, 2016, **116**, 8105–8145.
90 A. D. Horton, *Organometallics*, 1996, **15**, 2675–2677.
91 P. Kelley, S. Lin, G. Edouard, M. W. Day and T. Agapie, *J. Am. Chem. Soc.*, 2012, **134**, 5480–5483.
92 M. Tobisu, T. Morioka, A. Ohtsuki and N. Chatani, *Chem. Sci.*, 2015, **6**, 3410–3414.

2 CHAPTER TWO – $sp^2\text{C-O}$ BOND ACTIVATION BY AN ISOLABLE RUTHENIUM(II) *BIS*(DINITROGEN) COMPLEX: THEORY AND EXPERIMENT

2.1 INTRODUCTION

2.1.1 Biomass viability

The finite nature of fossil fuels has driven the exploration to find alternative renewable resources to obtain our bulk chemicals.¹ Lignocellulosic biomass has gained interest as a potential resource that can meet some of the demands to replace fossil fuels.² Lignocellulosic biomass can be broken down into its three components: cellulose, hemi-cellulose and lignin. It is lignin which provides the most attractive component in biomass as it contains the highest carbon to oxygen atom ratio as well as containing aromatic rings in its structure and therefore can potentially provide some of the demand to supply benzene derivatives traditionally obtained from petroleum. The huge structure of lignin first needs to be depolymerised before it can be utilised further as a feedstock and this involves the cleavage of strong carbon–carbon and strong carbon–oxygen bonds. Depolymerisation of this massive polymer then results in the formation of structurally related compounds to monolignols such as coniferyl alcohol and sinapyl alcohol (Figure 2.1). One functional group prevalent in these compounds even after the depolymerisation process is aryl methyl ether group ($\text{C}_{\text{Ar}}\text{-OMe}$). These methoxy groups are synthetic dead-ends due to their low reactivity and therefore a possible route to upgrade these aromatic molecules could involve cross-coupling reactions *via* the cleavage of these strong $\text{C}_{\text{Ar}}\text{-OMe}$ bonds.

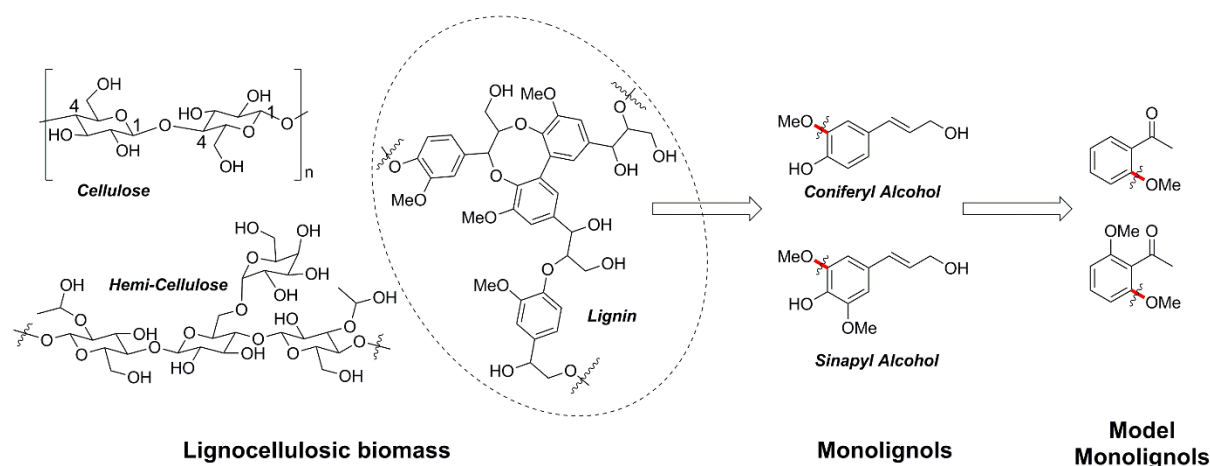


Figure 2.1 Breakdown of Biomass

The area of C–O bond activation and functionalisation mediated by organometallic reagents was pioneered by Wenkert *et al.* in 1979. Wenkert and co-workers reported the coupling reaction of

alkenyl ethers and aryl ethers with Grignard reagents using catalytic amount of the nickel species $[\text{NiCl}_2(\text{PPh}_3)_2]$ to generate new C–C bond.³ Since the original publication by Wenkert *et al.* the stagnation of this area of research ensued for the next few decades and has only recovered in the last 20 years with a small number of research groups investigating C–O bond activation reactions with organometallic reagents and catalysts.

The following summation of the literature will concentrate on C–O activation of substrates relevant to monolignols, mediated by nickel and ruthenium complexes and specifically investigations which cast a light on the mechanism operating in these reactions.

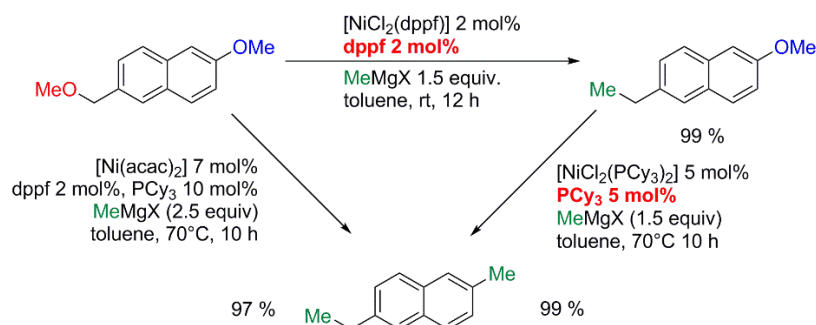
2.2 C–O ACTIVATION

2.2.1 Nickel

In 2008, Shi *et al.* demonstrated the chemoselective cleavage of $sp^2\text{C–OMe}$ bond and $sp^3\text{C–OMe}$ bonds in 2-methoxy-6-(methoxymethyl)naphthalene to generate a new C–C bond from the reaction with Grignard reagents. This reaction was catalysed by nickel phosphine complexes (Scheme 2.1).⁴ Product formation depended on the nature of the external phosphine ligand used in the catalyst system with 1,1'-bis(diphenylphosphino)ferrocene (dppf) favouring $sp^3\text{C–OMe}$ bond cleavage of the substrate and tricyclohexylphosphine (PCy_3) favouring $sp^2\text{C–OMe}$ bond cleavage of the substrate. One pot synthesis containing both dppf and PCy_3 ligands and $[\text{Ni}(\text{acac})_2]$ as the catalyst precursor resulted in the formation of 2-ethyl-6-methylnaphthalene with both C–OMe bonds converted into new C–C bonds. Control reaction of 2-(methoxymethyl)naphthalene with MeMgBr mediated by $[\text{NiCl}_2(\text{PCy}_3)]/\text{PCy}_3$ catalyst system resulted in only 12 % yield of the methylated product. In comparison, the same reaction but using $[\text{NiCl}_2(\text{dppf})_2]$ as the catalyst precursor and dppf as the external phosphine ligand resulted in >90 % yield of product. These results confirmed the preference of $sp^3\text{C–OMe}$ bond cleavage by a $[\text{NiCl}_2(\text{dppf})_2]/\text{dppf}$ system, however it was not clear whether this same system could also mediate $sp^2\text{C–OMe}$ cleavage but at a slower rate than $sp^3\text{C–OMe}$ cleavage and therefore whether having both dppf and PCy_3 in the same reaction mixture was required to form the final product 2-ethyl-6-methylnaphthalene.

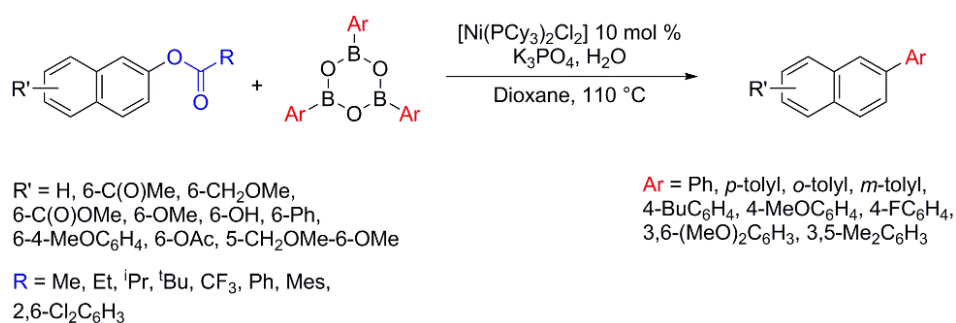
No discussion of the identity of the active nickel species involved during the bond cleavage process was reported which may have shed some mechanistic understanding as to why the phosphine ligand affected the chemoselectivity of this reaction. The most apparent conclusion would be the denticity of the ligand, dppf being bidentate and PCy_3 being monodentate. The labile nature balanced with the stability of these phosphine ligands could determine the pathway undertaken by the reaction *i.e.* $sp^3\text{C–O}$ versus $sp^2\text{C–O}$ activation. The ability of dppf ligand to bind *via* two sites or one site may infer more stability for the active nickel species to cleave the stronger C–O bond and prevent an

unnecessary vacant site from opening up at the metal centre to undergo off-cycle reactions that could inhibit the cleavage reaction.



Scheme 2.1 Shi *et al.*⁴: sp^3 versus sp^3 C–O activation

Following up this work, Shi *et al.* published their findings on Ni mediated C–O activation of aryl carboxylate esters and the subsequent cross-coupling with boroxines (Scheme 2.2).⁵ Aryl carboxylate esters are much more affordable starting substrates than aryl methyl ethers and therefore would be a more attractive starting aromatic to valorise. Carboxylate esters also has the advantage of being a good leaving group in comparison to methoxy group. Using 10 mol % $[\text{Ni}(\text{PCy}_3)_2\text{Cl}_2]$, K_2PO_4 as the base and water as an additive, they found success in cross-coupling a range of aryl carboxylate esters with different aryl boroxines. The role of water in this reaction was anticipated to hydrolyse boroxine to boronic acid as it is known that they exist in equilibrium to each other.⁶ The proposed mechanism of this reaction underwent the classic 3 step process (Figure 2.2): (i) oxidative addition, (ii) ligand transfer and transmetallation and finally (iii) reductive elimination. However, no further investigation to validate this proposal was undertaken.



Scheme 2.2. C–O cleavage of aryl carboxylate esters

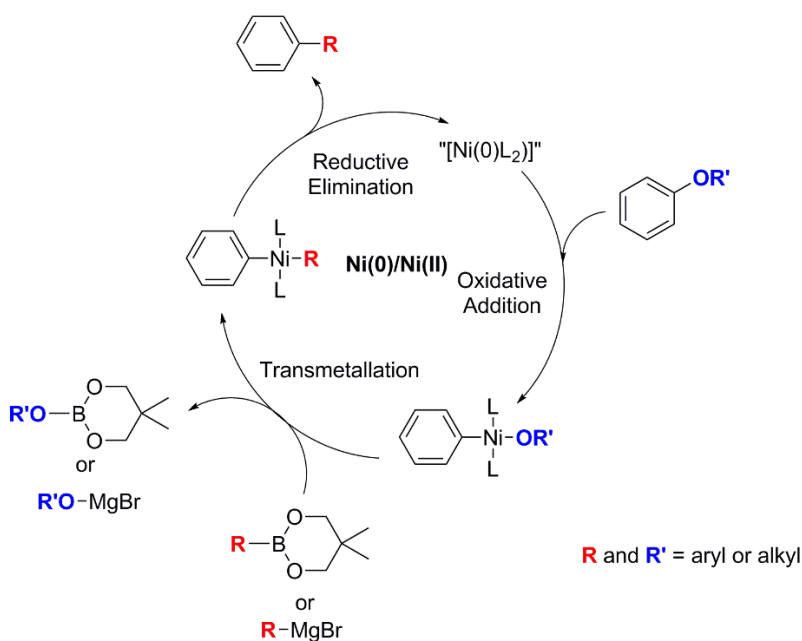


Figure 2.2. Generalised Ni(0)/Ni(II) redox mechanism for C–O bond cleavage

The importance of the phosphine groups on nickel for the success of C–O cleavage was further explored by Wang *et al.* using square planar nickel(II) complexes⁷ to cleave C–O bonds in methoxynaphthalene derivatives (Figure 2.3).⁸ Simply changing the R group on the phosphine ligand changed the activity of the catalyst with the most active group being *isopropyl* > *cyclohexyl* > *phenyl* group. This trend would support the unsurprising indication that the electron density induced to the Ni centre by the phosphine ligand plays an important role on the success of bond cleavage – the more electron rich the Ni centre the stronger the donation from the metal d-orbital into the antibonding orbital of the C–O bond to weaken it. It would be pertinent to test these Ni(II) catalysts synthesised by Wang *et al.* on methoxybenzene derivatives as opposed to naphthalene derivatives. The greater reactivity resulting from π -extended conjugation substrates makes them more likely to undergo these cleavage reactions and therefore it would be interesting to note if these complex synthetic ligands are necessary to perform these C–O functionalisation reactions or if the commercial ligands used by Shi *et al.* are equally as successful.⁴

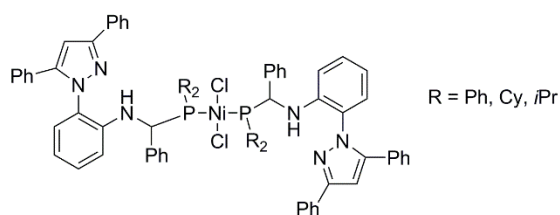


Figure 2.3. Phosphine ligand used by Wang *et al.*

In 2009 Liu *et al.* published a computational study on the work by Shi *et al.* on their Ni-catalysed C–O cleavage of aryl carboxylates and subsequent cross-coupling with arylboronic esters reactions (Scheme 2.2).⁹ Liu *et al.* computed a viable pathway that underwent the traditional Ni(0)/(Ni(II)) redox process (Figure 2.2). The calculations showed that a nickel monophosphine complex mediated the C_{Ar}–O cleavage step with the highest transition state found for the oxidative addition step being $\Delta G^\ddagger = 22.9$ kcal mol⁻¹ (**TS1**) to generate a Ni(II) carboxylate complex (**INT2**) (Figure 2.4). A pathway involving a nickel *bis*-phosphine species cleaving the C_{Ar}–O bond was also analysed and was found to be unfavourable with the energy barrier calculated as $\Delta G^\ddagger = 54.9$ kcal mol⁻¹. From **INT2**, the highest energy barrier for the transmetallation step was $\Delta G^\ddagger = 31.2$ kcal mol⁻¹ through **TS2** and this also represented the rate determining step of the mechanism. Under the experimental reaction conditions (base, water and boroxine) boronic acid and PhB(OH)₃⁻ anion existed in solution and it was the anion which was calculated as the favoured active species which participated in the transmetallation step to generate **INT3**. The corresponding base-free transmetallation step was also calculated and was significantly higher ($\Delta G^\ddagger = 54.7$ kcal mol⁻¹) showing the important role the base has to play in these reactions to generate the active transmetallation anionic species. Finally, the formation of product was a downhill process to discharge B(OH)₃ as a by-product, release the biphenyl product and regenerate the catalyst. It is interesting to note that the highest transition state was calculated to occur during the transmetallation process. This would suggest the rate determining step was found after C–O bond cleavage. If kinetic experiments were performed, the results would at least be able to substantiate the computational finding as the reaction should be first order with respect to both the substrate and importantly boroxine, base and water.

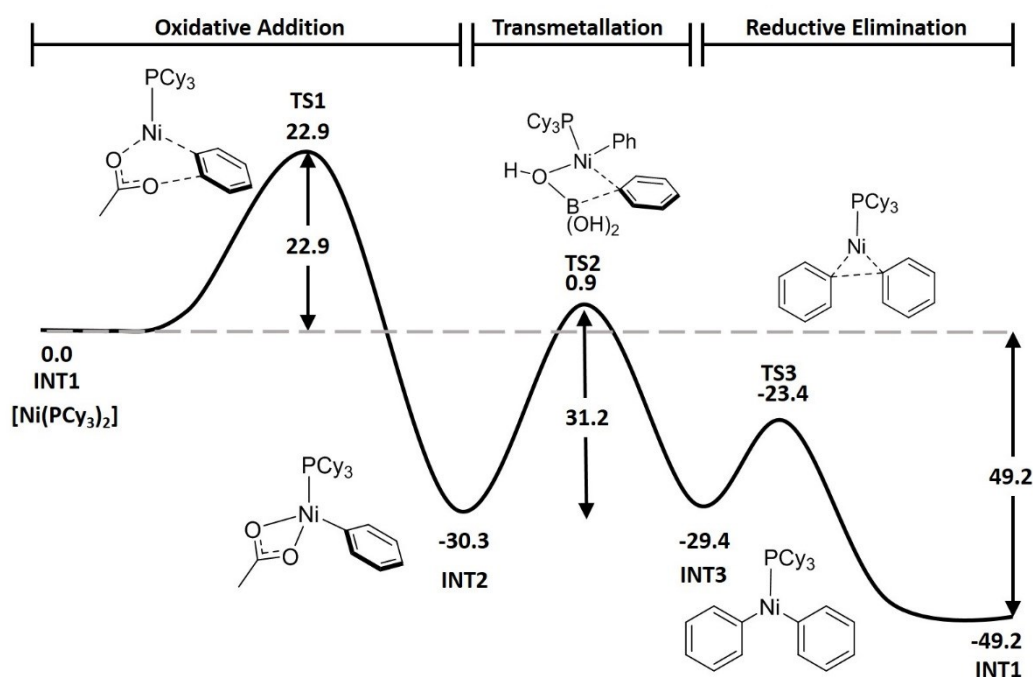
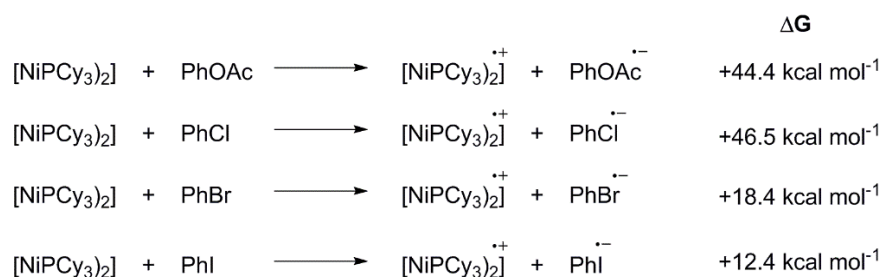


Figure 2.4. Simplified reaction profile of C–O cleavage of aryl carboxylates. Gibbs free energy in kcal mol⁻¹

An alternative reaction mechanism whereby the oxidative addition of C_{Ar}–O bond occurred *via* stepwise electron transfer and not concerted fashion was also calculated by Liu *et al.*⁹ The free energies of electron transfer of from [Ni(PCy₃)₂] to PhOAc, PhCl, PhBr and PhI were calculated (Scheme 2.3). The trend observed matched previous work by Kochi *et al.*¹⁰ on the ability to form Ni(I) species from reaction of Ni(0) species with ArX and found when X = I and Br, significant quantities of Ni(I) species was formed but when X = Cl no Ni(I) species was observed. Based on this high transition state energy for oxidative addition by electron transfer of PhOAc (+44.4 kcal mol⁻¹), it suggested PhOAc should prefer to undergo concerted oxidative cleavage of the C_{Ar}–O bond and unlikely through the Ni(I) species route.



Scheme 2.3. Oxidative addition of PhX (X = OAc, Cl, Br, I) via stepwise electron transfer

As well as cross-coupling reactions of aryl methyl ethers with boronic acids, the cross coupling reactions of aryl methyl ethers with Grignard reagents mediated by Ni(0) species has also been proposed to go through the classic Ni(0)/Ni(II) redox mechanism (Figure 2.2). In 2015, Uchiyama *et al.* looked to rationalise the high reactivity demonstrated by Ni in these Kumada-Tamao-Curriu cross-coupling reaction *via* C_{Ar}–OR (R = alkyl or aryl) cleavage (*vide supra*).¹¹ Uchiyama *et al.* modelled the reaction of anisole coupling with [PhMg(OMe₂)Br]₂ to generate biphenyl as the product with the reaction mediated by [Ni(PCy₃)₂] as the pre-catalyst. The study found that the oxidative addition of the C_{Ar}–OMe across a Ni(0) species was high ($\Delta G^\ddagger = 36.9$ kcal mol⁻¹) and therefore an alternative pathway was studied. Formation of the Ni(0)-ate species proceeded smoothly from the starting materials with formation of **INT1** (the organisation and association of the reactants) then migration of the phenyl group from the Grignard reagent to the Ni(0) centre generated **INT2**, the Ni(0)-ate species. The NPA charge was analysed within the structure of **INT2** and confirmed that the [Ph–Ni–Ph] unit was negative (–0.23) and the [Mg(OMe₂)Br] unit was positive (+0.85) supporting the assignment of the Ni(0)-ate complex. Cleavage of the C_{Ar}–OMe bond through a 5-membered transition state (**INT2** to **TS2**) was endergonic ($\Delta G^\ddagger = 15.5$ kcal mol⁻¹) to form a Ni(II) species **INT3** (Figure 2.5). In this reaction mechanism, the magnesium helped to stabilise the transition state by acting as a Lewis acid and coordinating with the oxygen in the –OMe fragment to make it a better leaving group. The cleavage of the C_{Ar}–OMe bond also represented the highest transition state across the whole reaction pathway. From **INT3** a facile

reductive elimination step gave the biphenyl product. Absence of the formation of a Ni–OMe fragment in this reaction profile would therefore avoid β -hydride elimination pathway and therefore avoid formation of the by-product PhH instead of the desired biphenyl which corroborated with experimental observations whereby no PhH formed in the reaction.¹²

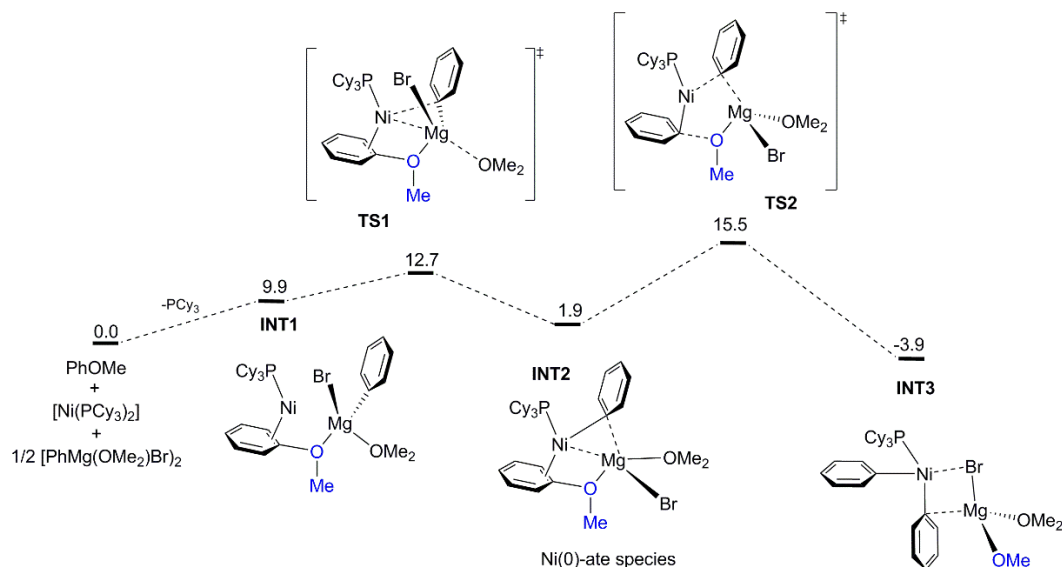
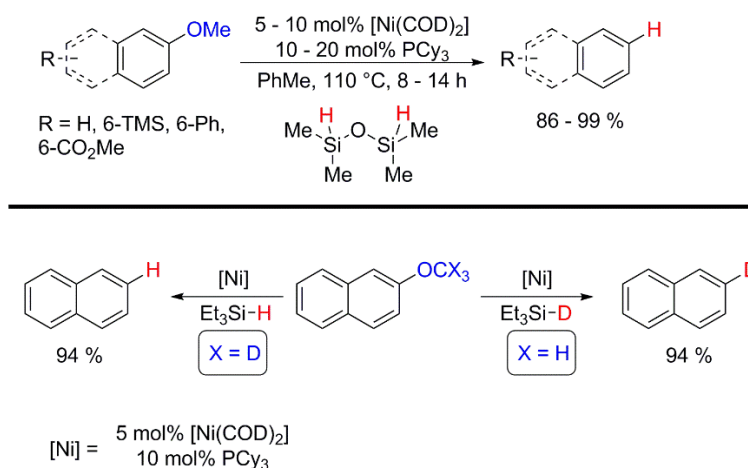


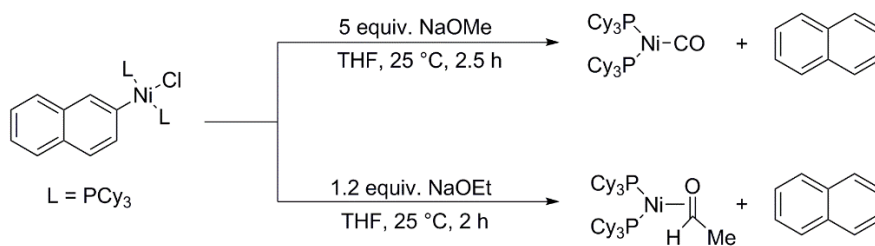
Figure 2.5. C–O bond breaking of anisole with "Ni(0)-ate" complex (CP2). Gibbs free energy in kcal mol⁻¹

Moving away from Grignard reagents and organoboranes as the nucleophiles in these cross coupling reactions, in 2010 Martin *et al.* reported the reduction of C–O bonds of aryl methyl ether substrates using [Ni(COD)₂] as the catalyst precursor in combination with PCy₃ as the external ligand and tetramethyldisiloxane (TMDSO) as the reductant. The reaction conditions were able to tolerate silyl, ester, amide and acetal functional groups to give the products of C–O bond activation in varying yields (55 – 99 %) (Scheme 2.4).¹³ Martin *et al.* noted that the tolerance of tertiary amines and N-heterocycles indicated the low Lewis acidity of the active catalyst, however the conversion to product was reduced significantly if the N-heterocycle group was *meta* or *para* to the C–O bond. Deuterium labelling experiments were carried out in order to ascertain the mechanism operating in these reactions. Martin and co-workers found that they could incorporate deuterium exclusively when Et₃SiD was used as the reductant ruling out any β -hydride elimination of the cleaved methoxy group (Scheme 2.4). The interrogation of the mechanism of this reaction was followed up in 2013 by Martin *et al.* in a combined experimental and computational investigation of these reactions.¹⁴ Additional control experiments beyond the deuterium labelling experiments indicated the nickel catalysed C–OMe cleavage reaction only proceeded in the presence of catalyst *and* silane and therefore strengthened the argument that β -hydride elimination from a C_{Ar}–Ni–OMe intermediate seemed unlikely.



Scheme 2.4. (Top) C–O cleavage of aryl ethers with [Ni(COD)₂] / PCy₃. (Bottom) Deuterium labelling experiment

From these empirical observations Martin *et al.* investigated the mechanism of this nickel catalysed reduction of C_{Ar}–OMe bond reaction in more detail. Oxidative addition of the C_{Ar}–OMe bond across a Ni(0) species was hypothesised to be the first step of the reaction to form the C_{Ar}–Ni–OMe intermediate. Isolation of this postulated C_{Ar}–Ni–OMe intermediate directly from the reaction mixture was unsuccessful. An alternative approach to directly synthesise the C_{Ar}–Ni–OMe intermediate through the metathesis of [Ni(C₁₀H₈)(PCy₃)₂Cl] with NaOMe resulted in formation of [Ni(PCy₃)₂(CO)] and naphthalene. In comparison reacting [Ni(C₁₀H₈)(PCy₃)₂Cl] with NaOEt resulted in the formation of [Ni(PCy₃)₂(CH₃CHO)] complex whereby the ethanal was coordinated to the nickel centre in an η^2 -fashion (Scheme 2.5). Both the nickel carbonyl and nickel ethanal complex were characterised by X-ray crystallography. The formation of these nickel species was ascribed to the facile β -hydride elimination from alkoxide fragments however as the nickel species were not observed in the reaction, the oxidative addition of C_{Ar}–OMe bond seemed unlikely to be operating in the mechanism.



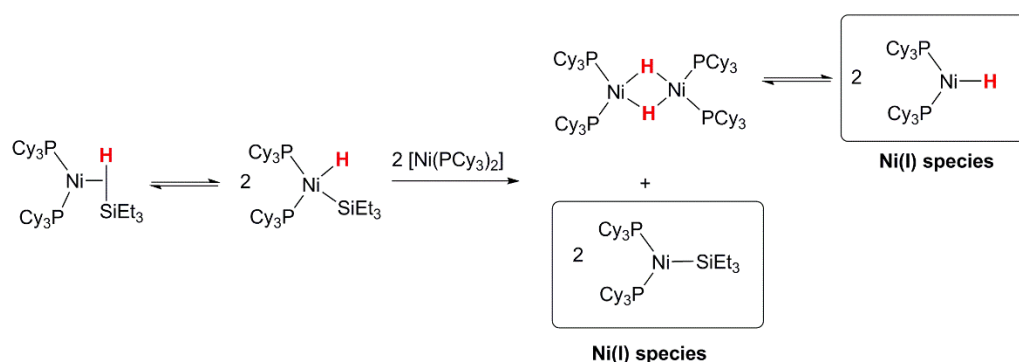
Scheme 2.5. Formation of undesired Ni species in attempt to isolate C_{Ar}–Ni–OMe intermediate

Kinetic studies were performed revealing first order dependence on both the catalyst and the substrate but also the silane. This result strengthened the argument that oxidative addition of the C_{Ar}–OMe was unlikely to be involved in the mechanism of the reaction as no dependence on silane would have been observed in the kinetic experiment. However, the *caveat* to this conclusion was the

assumption that the bond breaking step was the rate determining step in the reaction as it is often postulated to be in the traditional oxidative addition, transmetallation, reductive elimination mechanism.

Nevertheless, an alternative mechanism was proposed involving Ni(I) intermediates. Monitoring the initial time period of the reaction by gas chromatography, ^{29}Si NMR and *in-situ* IR spectroscopy they found that a longer induction period was observed when using Et_3SiD compared to Et_3SiH . Also, during the facile consumption of the silane no new peaks appeared in the ^{29}Si NMR or IR spectra for any intermediates that would have formed. With no experimental evidence for Ni(I) intermediates, Martin *et al.* probed the mechanism by computational methods.

DFT calculations showed a viable pathway to form potentially two active Ni(I) intermediates starting from $[\text{Ni}(\text{COD})_2]$ precursor. Ligand substitution gave $[\text{Ni}(\text{PCy}_3)_2]$ which underwent oxidative addition with SiEt_3H to give $[\text{Ni}(\text{H})(\text{SiEt}_3)(\text{PCy}_3)_2]$. $[\text{Ni}(\text{H})(\text{SiEt}_3)(\text{PCy}_3)_2]$ reacts with an additional equivalent of $[\text{Ni}(\text{PCy}_3)_2]$ to undergo a comproportionation reaction to give $[\text{Ni}(\text{SiEt}_3)(\text{PCy}_3)_2]$ as one of the Ni(I) species and a dimeric nickel hydride species with the monomeric form $[\text{Ni}(\text{H})(\text{PCy}_3)_2]$ as the second Ni(I) species (Scheme 2.6). Evidence of the viability of this pathway was demonstrated by the synthesis and characterisation by X-ray crystallography of an analogous dimeric nickel hydride species where the phosphine ligand was the bidentate 1,2-bis(dicyclohexylphosphino)ethane (dcpe) ligand.



Scheme 2.6. Formation of Ni(I) species

Reaction pathways involving both Ni(I) species were calculated and the favoured profile was found to involve the $\text{Ni}(\text{I})\text{--SiR}_3$ complex ($\text{R} = \text{Me}$ for the modelled mechanism) due to the propensity for the $\text{Ni}(\text{I})\text{--H}$ species to exist as a dimer and not a monomer. Calculations show that dimerization of the $\text{Ni}(\text{I})\text{--H}$ species was exergonic by about $15.5 \text{ kcal mol}^{-1}$ and therefore unlikely for the active monomeric $\text{Ni}(\text{I})\text{--H}$ species to enter the catalytic cycle.

Focusing on just the $\text{Ni}(\text{I})\text{--SiMe}_3$ species, a viable pathway from starting materials to product was located. The reaction mechanism was summarised as (i) formation of active $\text{Ni}(\text{I})\text{--SiEt}_3$ species, (ii) coordination of the substrate in an η^2 -fashion on the arene ring followed by insertion of Ni--SiMe_3

bond into naphthyl ring to generate a benzyl nickel species, (iii) elimination of MeOSiR_3 as by-product with concomitant migration of the nickel to form naphthyl–Ni–(PCy_3)₂ species and finally (iv) a reversible σ -bond metathesis with an incoming silane to release the product and regenerate the active $\text{Ni(I)}\text{--SiEt}_3$ species (Figure 2.6). The highest transition state of this reaction pathway was the Ni–SiMe₃ insertion into the backbone of the naphthalene ($\Delta G^\ddagger = 32.9 \text{ kcal mol}^{-1}$). This insertion step involved the Ni species, the substrate and importantly the silane which corroborates with the results from the kinetic studies. In addition, the rate determining step also does not involve any Ni–H or Si–H bond breaking which again aligns with the lack of kinetic isotope effects observed experimentally. This study represented an alternative mechanism in operation from the traditional Ni(0)/Ni(II) redox process often postulated for these bond breaking reactions.

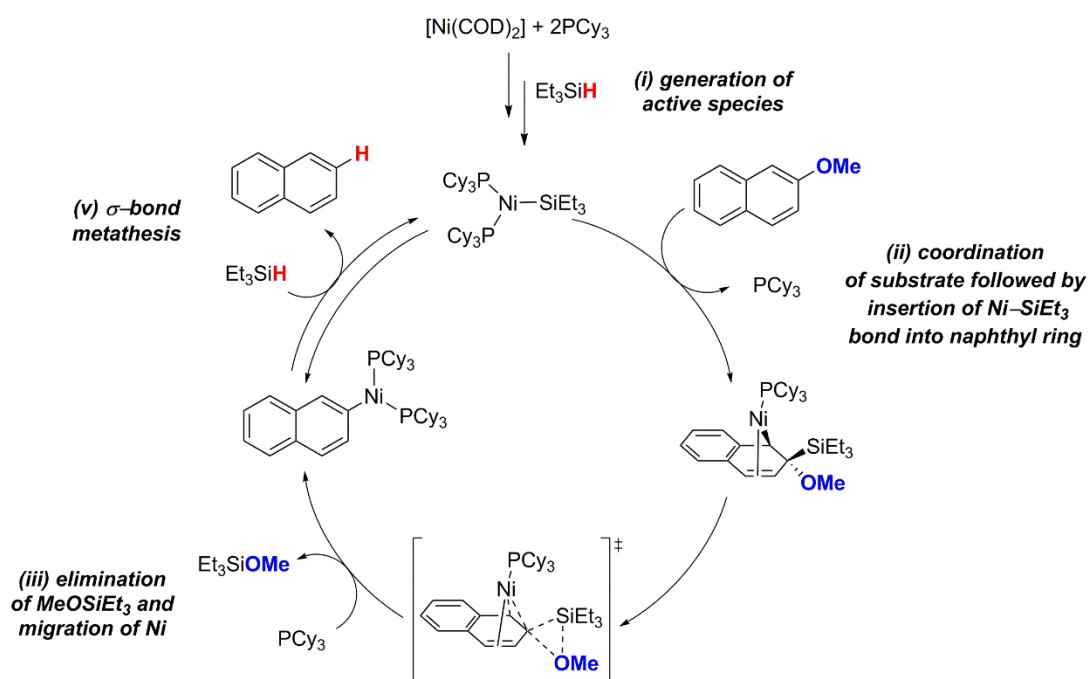
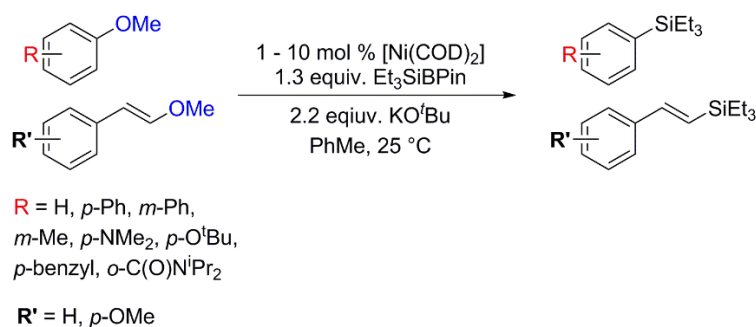


Figure 2.6. Proposed catalytic cycle of reduction of aryl methyl ether with Ni(I) species

Continuing their research into nickel mediated C–O cleavage, in 2017 Martin *et al.* reported the catalytic *ipso*-silylation of aryl methyl ethers under mild conditions with $[\text{Ni}(\text{COD})_2]$ but notably without the need for external ligands (Scheme 2.7).¹⁵ The reaction was able to tolerate a wide range of functional groups and without the need to use biased aryl methyl ether substrates to direct reactivity. The importance of the nature of the base used was emphasised during the optimisation process whereby using bases with cations besides K^+ failed to yield any product. Furthermore, the reaction was sensitive to anionic component of the base and a balance between nucleophilicity and steric bulk was required, with KOMe and potassium *bis*(trimethylsilyl)amide (KHMDs) also failing to yield product.



Scheme 2.7. Ipsso-silylation of aryl methyl ethers

A preliminary study into the mechanism of this *ipso*-silylation reaction pointed towards a “Ni(0)-silyl-ate species” as a key intermediate in catalysis. The suggestion was not too dissimilar to that proposed by Uchiyama *et al.* in related methodology (Figure 2.5).¹¹ Based on the empirical data, Martin and co-workers proposed that a $[\text{Ni}(\text{COD})\text{SiEt}_3]\text{K}$ complex was generated *in-situ* which was the active species in the reaction. This “Ni(0)-silyl-ate species” could then react with the aryl methyl ether substrate *via* 2 pathways: (i) a $\text{S}_{\text{N}}\text{Ar}$ fashion assisted by complexation of the K^+ counter cation with the lone pair of the ethereal oxygen atom or (ii) a “non-classical” oxidative addition of the $\text{C}_{\text{Ar}}\text{--O}$ bond again assisted by the K^+ counter cation.

In subsequent work, Fu *et al.* investigated this silylation reaction by DFT calculations and found that a similar reaction pathway postulated by Martin *et al.* was a viable pathway and indeed generation of a “Ni(0)-silyl-ate species” undergoing oxidative addition of $\text{C}_{\text{Ar}}\text{--O}$ through a 3-centred transition state, stabilised by the K^+ cation, was the most favoured pathway (Figure 2.7).¹⁶ NBO analysis of this 3-centred transition state showed strong $\sigma(\text{C--O}) \rightarrow \sigma^*(\text{Ni--Si})$ interaction, in agreement with an oxidative addition pathway. The study concluded that both the silyl anion and K^+ cation played an important cooperative role in aiding the nickel centre to mediate C--O cleavage. The K^+ cation helped to stabilise the transition state through noncovalent interactions and therefore lowering the energy of the transition state. The silyl anion increased electron density on the nickel centre which in turn allowed the $\sigma^*(\text{Ni--Si})$ orbital to be a better acceptor of electron density from $\sigma(\text{C--O})$ orbital, however exactly how the $\sigma^*(\text{Ni--Si})$ became a better acceptor was not entirely obvious in terms of the absolute energies of these orbitals.

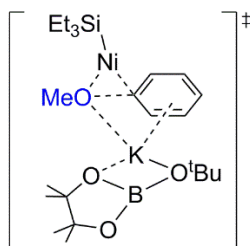
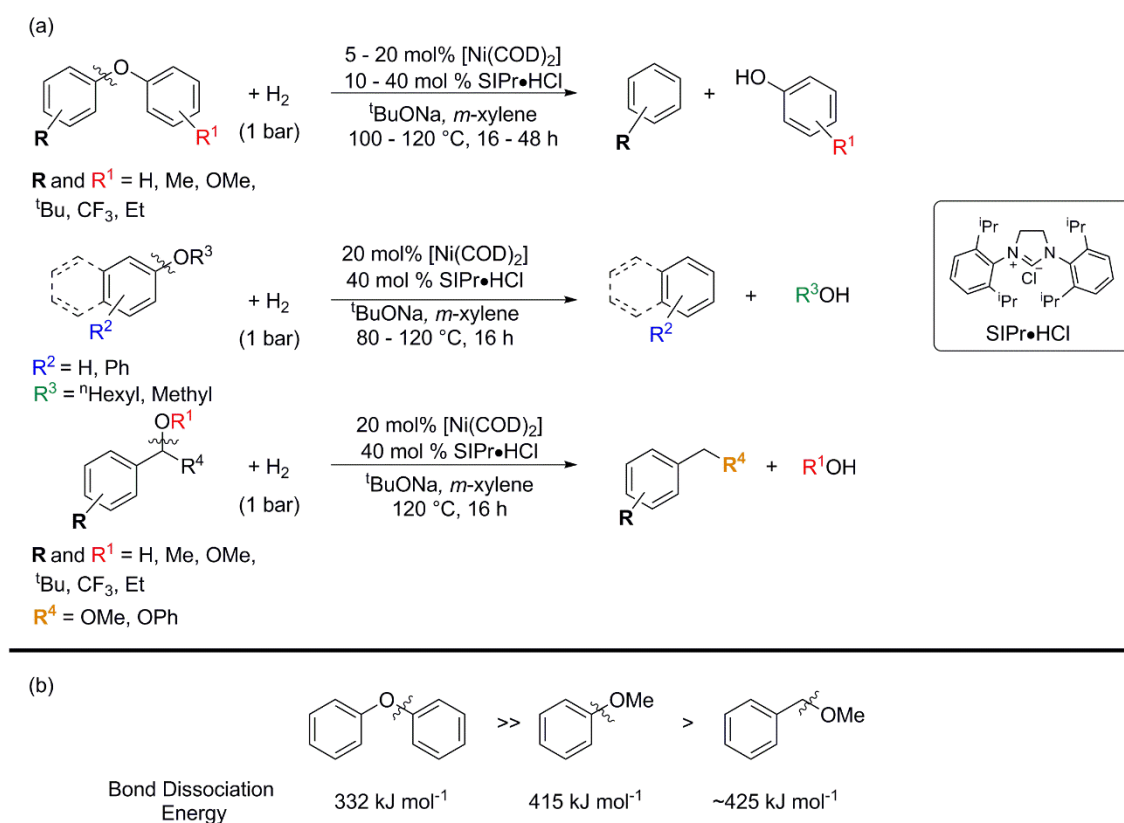


Figure 2.7 Transition state of C--O cleavage step by “Ni(0)-silyl-ate” species stabilised by K^+ cation

In 2011, Hartwig *et al.* reported the nickel catalysed hydrogenolysis of a number of aryl ether substrates.¹⁷ Hydrogenolysis of C–O bonds has traditionally been problematic as hydrogen is a less reactive nucleophile than the main group based nucleophiles used to date (Grignard reagents, organoboranes and organosilanes). Using hydrogen as the reductant could also potentially deactivate the active catalyst in a reaction. After initial screening with different nickel precursors and phosphine ligands a [Ni(COD)₂]/NHC (*N*-heterocyclic carbene) system was found to be the most active at C–O bond cleavage of a wide range of biaryl ether substrates and alkyl aryl ether substrates (Scheme 2.8). An important distinction of these reactions was the selective cleavage and reduction of the C–OR bond of these aryl ethers over the reduction of the electron deficient arene rings which heterogeneous reactions have historically struggled to avoid.¹⁸ The reaction conditions were also successful in the hydrogenolysis of benzyl ethers and therefore demonstrating the success of the cleavage of both *sp*²C–O and *sp*³C–O bonds.



Scheme 2.8.(a) C–O activation of biaryl ethers, alkyl aryl ethers and benzyl ethers, (b) Relative reactivity of ethers towards hydrogenolysis of C–O bonds

Competition reactions indicated the rate of cleavage and subsequent reduction of the C–O bond was fastest for biaryl ethers compared to alkyl aryl ethers which in turn was faster than benzyl ethers. This trend was not too surprising looking at the relative bond strengths of the average respective C–O bonds (Scheme 2.8).¹⁹ Pushing the capabilities of the reaction further, model substrates containing

4-O-5 and α -O-4 lignin linkages were tested out to yield the corresponding depolymerised derivative products: anisole, benzene and phenols in moderate yields. On the other hand, under basic conditions and importantly without the need for catalyst, model substrates containing β -O-4 linkages were still cleaved to give guaiacol as the main product in line with literature precedence.²⁰ The mechanism of these reactions was not probed in detail however Hartwig *et al.* envisioned a number of active nickel species that could be involved in the reaction: nickel hydride, Ni(0) complex and even an anionic nickelate species due to the increased reactivity observed using a strong base. Additionally, the homogeneity of the reaction was investigated. Addition of 300 fold excess of mercury with respect to the nickel catalyst into a standard hydrogenolysis reaction resulted in no decrease in conversion or product yields suggesting the active catalyst in the reaction was homogeneous. However, Martin *et al.* noted in their studies¹⁴ that mercury can react with $[\text{Ni}(\text{COD})_2]$ and does not just form an amalgam with mercury if heterogeneous nickel was present,²¹ so it was interesting that Hartwig *et al.* saw no change in their reactivity. Nevertheless, there are discrepancies with using mercury poisoning as a test for homogeneity of a catalytic reaction.^{22,23} It is worth noting that Hartwig *et al.* have also researched the hydrogenolysis of these biaryl ethers under heterogeneous conditions with nanostructured nickel catalysts (0.25 mol %) and therefore the possibility that heterogeneous nickel was operating in the $[\text{Ni}(\text{COD})_2]/\text{NHC}$ system cannot be ruled out entirely irrespective of the mercury poisoning test.^{24,25}

Following on from this work by Hartwig and Sergeev¹⁷, Surawatanawong *et al.* reported a computational analysis on the mechanism of the hydrogenolysis of biaryl ethers mediated by Ni-NHC system.²⁶ Surawatanawong *et al.* found the most viable mechanism of this reaction involved 3 steps: (i) oxidative addition, (ii) σ -complex assisted metathesis (σ -CAM) and (iii) reductive elimination (Figure 2.8). The first step in this reaction involved the substitution of the COD ligands with one free SIPr ligand and one substrate molecule to form $[\text{Ni}(\text{SIPr})(\eta^6\text{-PhOPh})]$ which was a slightly endergonic process of 5.1 kcal mol⁻¹. $[\text{Ni}(\text{SIPr})(\eta^6\text{-PhOPh})]$ can then readily undergo a rearrangement into $[\text{Ni}(\text{SIPr})(\eta^2\text{-PhOPh})]$ (**INT1**). Alternative active species were also calculated and coordination of the substrate through the oxygen instead was found to be less favourable compared to the π -coordination of the arene ring which can accept π -back donation from the filled d-orbital of the Ni(0) species. From **INT1** oxidative addition of the C_{Ar}-O occurred through a 3-centred transition state **TS1** ($\Delta G^\ddagger = 28.6$ kcal mol⁻¹), to give a Ni(II) species (**INT2**). The oxidative addition of the C_{Ar}-O was also the highest barrier for the whole reaction pathway. From **INT2** dihydrogen complexes at the vacant side onto the nickel centre in an η^2 -fashion to form **INT3** which was a slightly exergonic process ($\Delta\Delta G^\ddagger = -0.6$ kcal mol⁻¹). The arrangement of ligands around **INT3** was set up for σ -CAM process whereby the H-H and Ni-C bonds were broken simultaneously with concomitant formation of C-H and Ni-H bond to release benzene as one of the product and formation of **INT4**. This process was incredibly favourable ($\Delta\Delta G^\ddagger = -18.7$ kcal mol⁻¹). Subsequently, **INT4** underwent reductive elimination to release phenol as the other product and complexation of another substrate helped to regenerate the active species **INT1**. As well as

calculating the mechanism of the reaction, the lack of hydrogenation products observed experimentally was explained by the high energy barrier ($\Delta G^\ddagger = 43.6 \text{ kcal mol}^{-1}$) calculated from **INT1** to form cycloalkanes, so the oxidative addition and subsequent hydrogenolysis of the substrate was the favoured pathway for the reaction to take.

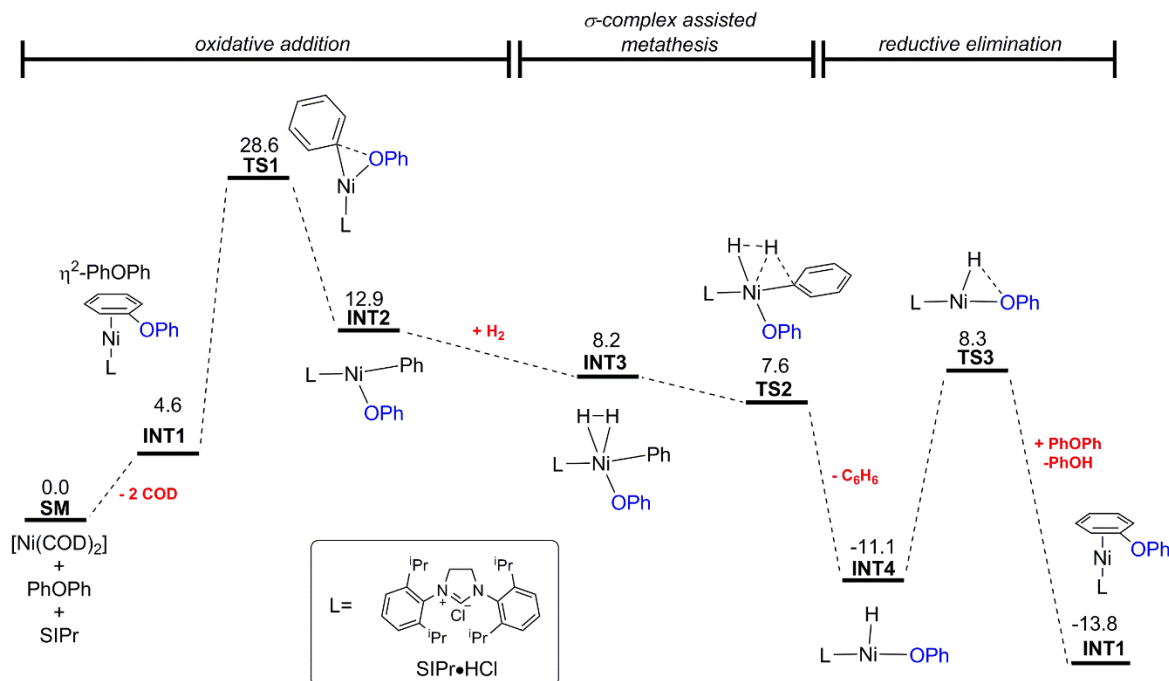


Figure 2.8. Free energy profile of hydrogenolysis of biaryl ether. Gibbs free energy in kcal mol⁻¹

A follow up paper to this work was published in 2016 by Wu *et al.*²⁷ Wu and co-workers sought to address the most salient point omitted by Surawatanawong *et al.*: what was the role of the excess base? Beyond deprotonating the imidazolium salt (SIPr•HCl) to generate the free carbene, the base was also considered to form a favourable active anionic species $[\text{Ni}^0(\text{SIPr})(\text{O}^t\text{Bu})]^-$ (**INT2**) (Figure 2.9) and this species participated in the oxidative cleavage of the C_{Ar}–O bond of PhOPh through a high energy barrier of $\Delta G^\ddagger = 33.4 \text{ kcal mol}^{-1}$ through **TS1**. The addition of the *tert*-butoxide ligand on nickel helped to stabilise the transition state of the C–O cleavage step as well as the resulting anionic intermediate generated, **INT4**. However looking at both energy profiles, even though formation of anionic species was more favoured over the Ni(0) species postulated by Surawatanawong *et al.*, the highest energy barrier was found at $\Delta G^\ddagger = 33.4 \text{ kcal mol}^{-1}$ for the bond cleavage step in Wu *et al.*'s reaction pathway which was higher than the highest energy barrier found in the pathway calculated by Surawatanawong *et al.* ($\Delta G^\ddagger = 28.6 \text{ kcal mol}^{-1}$). The caveat of this conclusion was that different functionals and basis set were used between both investigations and therefore direct comparison of numbers is not accurate. Nevertheless, the probability and complexity of the different pathways that this reaction can undertake

may depend on slight alterations to the reaction conditions and both mechanisms may be relevant to C–O bond activation.

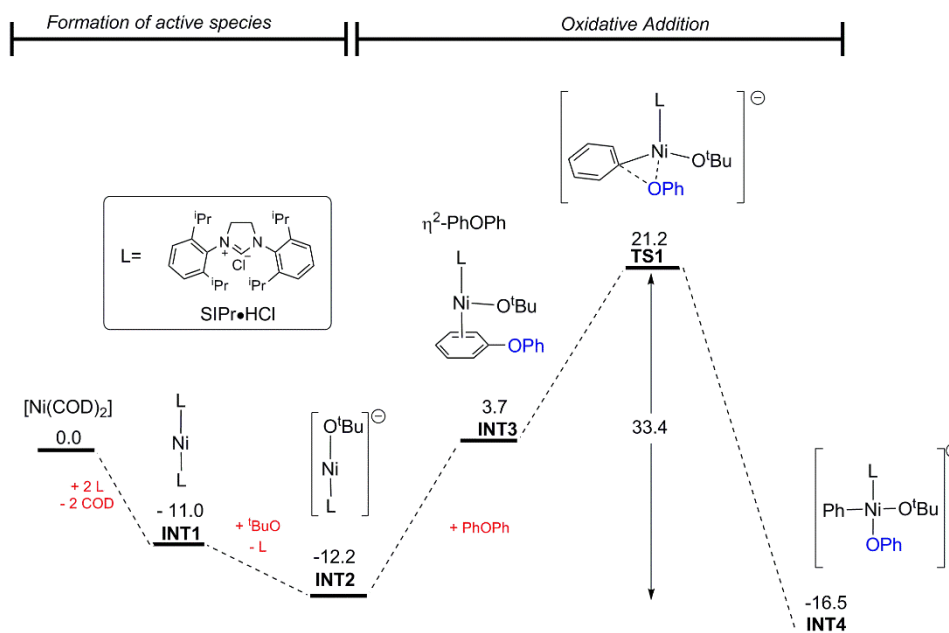
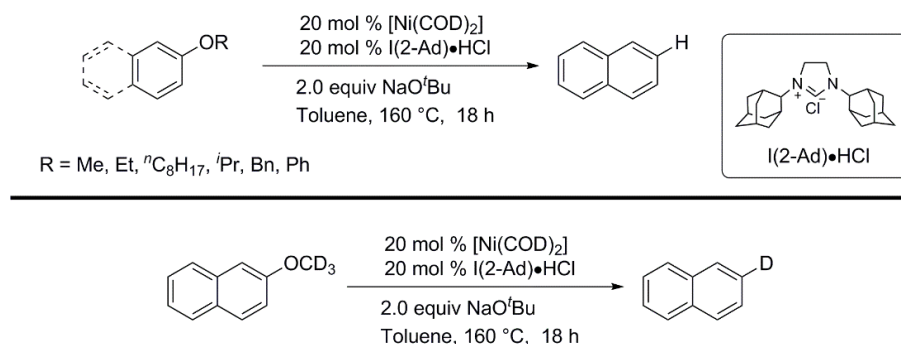


Figure 2.9 Free energy profile the formation of the active anionic species **INT2** and subsequent cleavage of C_{Ar}–O bond. Gibbs free energy in kcal mol⁻¹

More recently in 2015, Chatani *et al.* demonstrated a novel procedure for the reductive cleavage of aryl alkyl ethers but in the absence of an external reductant *i.e.* no silanes or dihydrogen using a $[\text{Ni}(\text{COD})_2]/\text{I}(2\text{-Ad})\cdot\text{HCl}$ ($\text{I}(2\text{-Ad}) = 1,3\text{-bis}(2\text{-adamantyl})\text{-imidazolium}$) system with excess NaO^tBu (Scheme 2.9).²⁸ Chatani and co-workers postulated that the mechanism of this reaction underwent initial oxidative addition of a C_{Ar}–OMe bond across a Ni(0) complex to generate C_{Ar}–Ni–OMe intermediate which underwent facile β -hydride elimination to generate a Ni–H species and it was the Ni–H species which was the reductant in the reaction. When the R group was benzyl, cleavage occurred at both the C_{Ar}–O and C_{Bn}–O position however when R group was Ph, product formation was only 5 % yield. This result would corroborate with the postulated mechanism undergoing β -hydride elimination at the cleaved fragment to form the necessary Ni–H species acting as the reductant and therefore as the Ph group has no β -hydrides, no Ni–H species were formed resulting in low conversion. To further substantiate the mechanism, deuterium labelling experiment was performed and 96 % of the naphthalene product recovered contained deuterium at the cleaved position (Scheme 2.9 - bottom). Furthermore, decomposition product “Ni(CO)” species was observed in the reaction over time which were catalytically inactive and in line with a β -hydride elimination process however no mention of the remaining identity or destination of the cleaved fragment after undergoing β -hydride elimination was found in the paper.

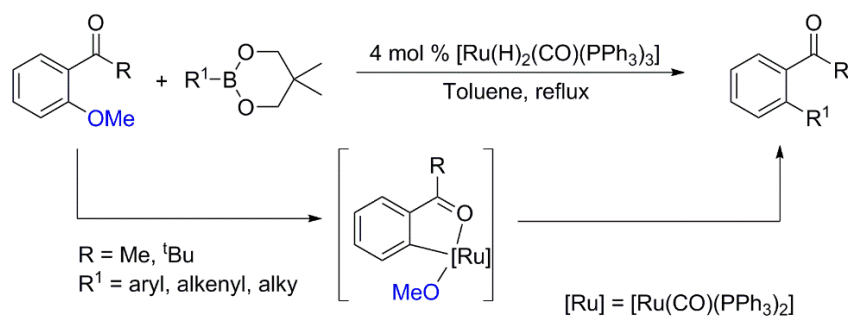
This reaction demonstrated divergent behaviour to what was observed by Martin *et al.*¹⁴ whereby no reaction was observed in their reduction of aryl methyl ethers without any silane present. The use of I(2-Ad) was obviously key to the success of the reaction however no comment about the ligand was provided and in addition, it would be interesting to perform calculations to analyse the nature of the postulated Ni–H species and whether it was a viable reductant source in the reaction.



Scheme 2.9. (Top) Reductive cleavage of aryl alkyl ethers. (Bottom) Deuterium labelling experiment

2.2.2 Ruthenium

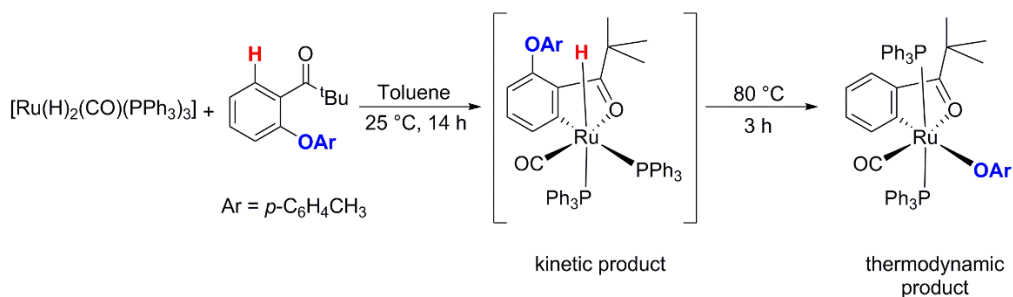
Aside from nickel mediated C–O cleavage reactions, ruthenium mediated reactions have also found success in recent years. In 2004, Kakiuchi *et al.* reported the catalytic functionalisation of aromatic ethers bearing a ketone directing group with organoborane compounds mediated by [Ru(H)₂(CO)(PPh₃)₃] (Scheme 2.10).²⁹ This work followed a series of papers on chelation assisted bond activation chemistry investigated by Murai *et al.*^{30,31} For example, reactions that cleaved C(O)–OR bonds of esters using pyridine as the directing group and also C–H activation of acetophenone substrates whereby the ketone functionality assisted in chelation of the substrate to the ruthenium centre. The investigation noted that a ketone directing-group was needed for bond activation chemistry as anisole failed to give any product, and also where the substrate had more than one C–O bond on the aryl ring, the C–O bond *ortho* to the ketone was cleaved preferentially. When 2,6-dimethoxyacetophenone was used as the substrate both the mono-substituted and di-substituted product were formed. It was observed when 2-methoxypivalophenone was the substrate C–O functionalisation was achieved exclusively and the *ortho* C–H position was left intact. No explanation was given for this selectivity in this paper however a possible reaction involving formation of a 5-membered cyclometallated intermediate was proposed (Scheme 2.10).²⁹



Scheme 2.10. C–O cleavage of acetophenone substrates via a 5-membered intermediate

It is worth noting that the speculated 5-membered cyclometallated intermediate was analogous to an intermediate proposed in the *ortho* C–H functionalisation of acetophenones.³¹ In 2005, Kakiuchi and co-workers published a detailed experimental analysis on the mechanism of C–H functionalisation reaction.³² Intermolecular and intramolecular deuterium labelling experiments showed that the rate determining step most likely involved C–H bond cleavage step. In addition, a higher kinetic isotope effect (KIE) was observed for the intramolecular competition. This led the group to ascertain that the intermediate formed during the reaction was coordinated to the ruthenium. A second observation from their investigation deduced that a sacrificial hydrogen trap was required for high yield of product to prevent hydrogenation of the ketone functionality of the substrate.

In 2006, the isolation and single crystal X-ray crystallographic data of the postulated 5-membered intermediate from the C–O activation of an aryl ether substrate (2,2-dimethyl-1-(2-*p*-tolylphenyl)propan-1-one) was achieved.³³ In later studies this 5-membered intermediate was shown to be catalytically competent in these functionalisation reactions of acetophenone substrates to unambiguously show that these 5-membered structures were active intermediates in these reactions.³⁴ It was discussed that at 25 °C the intermediate from the C–H activation at the *ortho* position was initially observed by NMR spectroscopy, and only after the reaction was heated to 80 °C for 3 h that isomerisation to the C–O activated product was completed to form the 5-membered intermediate (Scheme 2.11). This suggested the C–H activation of the substrate was the kinetic product but the C–O activated product was the thermodynamic product.



Scheme 2.11. Products from C–H and C–O activation of 2,2-dimethyl-1-(2-*p*-tolylphenyl)propan-1-one

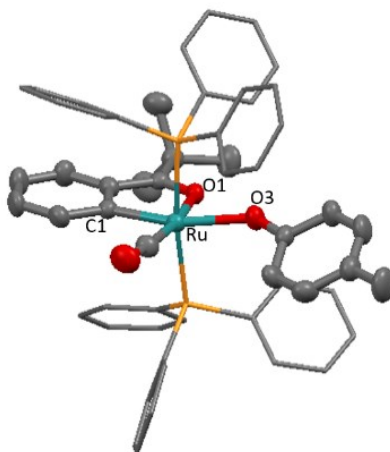
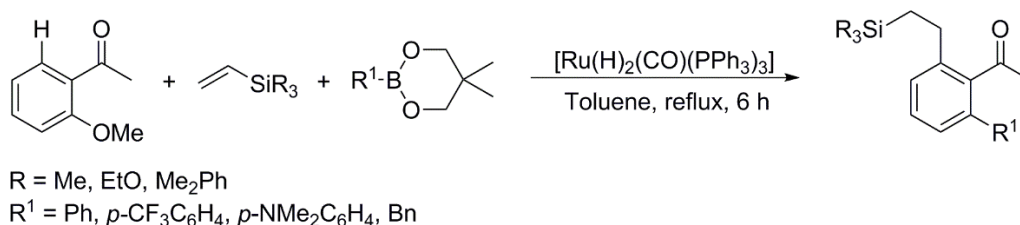


Figure 2.10. X-ray structure of product from C–O activation of 2,2-dimethyl-1-(2-*p*-tolylphenyl)propan-1-one

The difference in reactivity between C–H and C–O activation allowed for selective sequential C–C bond formation of 2-methoxyacetophenone using vinylsilanes and organoboranes (Scheme 2.12). Placing all reactants in the same vessel and monitoring the reaction products as a function of time the group deduced that (i) C–H/alkene coupling was faster than C–H/organoborane coupling and (ii) once Ru–OMe intermediate was formed from C–O cleavage, the transmetalation step with the organoborane was faster than potential β -hydride elimination pathway.

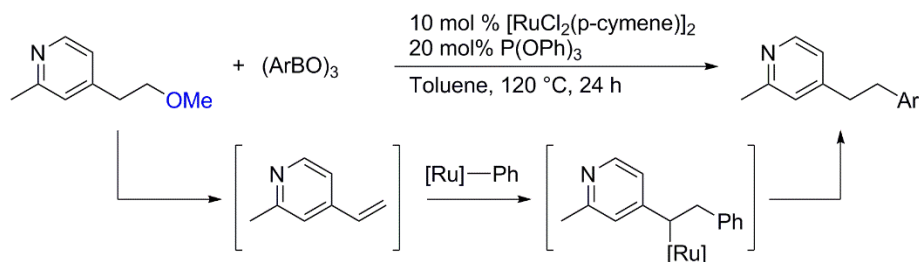


Scheme 2.12. Sequential C–C bond formation

A similar intramolecular competition reaction with C–OMe and C–NMe₂ bonds occupying the *ortho* positions of acetophenone substrate was also investigated.³⁴ [Ru(H)(OAc)(CO)(PPh₃)₃] was the catalyst precursor with CsF as an additive. Exclusive cleavage and functionalisation of the C–NMe₂ bond was observed which was understood as the unconventional chemoselectivity based on the fact that amino groups are more electron donating than methoxy groups so should proceed less favourably for an oxidative addition process across a transition metal centre. No further comment on this unconventional reactivity was made by Kakiuchi *et al.*^{35,36}

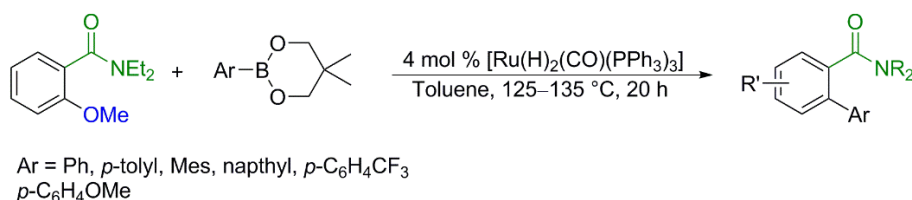
Expansion from *sp*²C–O bond cleavage to the *sp*³C–O bond cleavage of dialkyl ethers bearing pyridine group was demonstrated in 2011 by Kakiuchi *et al.* (Scheme 2.13).³⁷ While monitoring the

coupling reaction of 4-(2-methoxyethyl)-2-methylpyridine with (PhBO)₃ it was observed *via* ¹H NMR spectroscopy that 2-methyl-4-vinylpyridine was being produced. Starting directly from 2-methyl-4-vinylpyridine and placing this substrate under the same catalytic conditions, successful coupling with (PhBO)₃ was observed. This result indicated that these reactions go through a dehydroalkoxylation process, most likely assisted by the chelation of the –OMe to the ruthenium centre, to generate these vinyl pyridine intermediates before continuing with the coupling with the aryl boroxines.



Scheme 2.13. Chelation assisted *sp*³C–O activation. Ligands around Ru omitted for clarity

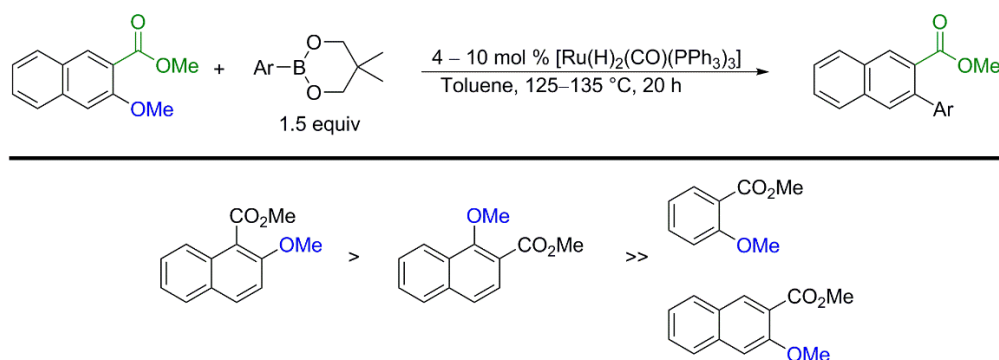
Expanding on the directing group assisted C–O cleavage of these aromatic substrates, in 2014 Snieckus *et al.* investigated how altering the directing group can affect the selectivity of the C–X (X = H, O) bond being broken. The exclusive *ortho* C–O bond cleavage of 2-methoxypivalophenone was originally attributed to the greater steric bulk from the R-group on the ketone directing group aligning towards the *ortho* C–H position and therefore shielding this position from attack leaving the *ortho* C–O position vulnerable. Snieckus *et al.* showed that changing the directing group from ketone to an amide group shut down the pathway for C–H functionalisation and the reaction yielded exclusive C–O functionalisation (Scheme 2.14).³⁸ From observing this selectivity, the reaction conditions were manipulated to build up complexity of simple aromatic substrates by undergoing Pd mediated Suzuki-Miyaura cross coupling followed by C–O functionalisation reactions. Nevertheless, no further scrutiny of the mechanism of this amide group assisted C–O functionalisation was discussed. These reaction conditions were further expanded by Snieckus *et al.* and included naphthalene derived substrates.³⁹



Scheme 2.14. Amide directed C–O activation

Following from this work Snieckus *et al.* also investigated the use of esters as directing groups in these reactions (Scheme 2.15).⁴⁰ The cross-coupling of naphthoates, exclusively at the *ortho* C–O

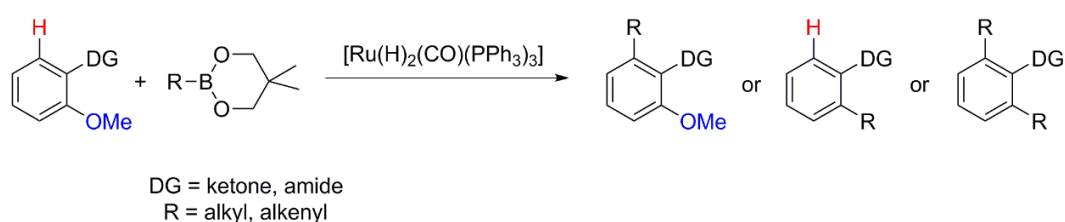
position, with organoborane substrates were successful whereas benzoates yielded only trace product. It was noted that naphthalenes are more reactive substrates due to the greater π -conjugation interred in the system. The group were able to identify an order of reactivity between isomeric naphthoates which followed the previous trend seen in their previous studies on naphthamides.³⁹ This work once again demonstrates the potential to add complexity to simple aromatic molecules based on orthogonal reactivity.



Scheme 2.15. (Top) Ester directed C–O functionalisation. (Bottom) reactivity order of isomeric naphthoates

Even though the investigations into the reactivity of ruthenium mediated C–X (X = H, O) functionalisation have provided a gateway towards synthetic advancement, much less investigation into the mechanism of these reaction, compared to the nickel counterpart, has been reported.

In 2017 Lin *et al.* reported a computational study on the mechanism C–X (X = H, O) bond functionalisation reactions of acetophenone substrates with organoborate substrates mediated by $[\text{Ru}(\text{H})_2(\text{CO})(\text{PPh}_3)_3]$.⁴¹ The study investigated the effect that different nucleophiles (organoboranes) and different directing groups had on the chemoselectivity of the reaction (Scheme 2.16). The mechanism of the C–H functionalisation reaction was broken down into 4 fundamental steps (i) oxidative addition of the C–H bond to a ruthenium(0) centre, (ii) ketone insertion in to the newly formed Ru–H bond (iii) transmetallation of the resulting Ru alkoxide with the organoborate substrate, and finally (iv) reductive elimination to release the product with the new C–C bond and regeneration of active species. For C–O functionalisation the fundamental steps were the same omitting step (ii) ketone insertion as no Ru–H bond is generated.



Scheme 2.16. Model C–X bond (X = H, O) functionalisation reaction examined by DFT

The first model reaction analysed was the C–X (X = H, O) functionalisation of 2-methoxyacetophenone with PhBneop (Bneop = 5,5-dimethyl-2-aryl[1.3.2.]dioxaboranane). The d⁸-square planar Ru(0) complex “[Ru(CO)(PPh₃)₃]” was invoked as the active species based on precedent in literature.^{42,43} From “[Ru(CO)(PPh₃)₃]” coordination of the carbonyl group of 2-methoxyacetophenone to the ruthenium centre generated (**INT1**) as the starting point of the reaction profile (Figure 2.11).

Focusing on the C–H bond activation pathway (red line), the highest transition state for the oxidative addition step was calculated to be $\Delta G^\ddagger = 2.1 \text{ kcal mol}^{-1}$ through a 3-centred transition state (**TS1**) to generate the favourable cyclometallated intermediate (**INT2**) ($\Delta G^\circ = -9.3 \text{ kcal mol}^{-1}$). The subsequent ketone insertion step, transmetallation step with PhBneop and reductive elimination of the product revealed that the highest activation barrier calculated throughout these three steps was $\Delta G^\ddagger = 23.4 \text{ kcal mol}^{-1}$ through **TS2** which was the transmetallation process of the migration of the Ph group from the boron centre to the ruthenium. Formation of the product from C–H functionalisation (2-methoxy-6-phenylacetophenone) and reformation of **INT1** was favourable ($\Delta G^\circ = -10.4 \text{ kcal mol}^{-1}$).

Focusing on the C–O functionalisation pathway, the highest transition state found for the oxidative addition step was $\Delta G^\ddagger = 12.8 \text{ kcal mol}^{-1}$ through a similar 3-centred transition state (**TS3**) to generate the cyclometallated intermediate (**INT3**) ($\Delta G^\circ = -11.3 \text{ kcal mol}^{-1}$). The highest energy barrier for the subsequent transmetallation and reductive elimination steps was calculated to be $\Delta G^\ddagger = 13.6 \text{ kcal mol}^{-1}$ through **TS4**. Again, formation of the product from C–O functionalisation (2-phenylacetophenone) and reformation of **INT1** was favourable ($\Delta G^\circ = -22.1 \text{ kcal mol}^{-1}$).

Comparing both C–X oxidative addition steps, the highest transition energy for this step was calculated for C–O activation (**TS1** *versus* **TS3**) however the resulting formation of the 5-membered cyclometallated intermediate (**INT2** *versus* **INT3**) was more favourable for the C–O activation pathway. This indicated a kinetic preference for C–H activation product but the thermodynamic product was *via* C–O cleavage which mirrored what was observed in experimental data.³³ Looking at the entirety of the C–X functionalisation pathway, the highest activation barrier was found during the transmetallation process for both pathways (C–H, $\Delta G^\ddagger = 23.4 \text{ kcal mol}^{-1}$; C–O, $\Delta G^\ddagger = 13.6 \text{ kcal mol}^{-1}$). Therefore, even though the actual bond breaking step was lower in energy for the C–H pathway rather than the C–O pathway, the subsequent functionalisation step was favoured for the C–O pathway. Therefore, the C–X functionalisation reaction was determined by the relative stability of the transition state structure of **TS2** *versus* **TS4** in the transmetallation step (Figure 2.11).

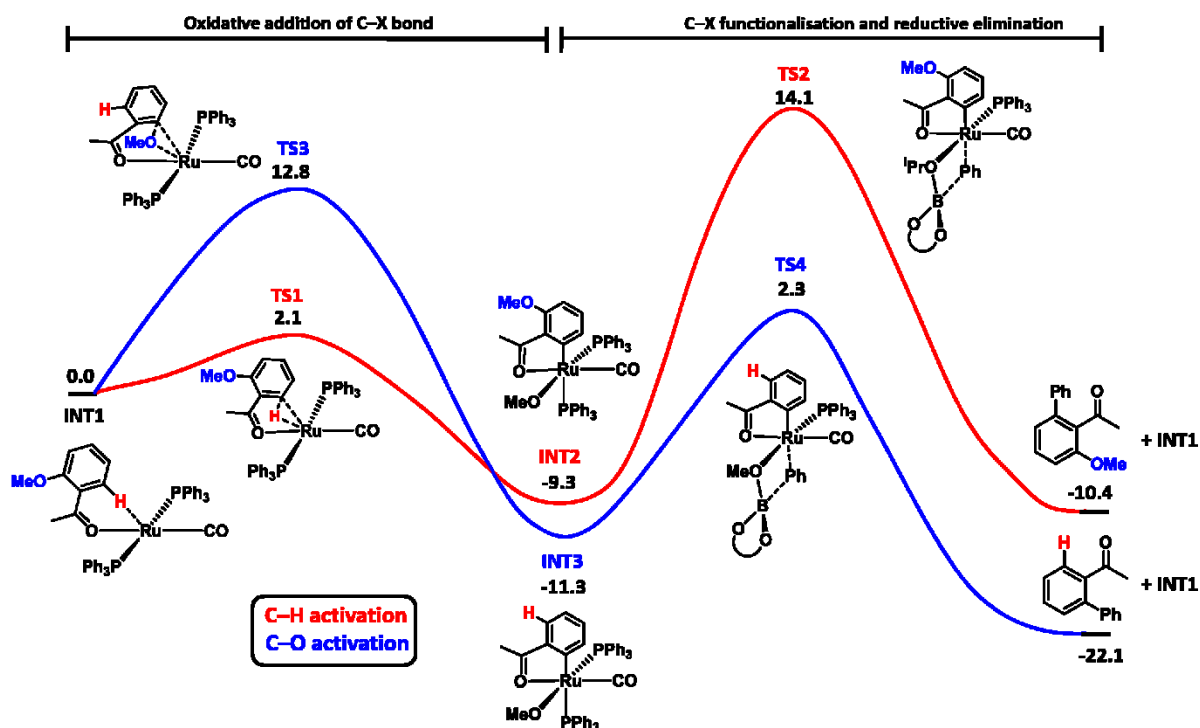


Figure 2.11. Calculated highest TS and selected stationary points for C–H (red) and C–O (blue) functionalisation. Gibbs free energies in kcal mol⁻¹

From the conclusion above, Lin *et al.* proposed that altering the organoborate coupling partner (nucleophile) should alter **TS2** and **TS4** respectively during the transmetallation step and therefore this step decides whether C–H or C–O bond functionalisation was observed. The previous steps for the oxidative addition of the C–X bond should not be altered by changing nucleophile, so the remaining calculations focused on the functionalisation steps.

Using SrBneop (Sr = (*E*)-styryl) Kakiuchi *et al.* found that an alkenyl group compared to an alkyl on the borane helped to shut down the C–O functionalisation pathway.⁴⁴ The C–X functionalisation of 2-methoxyacetophenone with SrBneop was modelled by DFT. Focusing on just the C–H pathway, the barrier for the important transition state during the transmetallation step was calculated to be $\Delta G^\ddagger = 10.2$ kcal mol⁻¹. The stabilisation was justified as the result of the π interaction of the alkenyl group stabilising the Ru(II) centre of intermediates and transition states. Lin *et al.* concluded that the barrier of the transition state of this transmetallation step was now lower than the energy of the C–O bond breaking step ($\Delta G^\ddagger = 12.8$ kcal mol⁻¹) and therefore the C–H cleavage step was no longer reversible resulting in both the C–H cleavage and functionalisation becoming the favoured pathway and why C–H functionalisation of 2-methoxyacetophenone with SrBneop was the major product. However, inspecting the actual energy barrier for the transmetallation step and not the absolute Gibbs free energy values, the barrier was calculated to be $\Delta G^\ddagger = 19.5$ kcal mol⁻¹ which was higher than the highest energy barrier for the C–O activation step therefore the conclusion by Lin *et al.* was not

valid. No report of the C–O functionalisation of 2-methoxyacetophenone with SrBneop was reported and therefore the comparison of the entirety of the both C–X functionalisation pathway could not be analysed to justify the experimental observations by Kakiuchi *et al.*⁴⁴

It was observed by Snieckus *et al.* (Scheme 2.14) that using an amide directing group on the substrates resulted in just *ortho*-C–O functionalisation regardless of whether alkyl Bneop or alkenyl Bneop was used as the nucleophile (*vide supra*).³⁸ The investigation by Lin *et al.* pointed towards the ketone insertion step as the important factor. Only the transition state for the C–X oxidative addition and transmetallation steps were calculated for the model reaction using the 2-methoxy-*N,N*-dimethylbenzamide as the substrate and SrBneop as the coupling partner. For the C–H pathway, without a ketone acceptor (sacrificial or the substrate) the highest transition barrier for the insertion of the unsaturated C=O bond of the amide into the Ru–H bond was calculated to be significantly higher in energy ($\Delta G^\ddagger \geq 40.2 \text{ kcal mol}^{-1}$ *N.B.* the intermediate structures were not calculated so the true energy barrier could only be calculated in comparison to the starting materials) compared to ketone directing group pathway ($\Delta G^\ddagger = 18.6 \text{ kcal mol}^{-1}$). This carbonyl insertion into Ru–H bond step was unnecessary for the C–O functionalisation pathway and therefore the C–H pathway was shut down in this instance and only C–O functionalisation product was observed when an amide directing group was used. Lin *et al.* hypothesised that repeating the reaction performed by Snieckus' group, with PhBneop as the nucleophile, but importantly adding a sacrificial ketone should allow both the C–H and C–O bond functionalisation to occur.

DFT calculations were also performed by other groups on the ruthenium mediated Murai-coupling of an alkene and acetophenone.^{42,43,45} Morokuma *et al.* showed carbonyl binding to the ruthenium centre was necessary for bond formation, moreover coordination of the substrate to the ruthenium catalyst was found to be favourable.⁴³ Importantly the active species was always assumed to be a “Ru(CO)(PPh)_n” (n = 2 or 3) species based on the experimental evidence that transfer hydrogenation of ketone was observed in parallel to the desired product formation in stoichiometric reactions. The same assumption was taken by Lin *et al.* in their investigation however DFT data reported by Clot *et al.* on a similar reaction but modelling with [Ru(H)₂(η^2 -H₂)₂(PMe₃)₂] as the pre-catalyst looked specifically at how the active species was generated in the Murai-type coupling reaction of acetophenone with ethene (Figure 2.12).⁴⁵ The investigation found that binding of the potential ligands around this ruthenium complex followed the expected trend: η^2 -C₄H₂ > η^2 -H₂ > ketone > σ -(C–H). This allowed Clot and co-workers to conclude that “[Ru(H)₂(PMe₃)₂]” was the most likely active species generated from substitution of one of the η^2 -H₂ ligand with ethene with the remaining η^2 -H₂ hydrogenating the bound ethene. The highest transition energy barrier for this process was found at $\Delta G^\ddagger = 6.7 \text{ kcal mol}^{-1}$. In comparison, the direct substitution of the two η^2 -H₂ ligands by the acetophenone was uphill by $\Delta G^\ddagger = 14.2 \text{ kcal mol}^{-1}$. The importance of the route to generating the active species should therefore not be neglected when investigation the mechanism of a reaction.

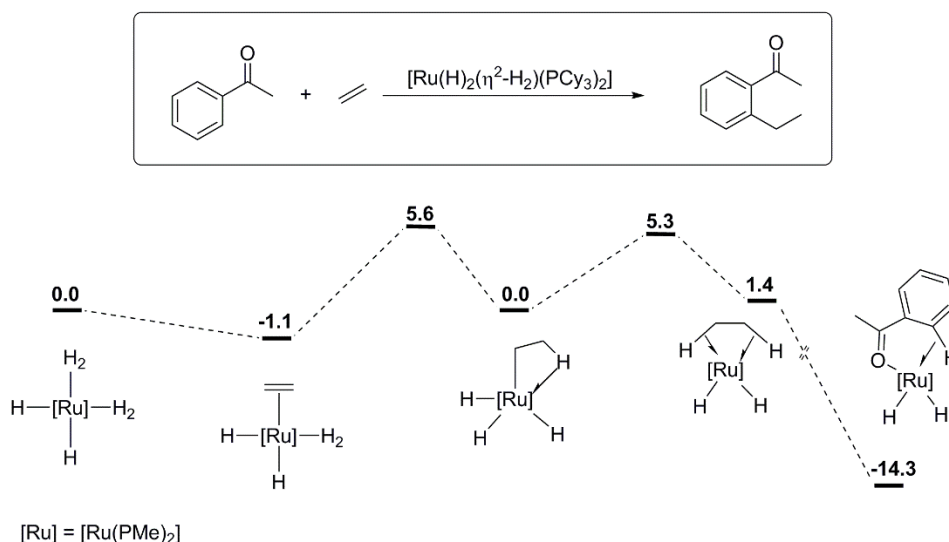


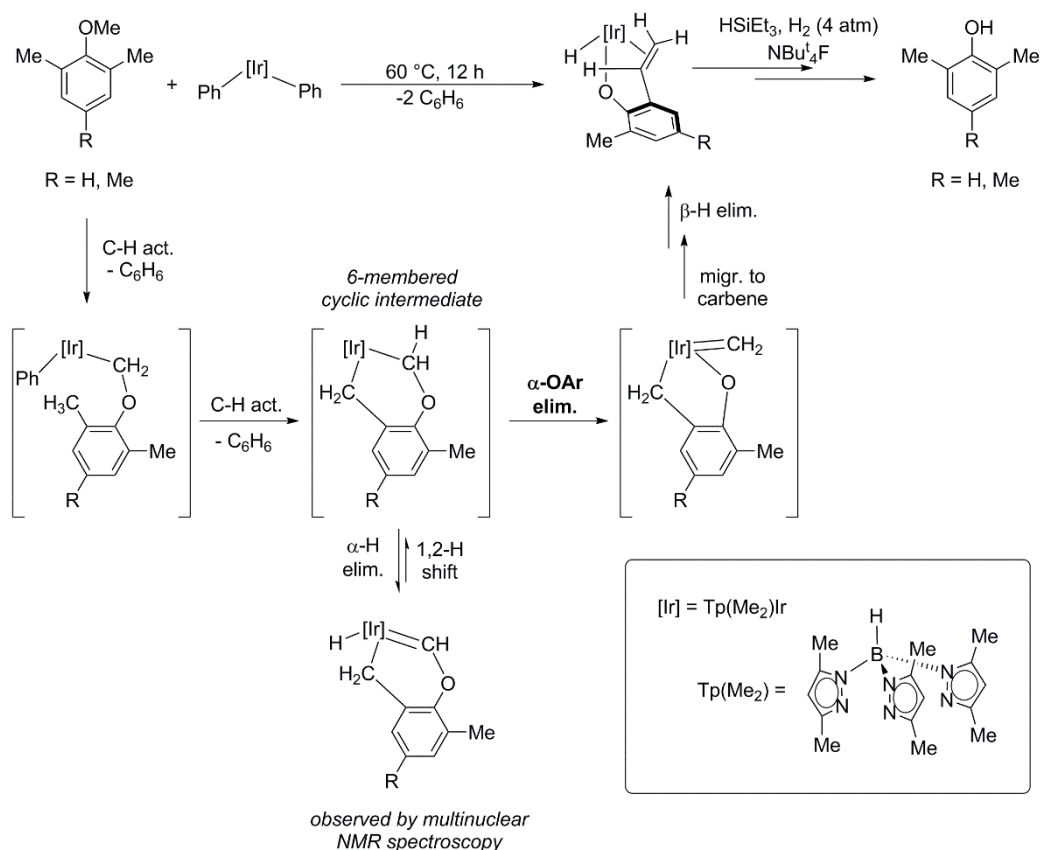
Figure 2.12. Lowest calculated energy reaction profile to generate reactive ruthenium species for the Murai coupling reaction of acetophenone with ethene. *Trans* PMe₃ omitted for clarity. Gibbs free energies in kcal mol⁻¹

The experimental and computation studies above highlight how a variety of nickel and ruthenium species can be formed depending on the reaction conditions and therefore understanding the initial steps before bond breaking of these C–X (X = H, O) cleavage reactions is incredibly pertinent. Different factors combine to alter the potential mechanistic pathway these reactions will ultimately undertake and therefore proposing the usual TM(0)/TM(II) (TM = Ni or Ru) may be too simplistic. In addition, analysing the entirety of a reaction profile may justify the chemoselective behaviour demonstrated in these reactions.

2.2.3 Iridium

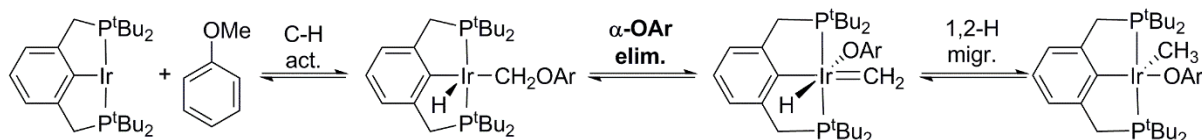
It is worth briefly highlighting some recent work into the mechanistic investigation of *sp*³C–O bond activation mediated by iridium complexes involving carbene intermediates. In 2006, Paneque and Carmona *et al.* reported the conversion of 2,6-dimethyl-substituted anisoles into the corresponding phenols involving formation and cleavage of C–H, C–C and C–O bonds (Scheme 2.17).^{46,47} It was proposed the mechanism of the reaction underwent initial *sp*³C–H activation of the –OMe group of the anisole followed by a second *sp*³C–H activation process of the *ortho*-Me group to generate a 6-membered cyclic intermediate. This intermediate underwent a reversible α-H elimination step to generate an iridium carbene intermediate that was detected by multinuclear NMR spectroscopy. In addition, this α-H elimination step was anticipated to be in competition with an α-OAr elimination process to form a different carbene species (not detected by multinuclear NMR spectroscopy). Following the C–O cleavage route, a further migratory insertion step and then a β-hydride elimination step yielded an iridium hydride aryloxy intermediate. The iridium hydride aryloxy compound can

be isolated and undergo further transformations (silylation and then hydrolysis) to form the desired phenol product.



Scheme 2.17. $[\text{Ir}(\text{Tp}(\text{Me}_2))\text{Ph}_2]$ mediated $\text{sp}^3\text{C}-\text{O}$ bond cleavage via a carbene intermediate.

In similar studies, Goldman *et al.* probed experimentally and computationally the $\text{sp}^3\text{C}-\text{O}$ cleavage of anisoles with an iridium pincer complex and also postulated the formation of a carbene intermediate in the mechanism of the reaction (Scheme 2.18).^{48,49} A positive kinetic isotope effect through deuterium labelling of the $-\text{OMe}$ group suggested a pathway involving initial C-H activation of methyl group as opposed to simple direct oxidative addition of the C-O bond. This mechanism was supported by DFT calculations and demonstrated an alternative mechanism to C-O cleavage reactions mediated by transition metals.



Scheme 2.18 Iridium pincer complex mediated $\text{sp}^3\text{C}-\text{O}$ bond cleavage via a carbene intermediate.

2.3 RESULTS AND DISCUSSIONS

The focus of this chapter will look at C–O bond activation of acetophenone substrates containing methyl ether and aryl ether motifs. From the work by Kakiuchi *et al.*^{29,31} the inclusion of a directing group was important for the success of bond cleavage to occur as the directing group not only provided a route of pre-complexation to the transition metal complex but helped to direct the *ortho*-position of the aryl group towards activation.

The ruthenium *bis*(dihydrogen) complex $[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$ (**1-2H₂**) was capable of X–H (X = C, N, O) bond activation but nothing has been reported concerning C–O activation.⁵⁰ Whether this was due to unsuccessful attempts to cleave C–O bonds or whether this area was never researched was not clear however this provided an opportunity to explore the reactivity of the analogous ruthenium *bis*(dinitrogen) complex $[\text{Ru}(\text{H})_2(\text{N}_2)_2(\text{PCy}_3)_2]$ (**1**). **1** provides more labile ligands in the form of the end on bound dinitrogen in comparison to the phosphines and carbonyl ligands ligated to the traditional ruthenium catalysts used for these C–H and C–O bond activation chemistry (*vide supra*).

The following body of work will combine experimental and computational analysis on the *sp*²C–O bond activation of acetophenone substrates mediated by a ruthenium *bis*(dinitrogen) complex (**1**). In addition, preliminary investigations into the functionalisation of the C–X (X = H, O) bond will be explored with main group reagents HBpin (pin = pinacolato) and B₂pin₂ as the coupling partner (Figure 2.13).

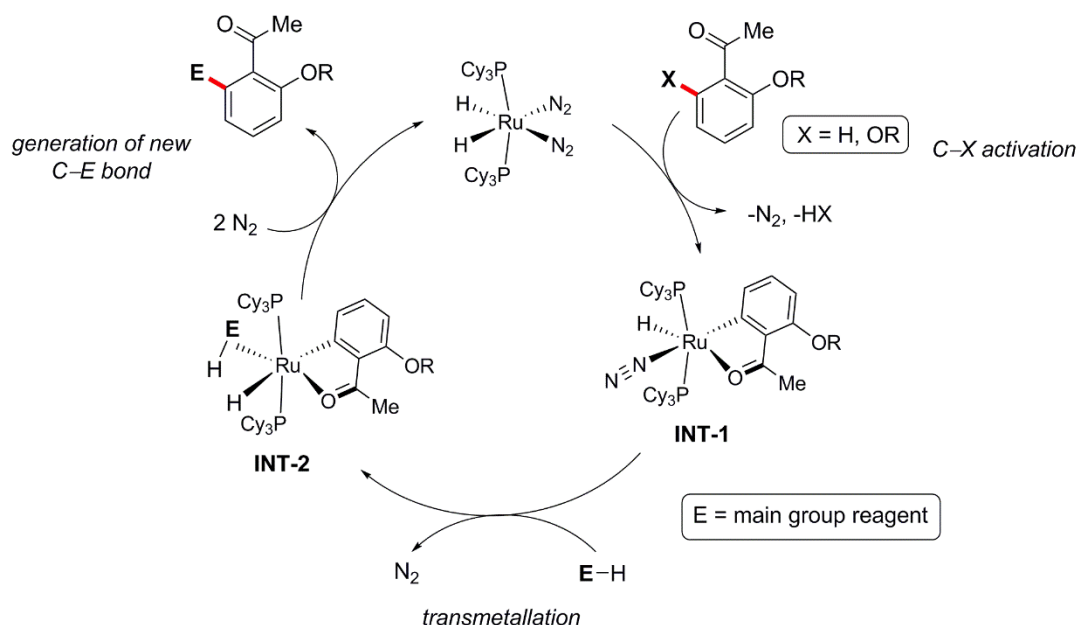
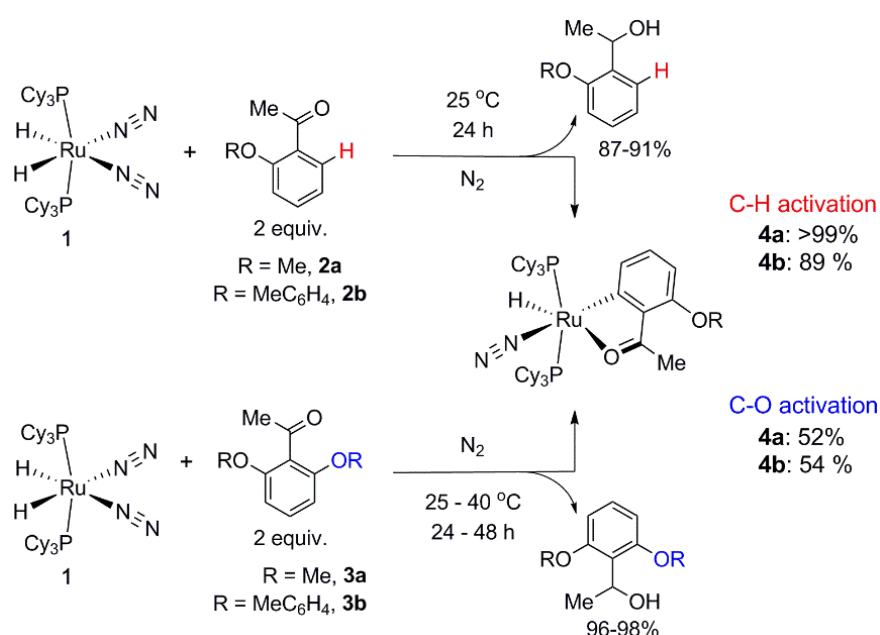


Figure 2.13. Idealised catalytic cycle on the functionalisation of C–X (X = H, O) bond in acetophenone substrates mediated by **1**

2.3.1 C–H activation

The reaction of the ruthenium *bis*(dinitrogen) complex $[\text{Ru}(\text{H})_2(\text{N}_2)_2(\text{PCy}_3)_2]$ with 2-methoxyacetophenone (**2a**) or 2-*p*-tolylloxyacetophenone (**2b**) in a 1:2 ratio proceeded rapidly at 25 °C to form the corresponding cyclometallated species **4a–b** from the *ortho*-C–H activation of one equivalent of substrate. This reaction was accompanied by transfer hydrogenation of the second equivalent of substrate to generate the arylethanol substrates (Scheme 2.19).⁵¹ When the reaction was performed with a 1:1 ratio of reagents, the same result was observed but 0.5 equiv. of **1** remained unconsumed. Synthesis of genuine samples of the arylethanol substrates allowed for doping of these substrates into the reaction mixtures and confirmed the formation of the transfer hydrogenation products.



Scheme 2.19. $sp^2\text{C–H}$ and $sp^2\text{C–O}$ activation of acetophenone substrates.

Complexes **4a** and **4b** were characterised by distinctive triplets in the hydride region of the ^1H NMR spectrum at $\delta = -14.89$ (t, $^2J_{\text{P–H}} = 24.5$ Hz) and -14.82 (t, $^2J_{\text{P–H}} = 24.1$ Hz) ppm respectively along with near identical $^{31}\text{P}\{^1\text{H}\}$ resonances (**4a**, $\delta = 39.1$ ppm; **4b**, $\delta = 39.9$ ppm). While ultimately resolved by X-ray diffraction studies (Figure 2.14), the retention of the dinitrogen ligand on ruthenium was supported by infrared absorptions for both Ru–H (**4a**, 1964 cm^{-1} ; **4b**, 1983 cm^{-1}) and N $\equiv$ N bonds (**4a**, 2078 cm^{-1} ; **4b**, 2106 cm^{-1}). The ruthenium-bound carbon atoms of the cyclometallated ligands were observed in the expected region of the ^{13}C NMR spectrum and correlated with the Ru–H resonance by ^1H - $^{13}\text{C}\{^1\text{H}\}$ HMBC experiments (**4a**, $\delta = 212.2$ ppm; **4b**, $\delta = 211.8$ ppm).

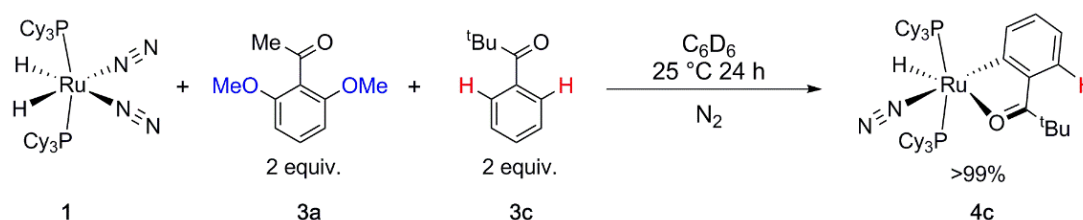
No *ortho*-C–O activation of the acetophenone substrates was observed by multinuclear NMR spectroscopy. Kakiuchi *et al.* demonstrated that 2,2-dimethyl-1-(2-*p*-tolylphenyl)propan-1-one first underwent *ortho*-C–H activation at 25 °C and the isomerisation of the product to the *ortho*-C–O activation product was not achieved until the reaction mixture was heated to 120 °C.³³ The reaction mixtures of the acetophenones with **1** were heated to 50 °C however no isomerisation to the *ortho*-C–O activation product was observed. Further attempts to force the isomerisation by photochemical conditions (400 W, Hg lamp) also failed.

Based on the observation above, the potential C–H activation pathway of these acetophenone substrates were blocked by investigation of substrates that only contained C–O bonds in the *ortho* position of the ketone directing group. The reactions of 2,6-dimethoxyacetophenone with **1** were investigated.

2.3.2 C–O activation

At 25 °C, addition of **1** to 2,6-dimethoxyacetophenone (**3a**) resulted in C–O bond activation, producing **4a** as the predominant ruthenium-containing product alongside transfer hydrogenation of the second equivalent of substrate to form the corresponding arylethanol product. Analogous reaction was performed using the biaryl ether substrate **3b** to form complex **4b** (Scheme 2.19). These results demonstrate that the ruthenium *bis*(dinitrogen) complex was capable of cleaving both *sp*²C–OMe and *sp*²C–OAr bonds, however slowly at 25 °C. The reaction conditions were optimised to 40 °C in order to increase the rate of reaction. The choice of this low temperature was determined as the ruthenium complex underwent side-reactions with itself at elevated temperatures along with H/D exchange with the deuterated solvent (CHAPTER 1).

In the case of substrates **2a–b**, despite the presence of both *ortho* C–H and C–O bonds, exclusive C–H activation was observed. Similarly, an intermolecular competition experiment in which **1** was reacted with 2 equiv. of **3a** and 2 equiv. of 2,2-dimethylpropiophenone led to exclusive formation of the C–H activation product **4c** (Scheme 2.20).



Scheme 2.20. Intermolecular competition between *sp*²C–H and *sp*²C–O activation

The propensity of [Ru(H)₂(η^2 -H₂)₂(PCy₃)₂] (**1-2H₂**) to effect the cyclometallation,⁵² and catalytic functionalisation,^{53,54} of the *sp*²C–H bond of aromatic substrates containing a suitable directing

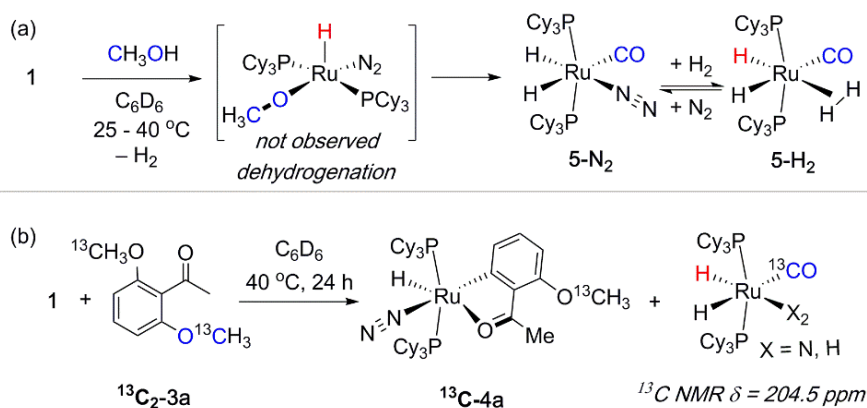
group was well established, however nothing has been reported concerning C–O bond activation. Reaction of **3a** with $[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$ under an atmosphere of H_2 failed to result in C–O bond cleavage of the acetophenone substrate with only transfer hydrogenation of the substrate to form the corresponding alcohol observed regardless of the reaction stoichiometry. Control reactions confirmed that C–O bond activation was sensitive to the nature of the ligands on ruthenium (N_2 versus H_2) but also sensitive to the atmosphere under which the reaction was conducted. Reaction of **1** with **3a** under argon proceeded to give **4a** over 5 h while that under N_2 required 24 h to reach completion: more accurately, $t_{1/2}(\text{N}_2) = 6.0$ h and $t_{1/2}(\text{Ar}) = 1.6$ h. In combination the experiments show that, while a labile N_2 ligand on ruthenium was necessary for C–O activation exogenous N_2 inhibits the rate of this reaction.

It was notable that, although both C–O cleavage reactions of **3** with **1** proceeded to give organometallics in approximately 50 % yield, neither contain the –OR fragment from the broken C–OR bond. Furthermore, transfer hydrogenation of the organic substrates occurred in both C–H and C–O activation reactions to form the arylethanol substrates as by-products to these reactions. These data raise a number of questions: What was the destination of the –OMe and –OAr groups following C–O bond cleavage? What was the source of dihydrogen for the transfer hydrogenation? And was transfer hydrogenation required to generate a reactive Ru-complex capable of effecting C–O bond cleavage?

2.3.3 By-Product

It was hypothesised that the initial side-products of C–O bond activation were the alcohols, methanol (from **3a**) and 4-methyl phenol (from **3b**), that go on to react with **1** at a faster or equal rate than the ethers themselves.

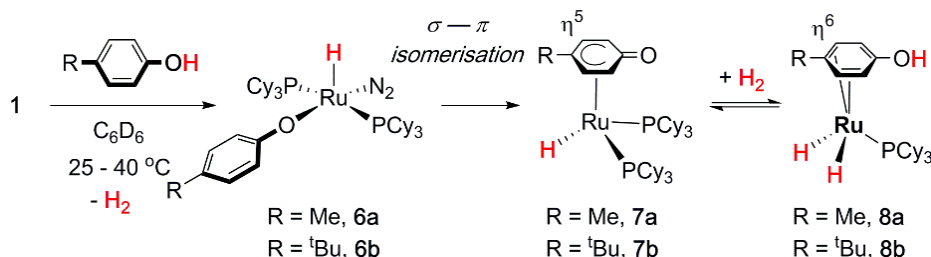
From the reaction of **1** with **3a**, cleavage of the methoxy fragment was expected to form methanol *in-situ*. In line with literature findings, methanol reacts rapidly with **1** to form an equilibrium mixture of **5-N₂**/**5-H₂**.^{55,56} These ruthenium carbonyl complexes were formed during reactions of the methyl ether **3a** with **1** in ~30 % yield as evidenced by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy. Additional evidence for the formation of a metal carbonyl under C–O cleavage conditions was provided by the reaction of **1** with double ^{13}C -labelled 2,6-dimethoxyacetophenone. Following the reaction by ^{13}C NMR spectroscopy revealed the formation of a new metal carbonyl characterised by a diagnostic resonance at $\delta = 204.5$ ppm. In combination, these experiments provide compelling evidence for the formation of a Ru-methoxide intermediate that readily decomposes to a metal carbonyl. For comparison, nickel alkoxide intermediates were prone to β -hydride elimination,^{12,28} and the formation of nickel carbonyl complexes has been reported during reactions that break strong C–O bonds of methyl aryl ethers.^{12,14}



Scheme 2.21. By-product from reaction of **1** with **3a**

From the reaction of **1** with **3b**, cleavage of the 4-methylphenoxide fragment was expected to form 4-methyl phenol as the alcohol. Monitoring the reaction of **1** with 4-methyl (or 4-tert-butyl) phenol as a function of time revealed the formation of a mixture of **6-8** prior to workup (Scheme 2.22).⁵⁷ The structural assignment was confirmed by a combination of $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy (including VT and 2D experiments) and X-ray crystallography. These experiments included the isolation and separation of **6b**, an analogue of **6a** which proved more amenable to purification by fractional crystallisation than **6a**.

The square-based pyramidal ruthenium-aryloxide complex **6a** was the major side-product observed in the C–O cleavage reaction of **3b** (~20% yield). This complex was characterised by a diagnostic resonance at $\delta = 41.9 \text{ ppm}$ in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum and a heavily shielded hydride resonance at $\delta = -25.86 \text{ (t, } ^2J_{\text{P-H}} = 19.2 \text{ Hz) ppm}$ in the ^1H NMR spectrum. Complexes **7a** and **8a** were also both observed during C–O bond activation of **3b** with **1**, albeit in smaller amounts than **6a** and were minor side-products of this reaction (~5% combined yield).



Scheme 2.22. By-product from reaction of **1** with **3b**

While analogous reactions between Ru(II) hydrides and phenols have been reported previously, there is a dearth of single crystal X-ray studies to support the proposed structures of the reaction products.⁵⁸ The reaction of $[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$ with phenol has been reported to form an analogue

of **7** (R = H) which converts to **8** (R = H) upon hydrogenation (Scheme 2.22).⁵⁵ Neither of these complexes have been structurally characterised nor have data been presented to support formation of σ -phenoxide intermediates despite the fact that $[\text{Ru}(\text{H})_2(\text{PMe}_3)_4]$ reacted with phenol to afford a σ -phenoxide complex *cis*- $[\text{RuH}(\kappa^1\text{-OC}_6\text{H}_5)(\text{PMe}_3)_4]$.⁵⁹ Wilkinson and co-workers have commented that $[\text{RuH}(\text{PPh}_3)_2(\eta^5\text{-C}_6\text{H}_5\text{O})\cdot(\text{C}_6\text{H}_5\text{OH})_2]$ formed a π -phenoxo complex that was reported to crystallise as a 1:2 adduct with phenol, while this finding was directly relevant to our structural characterisation of **7a**, the crystallographic data for the former complex were not available in the literature.⁶⁰

Complex **6b** contains, to the best of our knowledge, the first structurally characterised *trans*-relation ($\text{O-Ru-N} = 166.22(10)^\circ$) between a σ -aryloxide and dinitrogen ligand (Figure 2.14). Both the Ru–O bond length (2.0181(18) Å) and the Ru–N bond length (1.878(2) Å) were short. For comparison, the former distance can be compared to the range found in σ -phenoxide complexes (2.108(6) – 2.152(2) Å) and the latter to **4a–c** (1.975(2) – 1.9803(19) Å).^{57–59} These data were a reflection of the weaker *trans*-influence of the σ -aryloxide in comparison to the σ -aryl ligand,⁵⁹ and the π -basicity of the aryloxide increasing back-donation to the dinitrogen ligand. For comparison, *trans*-disposed ether and dinitrogen ligands in a monomeric ruthenium complex have M–O and M–N bond lengths of 2.117(3) and 1.946(3) Å respectively.^{61–63}

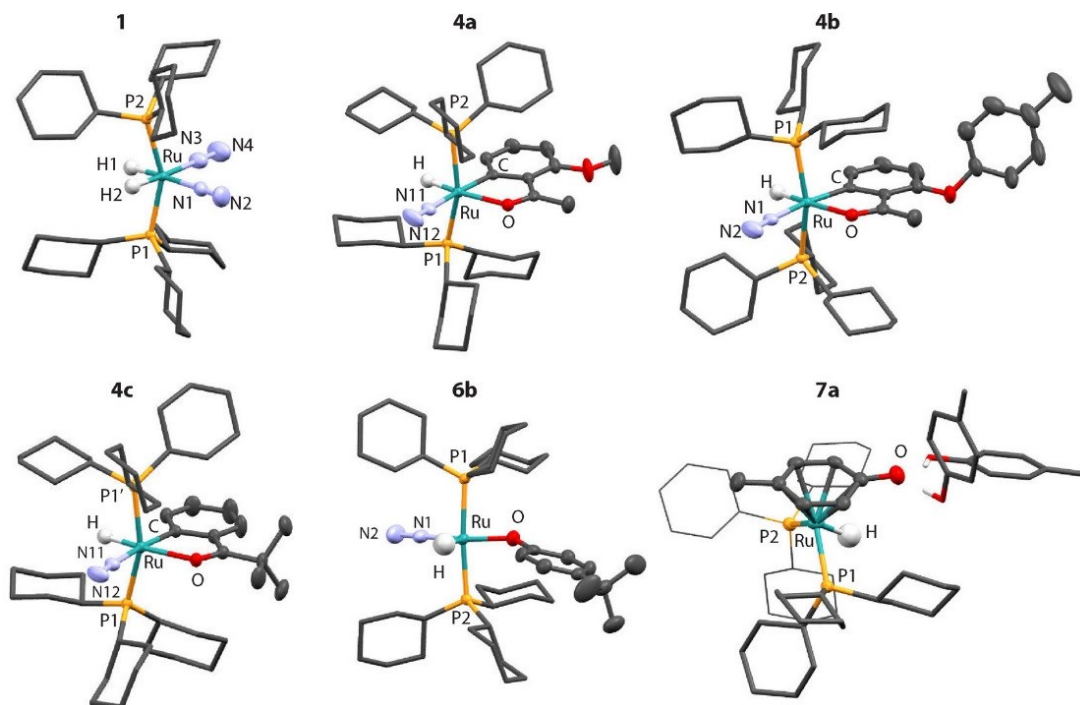


Figure 2.14. Crystal structures of **1**, products of C–X activation **4a–c** (X = H and O), and side products **6b** and **7a**

	1	4a	4b	4c
Ru–N	2.010(3)	1.978(2)	1.9803(19)	1.975(2)
	2.013(3)			
Ru–P	2.3382(7)	2.3529(7)	2.3562(6)	2.3459(5)
	2.3392(6)	2.3542(7)	2.3571(6)	2.3460(5)
N–N	1.134(4)	1.107(3)	1.105(2)	1.107(3)
	1.116(3)			
Ru–C		2.034(2)	2.042(2)	2.043(3)
O–Ru–C		76.89(7)	77.35(7)	76.49(9)

Table 2.1 Bond Lengths (Å) and Angles (°) in **1** and **4a–c**

Monitoring the C–X bond activation reactions as a function of time revealed that transfer hydrogenation of the ketone did not precede bond activation but rather occurred at the same time. Esteruelas *et al.* have also observed substrate hydrogenation during C–H bond activation of ketones promoted by ruthenium *POP*-pincer complexes.⁶⁴ Transfer hydrogenation of the first equiv. of substrate with **1** could be a potential route to generate coordinatively unsaturated Ru(0) complexes. These latter species have been suggested by DFT to play an important role in C–O and C–H bond activation (Figure 2.12) and was considered as potential intermediates in the key bond breaking events in the computational studies below (Scheme 2.23).

An alternative explanation for the observed transfer hydrogenation process was that **1** (or related species) could catalyse the hydrogenation of the ketone substrate. The H₂ required was potentially liberated during the C–X bond activation reactions. In the case of C–H activation, H₂ was formed from the breaking C–H and Ru–H bonds (Scheme 2.21). While in the case of C–OR activation, H₂ was generated by either dehydrogenation of the methoxide ligand to form the carbonyl complex **5-N₂/5-H₂** (R = Me) or during generation of the aryloxide **6a** (R = Ar) (Scheme 2.22).

In combination, the experimental data showed that: (i) facile C–O activation of aryl and methyl ethers occurred with the ruthenium(II) complex **1** below 40 °C provided the substrate contains a suitable directing group, (ii) the initial side-products of C–O bond activation were ruthenium–alkoxide/aryloxide complexes, (iii) C–O bond activation can be inhibited by addition of exogenous dinitrogen and (iv) C–H activation occurs at a faster rate than C–O bond activation. The computational studies presented below will rationalise these experimental data.

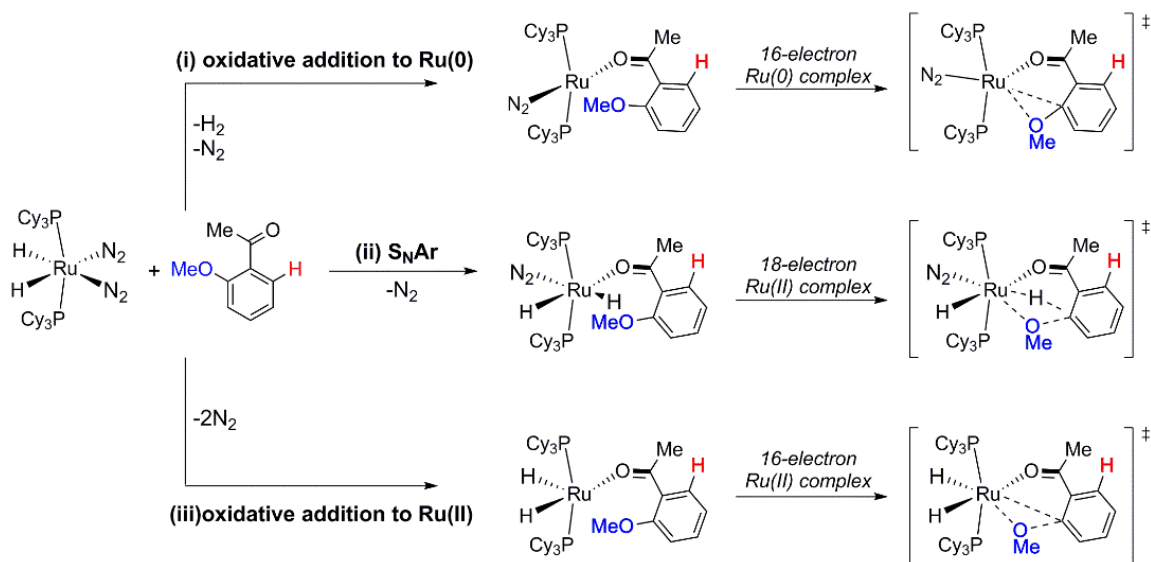
2.3.4 Mechanistic and DFT Studies

The following DFT and QTAIM calculations were performed by Dr Bryan J. Ward (Imperial College London). Potential reaction mechanisms were studied by DFT using the Gaussian 09 suite and

optimisations employed the BP86 functional.^{65–67} Ru and P centers were described with Stuttgart RECPs and associated basis sets (ECP28MWB for Ru and ECP10MWB for P).^{68–70} The P basis set was augmented with the addition of d-orbital polarisation ($\zeta = 0.387$).⁷¹ 6-31+G* basis sets were used for N and O and 6-31G** basis sets were used for all other atoms.^{72–74} Free energies are corrected for both benzene solvent (PCM approach) and dispersion effects (Grimme's D3 parameter set with Becke-Johnson (BJ) damping).^{75,76}

1.1.1.1 Plausible pathways for C–O activation

In analysing plausible mechanisms of C–O bond activation from **1** both the key bond breaking step and the energetics to form the reactive transition metal fragment that participates in this step were considered. Three plausible steps for C–O bond cleavage were postulated: (i) oxidative addition of the C–O bond to Ru(0), (ii) hydrodeoxygenation by hydride attack on the C–O bond of the Ru(II) coordinated substrate (S_NAr), and (iii) oxidative addition of the C–O bond to Ru(II) (Scheme 2.23).



Scheme 2.23. Plausible reaction pathways to obtain reactive Ru intermediate

Oxidative addition of C–O bonds of ethers to Ru(0) carbonyl complexes has been widely invoked in Ru-catalysed cross-coupling reactions of ethers with boronic esters.^{29,34,38–40} Lin *et al.* have recently calculated a low energy transition state for the oxidative addition of a C–O bond to the square-planar 16 electron complex *trans*-[Ru(PPh₃)₂(CO)(*o*-OMe-C₆H₄C(O)Me)] (Figure 2.11).⁴¹ Directing-group assisted C–H activation have been calculated to occur by similar facile Ru(0)/Ru(II) redox process.^{42,43} While the Ru(0)/Ru(II) mechanisms for C–X bond activation were becoming generally accepted, the question remained: what were the barriers to generate the reactive 16 electron fragments from the Ru(II) precursors employed in experiments? The results of the calculations that address this

question for **1** were summarised graphically alongside the highest energy transition states for the C–O activation step in Figure 2.15.

Oxidative addition of C–O bond to Ru(0): Although oxidative addition of a C–O bond to Ru(0) was facile (highest transition state for this process was calculated as 25.3 kcal mol⁻¹), formation of the required 16 electron intermediate was kinetically challenging. This species could be generated by either reductive elimination of H₂ from **1** or transfer hydrogenation of a further equivalent of the ketone substrate (as observed experimentally). The highest transition states for these processes reached 32–38 kcal mol⁻¹ (Figure 2.15, red line).

In contrast ligand exchange reactions to generate the reactive Ru(II) intermediates capable of C–O bond activation were lower in energy <30 kcal mol⁻¹ than generation of the Ru(0) intermediate. Therefore, it seemed less likely that oxidative addition of C–O bond to a Ru(0) was the pathway operating in this reaction as the step to generate the reactive Ru(0) species was higher than the steps to generate the Ru(II) species *and* the subsequent C–O bond activation steps by these reactive Ru(II) intermediates. Two pathways for C–O bond activation were considered plausible from these Ru(II) intermediates: S_NAr or oxidative addition.

S_NAr versus Oxidative addition of C–O bond to Ru(II): The transition state for the S_NAr path for C–O bond activation by hydrodeoxygenation (Figure 2.15, black line),^{77–79} was 1.8 kcal mol⁻¹ higher than the barrier involving oxidative addition of the C–O bond to Ru(II) to form Ru(IV) (Figure 2.15, blue line). While 3 different pathways for C–O bond activation were potentially competitive, the data suggested that the oxidative addition of C–O bond to the reactive Ru(II) intermediate was the lowest energy pathway of this reaction.

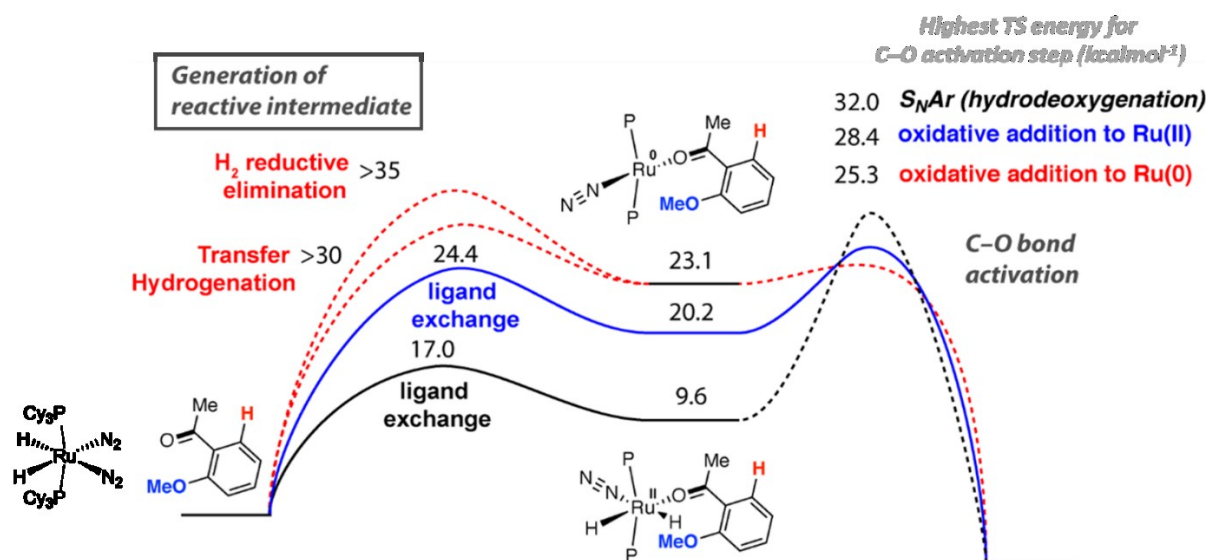


Figure 2.15. Comparison of the highest TS to generate reactive Ru intermediate and C–O bond activation. P = PCy₃

The following DFT calculations will show the oxidative addition of C–O bond to Ru(II) species to generate Ru(IV) species in more detail and compare the pathways for C–O and C–H cleavage that derive from common intermediates to reason our experimental observation that C–H activation was the kinetic pathway whereas C–O activation was the thermodynamic pathway.

1.1.1.2 Oxidative Addition to Ru(II) intermediate

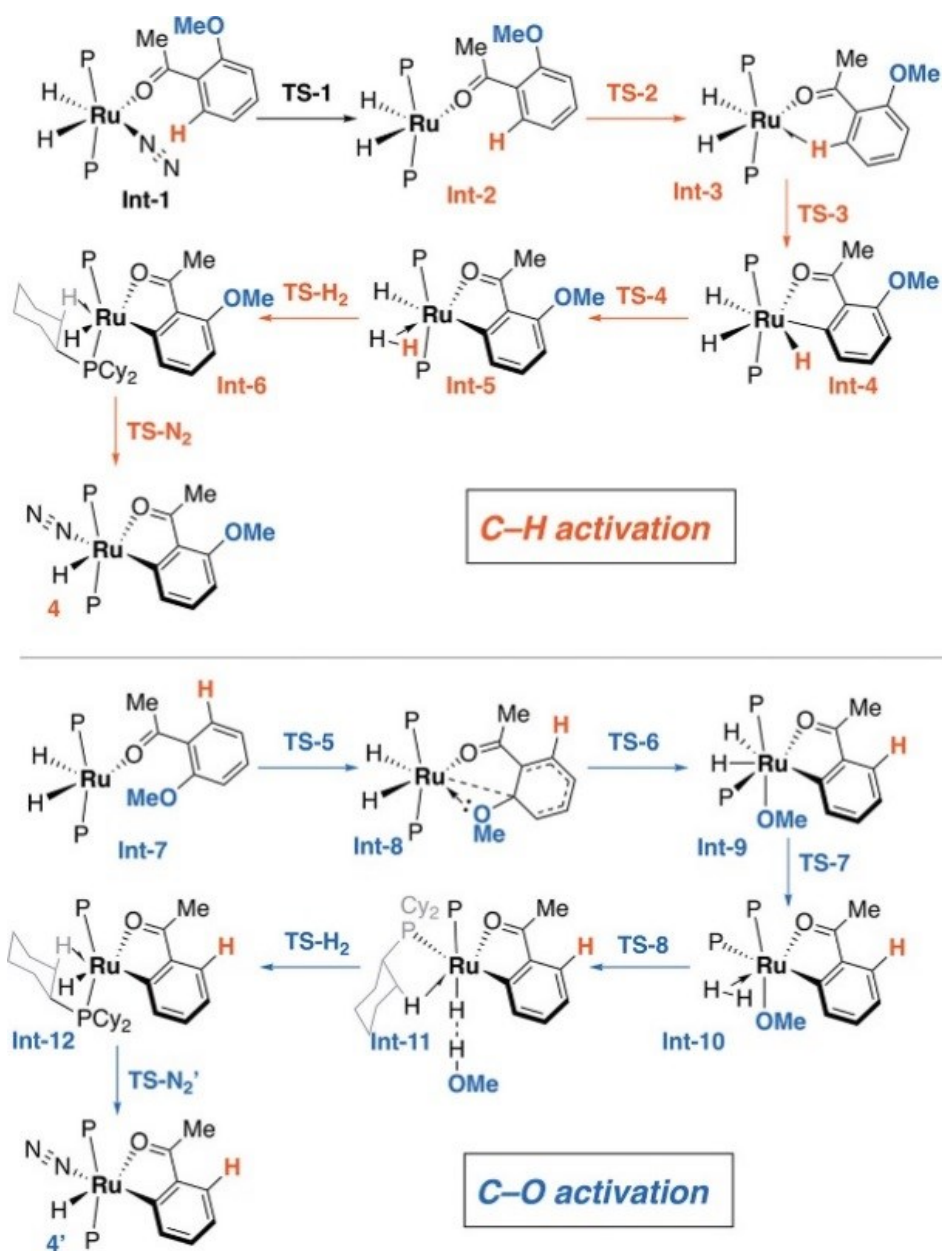


Figure 2.16. Structures of the intermediates in both C-H and C-O bond activation pathways. P = PCy₃

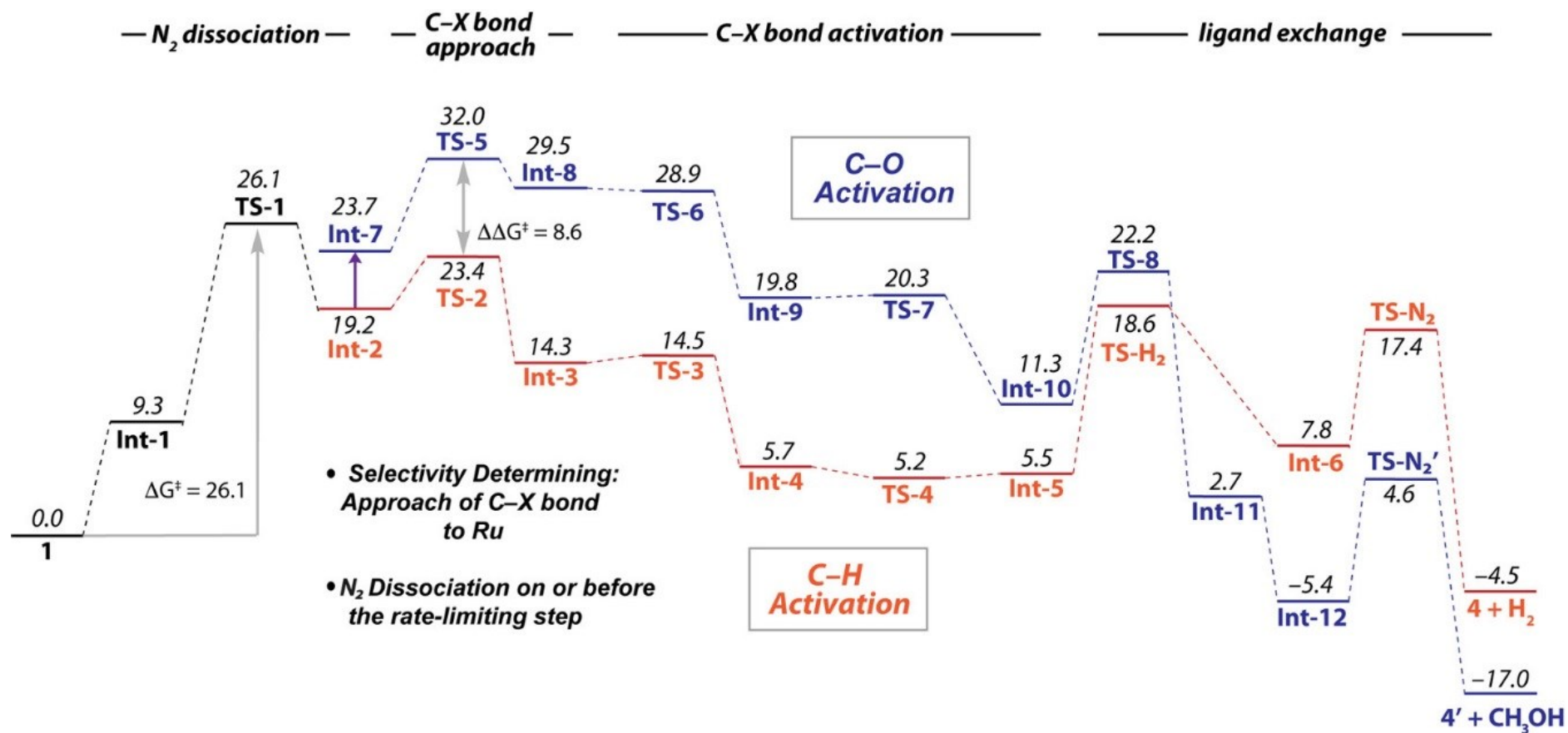


Figure 2.17. Calculated pathways for C-H (red) and C-O (blue) activation. Gibbs free energies in kcal mol⁻¹; liberated N₂ not shown.

Clot *et al.* have previously calculated the C–H activation of acetophenone by $[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PMe}_3)_2]$ and concluded that following displacement of two equivalent of H_2 by the ketone and formation of an agostic complex, the reaction proceeds by a σ -complex assisted metathesis (σ -CAM)-like mechanism (Figure 2.12).^{45,80} Importantly this study demonstrated that the directing group-assisted pathway was considerably lower in energy than those which did not involve coordination of the carbonyl group to ruthenium. In the current case, while modification of the substrate to **2a** and ruthenium precursor to **1** produced a near identical low energy reaction pathway for the C–H bond cleavage step, by considering the steps prior to coordination of the C–H bond further important features of this reaction have been identified (Figure 2.16 and Figure 2.17).

C–H Activation: Stepwise dissociation of two equivalents of N_2 from **1** with formation of the five coordinate intermediate **Int-2** was endergonic $\Delta G^\circ = +19.2 \text{ kcal mol}^{-1}$ and provided the highest energy transition state (**TS-1**) on the potential energy surface $\Delta G^\ddagger = 26.1 \text{ kcal mol}^{-1}$ (Figure 2.17). N_2 dissociation from **Int-1** can therefore be considered as the rate-limiting step for C–H activation. Therefore, the actual bond breaking and bond making processes from **Int-2** onwards are facile.

The second highest transition state in C–H bond breaking step was from **Int-2** to **Int-3** ($\Delta G^\ddagger = 23.4 \text{ kcal mol}^{-1}$) *via* **TS-2** – the approach of the C–H bond to ruthenium to form the agostic complex **Int-3**. The C–H bond cleavage transition state, **TS-3** was only $0.2 \text{ kcal mol}^{-1}$ higher in energy than **Int-3** and C–H bond cleavage was rapidly followed by H–H bond formation along a flat potential energy surface through **Int-4** (formally a Ru(IV) complex) arriving at **Int-5** (a Ru(II) complex) as the minimum.

QTAIM and NBO calculations supported the formulation of **Int-4** as a ruthenium(IV) trihydrido complex (Figure 2.18). A number of Ru(IV) hydrido complexes are known,^{81,82} and Sabo-Etienne and co-workers have recently characterised a Ru(IV) hydridotrisilyl complex of the form $[\text{RuH}(\text{SiR}_3)_3\text{L}_3]$ by neutron diffraction.⁸³ The reorganisation of hydrogen atoms within the equatorial plane of ruthenium(II) complexes is well known to proceed through low-energy, almost barrierless steps,^{52,84} and related fluxional exchange processes have been proposed to be facilitated by nascent H–H bond formation in the ground state due to donation from the σ -(M–H) orbital to the σ^* -(H–H) orbital.^{82,85}

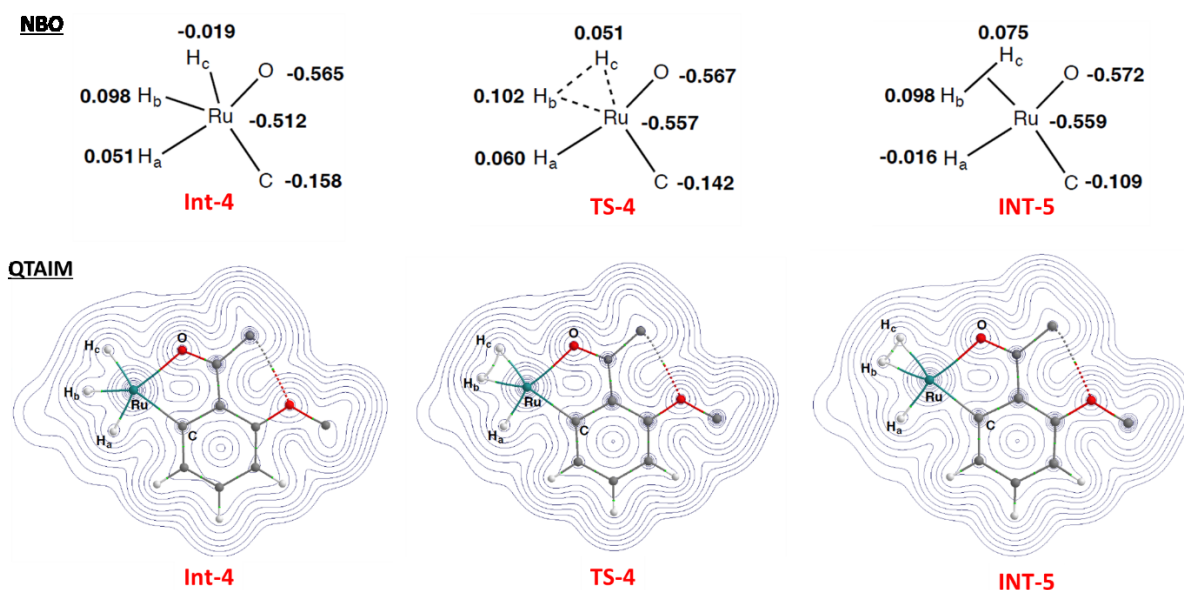


Figure 2.18. (Top) NBO, NPA charges of **Int-4**, **TS-4** and **Int-5** and (Bottom) Electron density contour plot overlaid calculated structures from QTAIM; bond critical points between atoms (green dots),

Dissociative substitution of H₂ in **Int-5** leaves a vacant site at Ru which was stabilised through a C–H agostic interaction from a tricyclohexylphosphine ligand intermediate to give **Int-6** and ultimately coordination of N₂ gives the experimentally isolated C–H activation product **4**.

C–O Activation: Considering the analogous pathway for C–O bond activation, the transition state for the approach of the C–O bond toward ruthenium, **TS-5**, was higher in energy than **TS-2** on the C–H activation pathway. The approach of the C–O bond was therefore the rate determining step and not the N₂ dissociation from **Int-1**. Once **Int-8** is formed, C–O activation, like C–H activation, was again facile and resulted in the generation of Ru(IV) intermediate **Int-9** at +19.8 kcal mol⁻¹ above the separated reactants. Formation of H₂ from **Int-9** via **TS-7** generated the Ru(II) complex, **Int-10**.

As with C–H activation, the bond breaking and making processes that occurred from **Int-8** to **Int-10** connected two Ru(II) complexes by Ru(IV) stationary points. Although in contrast to the C–H activation σ -CAM like mechanism (in which the H from the C–H bond effectively transfers directly on to the neighbouring hydride to form H₂), for the C–O activation pathway, as the C–OMe bond breaks a new H–OMe bond does not form directly. Instead addition of the C–O bond to Ru(II) occurred in concert with the reductive coupling of the two hydride ligands already present to form dihydrogen and this served to re-establish the Ru(II) oxidation state in **Int-10**. The nature of the C–X bond breaking step in this pathway was subtly different to C–H activation (*vide infra*).

Methanol formation proceeds from **Int-10** through **TS-8**, breaking the H–H and Ru–OMe bonds while simultaneously forming H–OMe and H–Ru bonds to generate **Int-11**. Cundari, Gunnoe

and co-workers have characterised related processes which involved the addition of H₂ (or C–H bonds) across Ru–OH and Ru–NH₂ bonds.^{86,87} Methanol remained bound to the outer-sphere of the ruthenium complex in **Int-11** through a dihydrogen bond (1.59 Å) and again the vacant site at Ru is stabilised through a C–H agostic interaction from a tricyclohexylphosphine ligand. Dissociation of methanol was facile leaving the five coordinate complex, **Int-11**, with *cis*-phosphine ligands. Due to the ease of the ligand re-organisation processes, **Int-11** can undergo an intramolecular isomerisation. The equatorial phosphine ligand reorganised to the axial site to yield **Int-12** (Figure 2.19), which retained a C–H agostic interaction. From **Int-12** dinitrogen readily coordinated to form the reaction products.

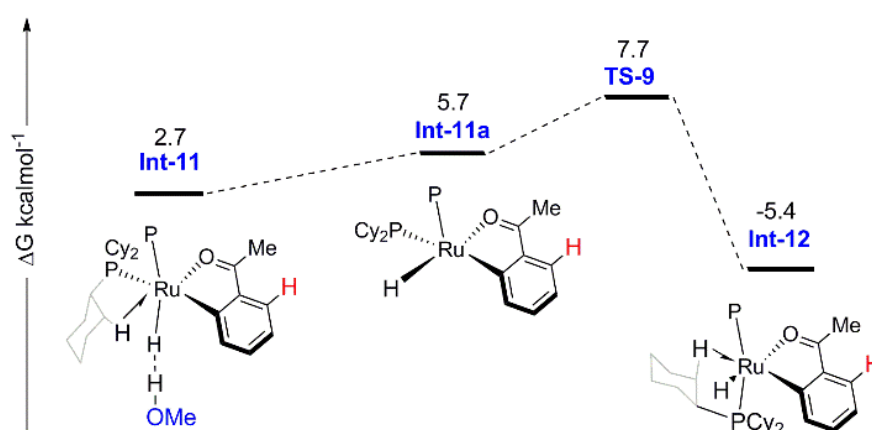


Figure 2.19. *cis-trans* isomerisation of PCy₃. P = PCy₃

Additional pathways were characterised for product formation from **Int-9**, these included: (i) H₂ formation accompanied by an intramolecular isomerisation of the phosphine ligands, (ii) direct O–H bond formation, and (iii) H₂ extrusion followed by β -hydride elimination of a ruthenium-methoxide intermediate. All three aforementioned pathways were in theory viable as the highest activation barriers of all these pathways were lower than that of the preceding rate-limiting C–O bond cleavage step.

Dehydrogenation of CH₃OH to form **5-N₂/5-H₂** by **1** was also investigated computationally. Formation of the carbonyl complexes occurred through well understood β -hydride elimination and C–H activation steps all of which were computed to be more accessible than the preceding C–O activation.^{88,89}

1.1.1.3 Selectivity Determining Approach of the C–X bond to ruthenium

Comparison of **TS-2** and **TS-5** explained the experimental observation that C–H activation was the kinetic pathway whereas C–O activation was the thermodynamic pathway. The Gibbs energy barrier for C–H activation was considerably lower than C–O activation ($\Delta\Delta G = 8.6$ kcal mol⁻¹). This difference in energy can be attributed to the approach of the C–O bond toward ruthenium being less favoured than the C–H bond due to repulsive non-covalent interactions (NCI) forcing ligand reorganisation (Figure 2.20a and Figure 2.20b). NBO analysis highlighted negative charge accumulation at both Ru and O(Me)

in **TS-5**. In contrast for **TS-2** the Ru(d π)---C-H(σ) repulsion was less significant. Consequently, as the C–O bond approached Ru, the acetophenone aryl ring was twisted out of the equatorial plane in **TS-5** as Ru interacted preferentially with the *ipso*-carbon (Figure 2.20c). The structural reorganisation required was facilitated by the flexibility of the coordinated phosphine ligands and it was clear despite the energetic penalty that accompanied the structural distortion, the elasticity of the P–Ru–P angle was important for C–O bond cleavage. A number of relevant ruthenium complexes with *cis*-disposed PCy₃ ligands are known.^{90–92}

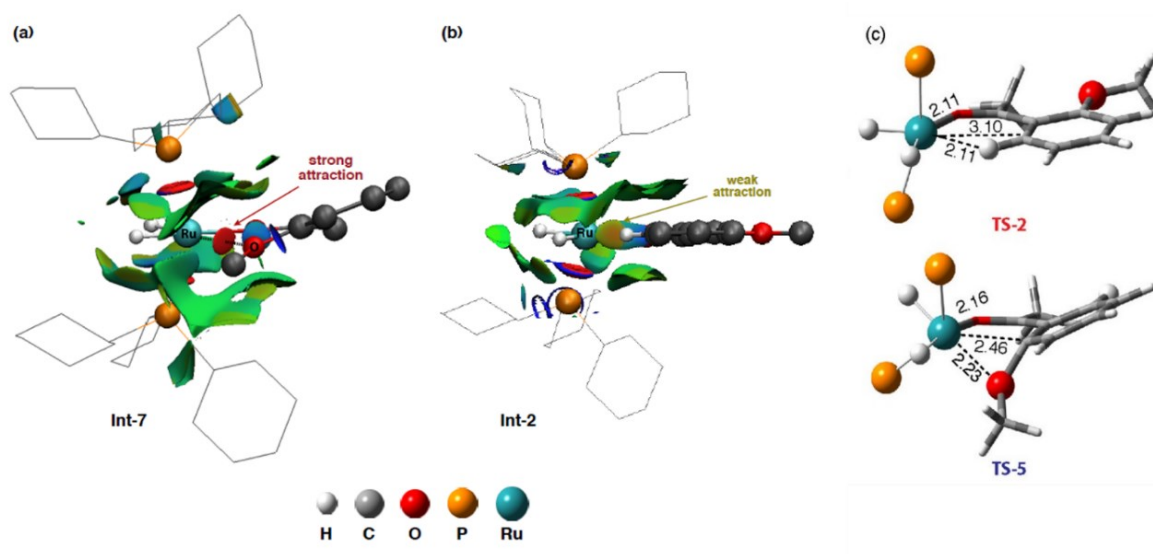


Figure 2.20. NCI plots of (a) **Int-7** (C–O) and (b) **Int-2** (C–H). (c) Molecular models of **TS-2** and **TS-5** with selected bond lengths (Å).

Breaking of the C–X bond: Both bond activation steps involved oxidative addition of the C–X bond to Ru(II). There were, however, subtle differences between the C–H and C–O cleavage mechanisms. As both pathways contained an early transition state for C–X bond activation the comparison of **Int-3** (C–H) and **Int-8** (C–O) allowed the key differences to be elucidated.

Second-order perturbation analysis allowed **Int-3** to be classified as a typical agostic complex. Donation from the σ -(C–H) orbital to the σ^* -(Ru–H) was accompanied by back-donation from a filled d-orbital of Ru to the σ^* -(C–H) (Figure 2.21a). NBO calculations showed that formation of this agostic complex from **Int-2** occurred with only minor perturbation of the electron density at the Ru and C centres (Figure 2.21b). It can be concluded that C–H bond breaking occurred by population of the σ^* -(C–H) orbital with electrons from Ru and formation of a Ru(IV) organometallic.

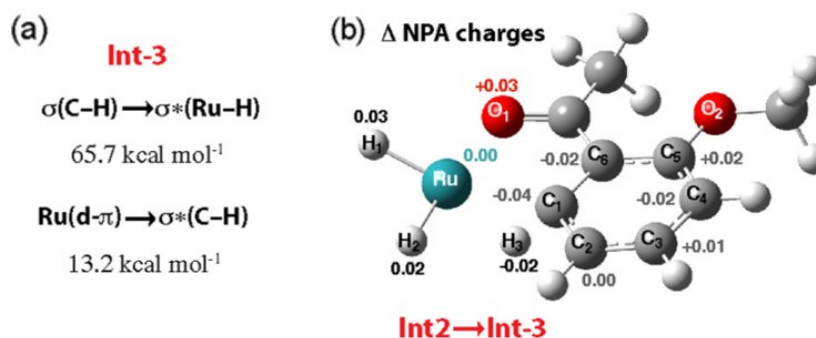


Figure 2.21. (a) Selected NBO second-order perturbation analysis data on **Int-3**. (b) NBO analysis showing the difference in NPA charges between **Int-2** and **Int-3**

In contrast, formation of **Int-8** from **Int-7** on the C–O activation pathway occurred with pyramidalisation at the *ipso*-carbon of the aromatic ring and accumulation of charge at both this site and, to a lesser extent, the *ortho*- and *para*-positions. Concurrently, the Ru centre underwent charge depletion (Figure 2.22b). While QTAIM analysis showed bond critical paths (bcp) between Ru–C, C–O and O–Ru in this intermediate, second order perturbation analysis from the NBO calculations suggested that it cannot be simply described as a σ -complex. No significant donation and back-donation to or from the $\sigma(\text{C-O})$ bond was calculated (Figure 2.22a). Moreover, the small positive $\nabla^2\rho_b$ and negative H_b (energy density) values at the bond critical points between Ru and C from the QTAIM data indicated the formation of a partially covalent bond. In combination the data suggest an asynchronous pathway for C–O bond activation in which Ru–C bond formation precedes Ru–O bond formation.

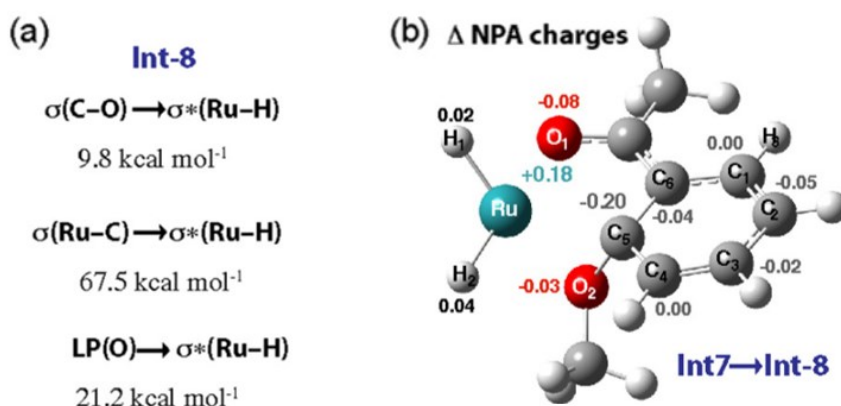


Figure 2.22. (a) Selected NBO second-order perturbation analysis data on **Int-8**. (b) NBO analysis showing the difference in NPA charges between **Int7/Int-8**

2.3.5 Expansion of scope

Aside from the four substrates depicted in (Scheme 2.19), a number of different substrates were tested in order to ascertain the scope and limitation of this ruthenium mediated C–X activation chemistry.

1.1.1.4 Directing group – (C(O)R, when R = ^tBu)

Kakiuchi *et al.*^{29,31,33} and Snieckus *et al.*^{38–40} alluded to the directing group having an effect on chemoselectivity of the reaction *i.e.* whether the *ortho*-C–H or *ortho*-C–O bond was cleaved. Kakiuchi *et al.* showed that the C–H activation pathway of an acetophenone substrate bearing both *ortho* C–H and C–O bonds could be shut down when the R group of the ketone was not a methyl group but a *tert*-butyl group. The argument was that sterics dictated the chemoselectivity of the reaction with the *tert*-butyl group preferring to arrange itself towards to the *ortho*-position with the smallest steric clash resulting in the blocked access of the metal complex to the C–H bond (Scheme 2.24). The computation study by Lin *et al.* has provided a more in-depth analysis based on the relative stability of the transition state of the intermediate during the transmetallation step with the organoborane substrate as to the origin of the chemoselective behaviour of the reaction (Figure 2.11).⁴¹

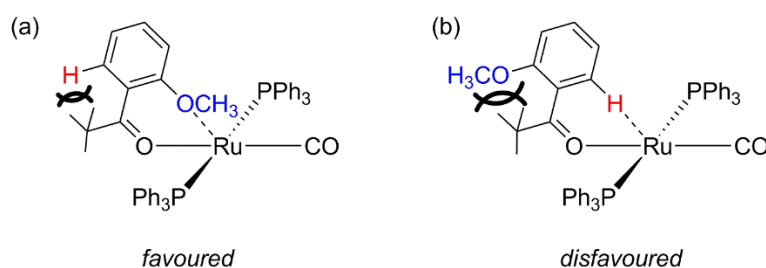
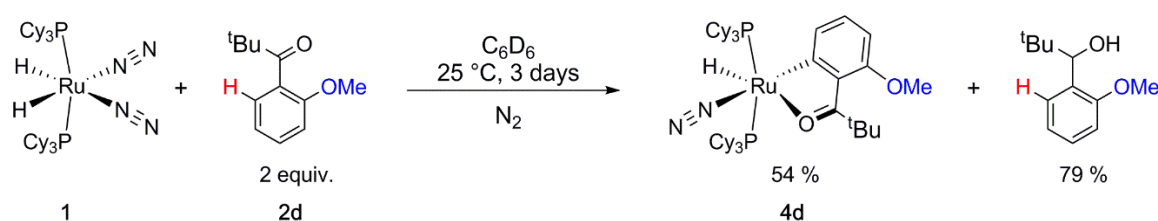


Figure 2.23. Steric argument for the chemoselectivity of C–H versus C–O bond activation of 1-(2-methoxyphenyl)-2,2-dimethylpropan-1-one

Repeating the reaction of 1-(2-methoxyphenyl)-2,2-dimethyl-1-propanone (**2d**) with **1** at 25 °C resulted in the *ortho*-C–H activation of the substrate to generate the cyclometallated species **4d** as well as one equivalent of the arylethanol product (Scheme 2.24). Complex **4d** demonstrated the same distinctive triplet for the Ru–H signal at $\delta = -14.16$ (t, $^2J_{P-H} = 26.2$ Hz) ppm as the analogous cyclometallated species **4a-c**, and with the corresponding $^{31}\text{P}\{^1\text{H}\}$ resonance at $\delta = 36.5$ ppm. This experiment showed that **1** was still able to mediate C–H bond activation of the substrate, in contrast to the result by Kakiuchi *et al.*²⁹ and confirming that the steric argument for the chemoselective behaviour may be too simplistic and that other factors can have a greater effect on the chemoselectivity of the reaction. The yield of **4d** was 54 % after 3 days at 25 °C with $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showing roughly half of **1** remaining unconsumed. The low yield of **4d** suggested that even though the C–H pathway was not shut down, the conversion to product was inhibited. Heating of the reaction mixture to 35 °C led to

the formation of a second product demonstrating a triplet at $\delta = -17.59$ ppm ($t, {}^2J_{P-H} = 19.3$ Hz) and with a corresponding ${}^3\text{P}\{^1\text{H}\}$ resonance at $\delta = 47.5$ ppm. The identity of this new organometallic species was never unambiguously established. Comparison of the data with **4c**, which would be the product from C–O activation, showed that this was not the product. It was anticipated that this minor impurity may be an artefact of another substrate formed in small amounts from the synthesis of 1-(2-methoxyphenyl)-2,2-dimethyl-1-propanone.



Scheme 2.24. C–H activation of 1-(2-methoxyphenyl)-2,2-dimethyl-1-propanone

1.1.1.5 Directing group – Hydrosilyl ether

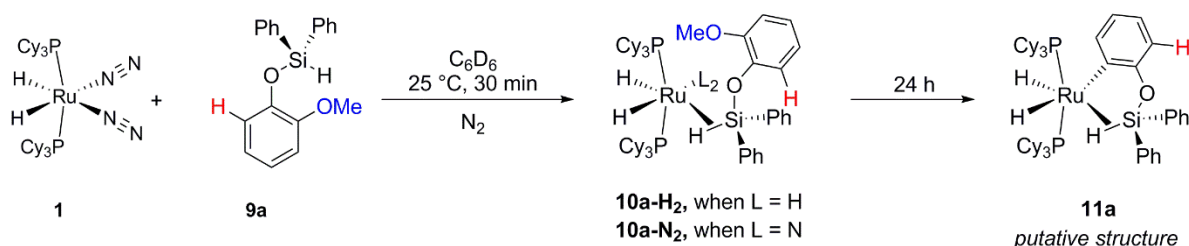
The ketone functionality of the acetophenone substrates used in this investigation can be made from the oxidation of phenol derivatives for example the structurally similar substrates to monolignols (Figure 2.1). An alternative functional group that could potentially serve as a directing group in these C–X bond activation chemistry was hydrosilyl ether group. Hydrosilyl ether can be constructed from the dehydrocoupling reaction of phenol derivatives with the required silane reagent and forming H_2 as the by-product. Alternatively, as in this investigation, the hydrosilyl ether group can be constructed *via* nucleophilic substitution reaction of the phenol with required silyl chlorides reagent (chloride salt as the by-product). The hydrosilyl ether group has a strong Si–O bond which should be resistant to being cleaved itself and also a Si–H bond that is able to complex to the ruthenium centre in an η^2 -fashion. Sabo-Etienne *et al.* has reported a number of interesting σ -silane complexes from the reaction of the ruthenium *bis*-dihydrogen complex, $[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$, with a number of silane complexes (Chapter 1, 1.2.5.2 Silicon).^{91–93}

The reaction of 1 equivalent of **1** with 1 equivalent of **9a** proceeded rapidly at 25 °C with a slight downfield shift and broadening of all the peaks corresponding to **9a** observed in the ${}^1\text{H}$ NMR spectrum (Scheme 2.25). In addition, a new broad peak in the up-field region of ${}^1\text{H}$ NMR spectrum at $\delta_{\text{H}} = -8.48$ ppm appeared indicative of complexation of the substrate and potential formation of a η^2 -Si–H motif in **10a**. For example, the same characteristic broadening of the resonances in the ${}^1\text{H}$ NMR spectrum was observed by Sabo-Etienne *et al.* for the reaction of **1-2H₂** with silanes to indicate successfully sigma complex formation (Chapter 1, 1.2.5.2 Silicon). In the ${}^3\text{P}\{^1\text{H}\}$ NMR spectrum two new broad resonances were observed at $\delta_{\text{P}} = 44.6$ and 53.0 ppm which were assigned as **10a-N₂** and **10a-H₂** respectively. Repeating the reaction of **1** with **9a** under an atmosphere of H_2 resulted in the

formation of just **10a-H₂** with only the resonance at $\delta_P = 53.0$ ppm observed in $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The broad resonance in ^1H NMR spectrum at $\delta_H = -8.48$ ppm also sharpened but was still broad (similar fluxional behaviour of hydrides observed for **1-2H₂**). In the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum, **10a-H₂** was characterised by a new downfield resonance at $\delta_{\text{Si}} = 14.3$ ppm (**9a**, $\delta_{\text{Si}} = -13.3$ ppm). Low temperature NMR spectroscopy failed to decoalesce the Ru–H resonance in **10a-H₂** however T_1 measurements were taken across 293 – 193 K temperature range (400 MHz) with a T_1 min value of 45 ms measured which was indicative of non-classical hydride behaviour,⁹⁴ however this was expected if an η^2 -H₂ ligand was present in the complex regardless of the presence of a η^2 -Si–H motif. In addition, no decoalescence was observed for the single resonance in $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at low temperature.

The reaction mixture of **1** and **9a** under an atmosphere of N₂ was left for 24 h at 25 °C and new characteristic resonances in ^1H NMR spectrum at $\delta_H = -8.31$ (td, $^2J_{P-H} = 15.0$ Hz and $^2J_{H-H} = 5.9$ Hz, Ru–H) and -9.88 (br s, η^2 -Si–H) ppm, in $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at $\delta_P = 76.5$ ppm and in $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum at $\delta_{\text{Si}} = 40.6$ ppm were observed. These new resonances were assigned to the speculated organometallic cyclometallated species **11a** from the C–O activation of the substrate (Scheme 2.25). No additional multinuclear NMR spectra data was performed due to low concentrations of the speculated **11a** formed in solution. However, ^1H – ^{13}C HMBC NMR spectroscopy could have provided the indicative cross peak between the Ru–H and Ru–C resonances to strengthen the argument for the formation of the cyclometallated product.

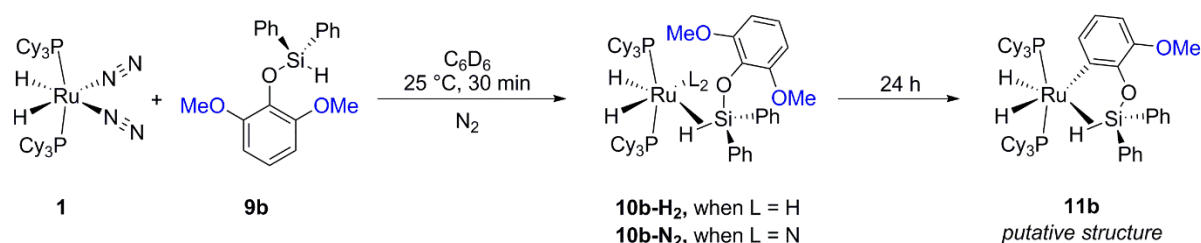
The ^1H NMR spectrum containing the mixture of **10a** and **11a** also contained a number of unassigned peaks including resonances characterised as Me fragments. This would indicate that potentially *ortho*-C–H activation of **9a** occurred instead of *ortho*-C–O activation however based on the reaction of **1** with (2,6-dimethoxy)diphenylsilane (**9b**) (*vide infra*) this seemed unlikely. Nevertheless, the assignment of **11a** as depicted in Scheme 2.25 was tentative and more data needs to be collected to confirm the formation of **11a**.



Scheme 2.25. Speculated products from reaction of **1** with **9a**

The analogous reaction of **1** with **9b** yielded similar results in terms of forming the ruthenium η^2 -Si–H complex initially **10b**. **10b** was characterised by resonances in ^1H NMR spectrum at $\delta_H = -8.49$ ppm and in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at $\delta_P = 44.7$ (**10b-N₂**) and 53.0 ppm (**10b-H₂**). Leaving the

reaction mixture overnight at 25 °C resulted in formation of the speculated cyclometalated species from the C–O activation of the substrate, **11b**. **11b** was characterised by resonances in the ^1H NMR spectrum at $\delta_{\text{H}} = -8.26$ (td, $^2J_{\text{P-H}} = 15.2$ Hz and $^2J_{\text{H-H}} = 2.9$ Hz) and -8.88 (br s) ppm and in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at $\delta_{\text{P}} = 77.4$ ppm and in $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum at $\delta_{\text{Si}} = 46.8$ ppm. The resonances in the multinuclear NMR spectra of **11b** did not match entirely with the resonances assigned to **11a**. This suggested that two different final products were formed from the reaction of **1** with **9a** and **9b** respectively and it seemed unlikely that *ortho*-C–H activation of **9a** occurred as this would have formed the same product **11b** (with the caveat that the formation of **11** was correct in both reactions).



Scheme 2.26. Speculated products from reaction of **1** with **9b**

The products and intermediates of these reactions were never successfully isolated as the yields of **11** were low and over time **11** decomposed to form $[\text{Ru}(\text{H})_2(\eta^6\text{-C}_6\text{D}_6)]$ and other unknown species. Although the assignment of the organometallic products **11** were tenuous based only on *in-situ* NMR spectra data, the formation of ruthenium σ -silane complexes (**10**) seemed probable.

From the reaction of **1** with **9**, the use of hydrosilyl ether as the directing group seemed successful in terms of complexation of the substrate to **1**. The formation of two different final products (**11**) was an interesting observation as this reactivity deviated from the formation of the same product observed between the reaction of **1** with **2** (one *ortho*-C–O bond) and **1** with **3** (two *ortho*-C–O bonds) respectively however more work will need to be performed to clarify formation of the products from the reaction of **1** with **9**.

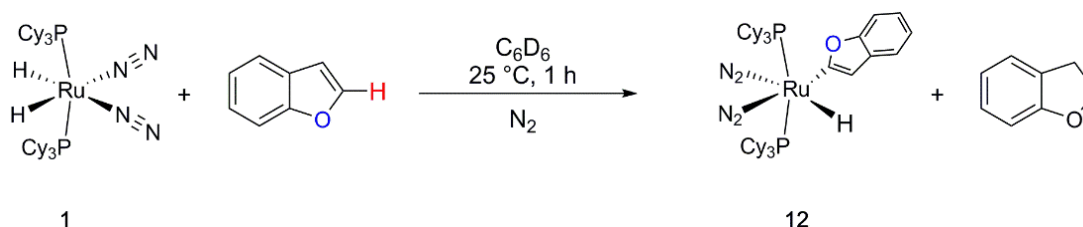
1.1.1.6 Absence of Directing group

The limitations of these C–X bond cleavage reactions were explored with the exclusion of a directing group in tested substrates. No reaction occurred between **1** and anisole or **1** with benzyl phenyl ether. Even upon extended heating and photolysis no reaction occurred except decomposition of **1**. This would suggest that a directing group was a pre-requisite to these reactions in order to bring the two reactants together in the right orientation.

Beyond acyclic ethers, the cyclic ether benzofuran was also investigated in these C–X bond activation reactions. Benzofuran is a by-product from coal gasification and therefore the ability to valorise this heteroaromatic would be another step towards utilising waste product.⁹⁵ Our group have

demonstrated the zirconocene catalysed C–O functionalisation of benzofuran with an aluminium dihydride reagent to generate new reactive C–Al bond.⁹⁶ In addition, there has been reports of successfully C–O bond activation of benzofuran *via* the precoordination of the arene ring of benzofuran before the bond cleavage step⁹⁷ and therefore the arene ring could replace the need of a directing group.

The reaction of 1 equivalent of **1** with 2 equivalents of benzofuran proceeded rapidly at 25 °C to give the product from the C–H activation at the 2-position of benzofuran as well as an equivalent of the transfer hydrogenation product 2,3-dihydrobenzofuran (Scheme 2.27). A broad resonance at $\delta_{\text{H}} = -15.58$ ppm was observed in the ^1H NMR spectrum with a corresponding resonance observed in $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at $\delta_{\text{P}} = 41.2$ ppm. Crystals suitable for single-crystal X-ray diffraction were grown to confirm the structure of the C–H activated product, **12**. Retention of the double bond motif of the benzofuran was confirmed by the measured bond length of C1–C9 bond which fell within the range of C–C double bond (1.32(2) Å) and in addition, the C9–H proton resonance was found in the aromatic region at $\delta_{\text{H}} = 6.55$ ppm. The C–H activation of benzofuran derivatives, mediated by ruthenium(II) catalysts, are known but only activation at the C3 position have been reported. Furthermore the C2 position was substituted by a directing group in order to direct the C3 position for bond activation chemistry.^{98,99} The assignment of **12** was incomplete and no ^{13}C NMR spectrum data was acquired. No low temperature NMR spectroscopy was performed as this may have alluded to the origin of the broad resonance exhibited by the Ru–H environment in ^1H NMR spectrum.



Scheme 2.27. C–H activation of benzofuran with **1**

12	
Ru–N	2.009(5) 2.014(9)
Ru–P	2.3696(18) 2.3857(18)
N–N	1.078(7) 1.111(8)
Ru–C	2.069(19)
P–Ru–P	169.96(6)

Figure 2.24. X-ray structure of **12** including selected bond lengths (Å) and angles (°). Hydride was not located on Fourier transform map.

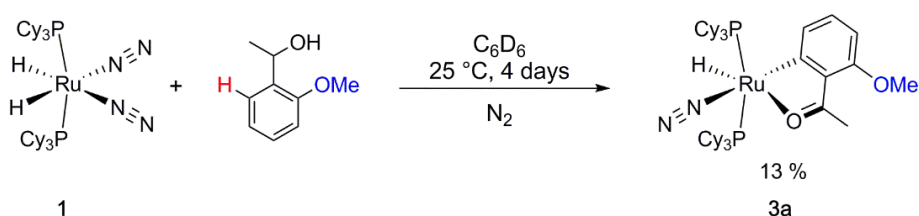
To probe if C–O bond activation of benzofuran occurred at higher temperatures, the reaction mixture containing **12** was heated to 40 °C however no change in the multinuclear NMR spectra was observed. No further reactivity of **12** was investigated.

The reaction mechanism of the C–H activation of benzofuran most likely will be different to what was reported with the acetophenone substrates and therefore the loss of H₂ may be important step to generate a reactive Ru(0) species for the bond activation chemistry. This hypothesis would agree with the crystal structure bearing two dinitrogen ligands still ligated on the ruthenium centre (Figure 2.24) in comparison to the cyclometallated products **4** (Figure 2.14). It would be interesting to react **1** with an acyclic ether bearing a reactive alkene bond and seeing if C–X cleavage was successful and whether loss of H₂ was important in this group of reactions.

1.1.1.7 Directing Group – ROH

It was demonstrated that the reaction of **1** with phenol derivatives generated aryloxide complexes (Scheme 2.22). The –OH group, though not a perfect directing group due to the fact it is non-innocent in these reactions, still potentially may provide some interesting results and insights. From the general reactions of **1** with the acetophenone substrates the corresponding transfer hydrogenation products were formed. The exploitation of the microscopic reversibility of hydrogen transfer reactions could allow the reaction to start from the arylethanol compound to circumvent the need for a 1:2 stoichiometry of **1** and the acetophenone.

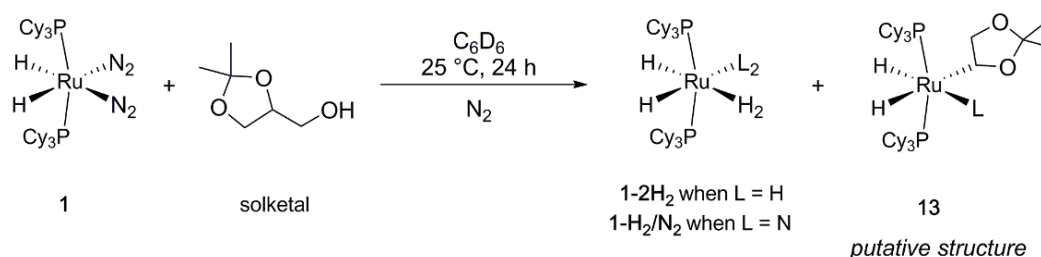
The reaction of **1** with 1-(2-methoxyphenyl)ethan-1-ol at 25 °C for 4 days resulted in formation of **4a** in 13 % yield (Scheme 2.28). This result demonstrates **1** was mildly capable of dehydrogenation reactions of secondary and primary alcohols (Scheme 2.21) however the ability for **1** to remove H₂ from an alcohol was most likely hindered by dissociation of N₂ (*vide supra*) to open up a vacant site around ruthenium. Performing the reaction in the presence of a hydrogen trap (3,3-dimethylbut-1-ene) to thermodynamically push the dehydrogenation of the arylethanol was unsuccessful as the rate of reaction of **1** with 3,3-dimethylbut-1-ene was faster and the dehydrogenation of **1** was observed instead to give the expected C–H activation of the ligated PCy₃ ligand (CHAPTER 1, Scheme 1.1). In addition, no reaction occurred between **1** with *tert*-butyl alcohol even after heating the reaction to 40 °C.



Scheme 2.28. Reaction of **1** with 1-(2-methoxyphenyl)ethan-1-ol

In line with investigating chemicals derived from biomass sources, solketal (2,2-dimethyl-1,3-dioxolan-4-yl)methanol), a derivation of glycerol, was investigated. Glycerol is created as a by-product

from the production of bio-diesel and has been proposed as a platform molecule for further transformation.¹⁰⁰ Solketal simplifies the reactivity of the substrate by only having one reactive hydroxyl group within the structure compared to three hydroxyl groups in glycerol, in addition solketal is less viscous than glycerol making it, on a practical level, easier to use. The reaction of **1** with solketal at 25 °C was facile and within 30 mins formation of the ruthenium *bis*(dihydrogen) complex **1-2H₂** and the intermediate [Ru(H)₂(η²-H₂)(N₂)(PCy₃)₂] **1-H₂/N₂** were observed by multinuclear NMR spectroscopy. In addition, the ¹H NMR spectrum of the reaction mixture showed broadening of the peaks between δ_H = 3.2 – 4.0 ppm for the methylene and methine protons of solketal suggesting complexation of the substrate. A second species was observed demonstrating a broad resonance in ¹H NMR spectrum δ_H = -7.06 ppm and two sharp singlets at δ_H = 2.08 and 3.52 with an integral of 6 and 2 respectively. A corresponding resonance in ³¹P{¹H} NMR spectrum at δ_P = 71.9 ppm was also observed. This species was speculated as a ruthenium complex with the 1,3-dioxolane-fragment bound at the 4-position (**13**) (Scheme 2.29). The formation of **1-2H₂** and **1-H₂/N₂** in this reaction indicated some dehydration process occurred and based on the reaction of **1** with methanol (Scheme 2.21) and phenol derivatives (Scheme 2.22) it seemed likely that β-hydride elimination process of the cleaved –CH₂OH fragment of solketal (*via* C–C cleavage) occurred to give **13** and formation of H₂ and CO which reacted with **1** to give **1-2H₂** and **1-H₂/N₂**. However, the ruthenium mono-carbonyl complex [Ru(H)₂(L)(CO)(PCy₃)₂] (L = N₂, H₂), expected to be formed from reaction of **1** with CO, was not observed in the NMR spectra, possibly due to low partial pressure of CO relative to H₂ and N₂. After 7 days at 25 °C full conversion to this unknown species was achieved however large scale synthesis of this reaction mixture failed to produce crystals suitable for X-ray crystallography. No ¹³C NMR spectroscopy was performed for this reaction.



Scheme 2.29. Speculated product formation of **13** from reaction of solketal with **1**

2.3.6 Functionalisation

The functionalisation of the activated C–X (X = H, O) of these acetophenone substrates was investigated in order to add chemical complexity and show proof of concept of utilising these substrates as building blocks for further transformations. The activation of the C–X bond by **1** resulted in the generation of the cyclometallated species **INT-1** which was the first step to the idealised proposed

catalytic cycle of upgrading these acetophenone substrates (Figure 2.13). The second step would require the ligand substitution of N_2 with an equivalent of a main group reagents, for example HBpin, to generate **INT-2** postulated to form a σ -complex based on the propensity for the analogous ruthenium *bis*(dihydrogen) complex to form σ -complexes with boranes^{101–104}, silanes^{83,92,105,106} and germanes¹⁰⁷ (Chapter 1). The final stage would be the release of the borylated product and regeneration of **1**. Generating a new C–B bond from C–O bond would set up these acetophenone substrates for the Suzuki–Miyaura cross-coupling reactions.^{6,108}

Based on the current data for the C–O activation of acetophenone substrates mediated by **1**, half of the ruthenium *bis*(dinitrogen) complex is lost through reactions of **1** with the cleavage of the methyl ether or aryl ether fragment. Therefore the role of the main group reagent, in this case, would also be two-fold: (i) acting as the transmetallation reagent and (ii) reacting with the cleaved –OR fragment instead of **1** to prevent deactivation pathway of the ruthenium complex which should allow for the turnover of the reaction to occur (Figure 2.25).

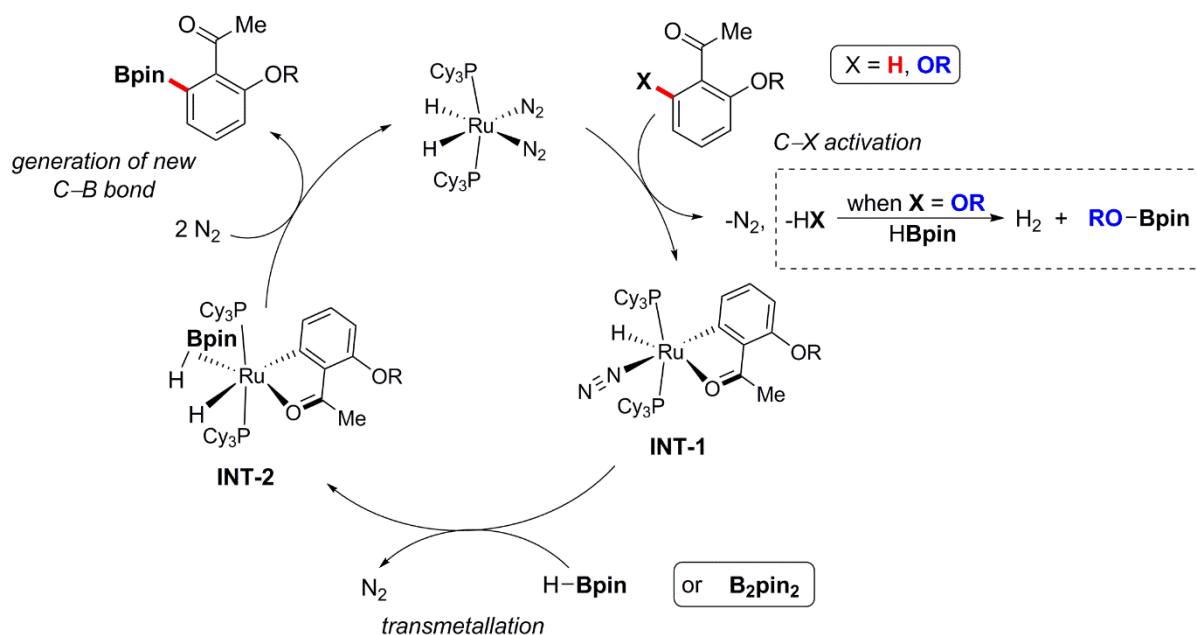


Figure 2.25. Proposed catalytic cycle of functionalisation of C–X (X = H, O) of acetophenone substrates

The substrate B_2pin_2 was initially tested as main group reagent in these C–X (X = H, O) functionalisation reactions as the anticipated side products generated from the reaction of the main group reagent with the cleaved fragments would be HBpin (which could react as main group partner as well Figure 2.25) and RO–Bpin respectively. The reaction of **1** with 2,6-dimethoxyacetophenone (**2a**) and B_2pin_2 in a 1:1:1 ratio at 40 °C resulted in formation of two new species and the aryl ethanol product from the transfer hydrogenation of the acetophenone substrate (Figure 2.26). Two new resonances were observed in the $^{11}\text{B}\{^1\text{H}\}$ NMR spectra at $\delta_{\text{B}} = 22.7$ ppm and 28.6 ppm that corresponded to the two new

species speculated as the hydroboration of 2,6-dimethoxyacetophenone across the carbonyl bond (**15b**) as well as the anticipated C–X functionalised product at the *ortho*-position (**14**) respectively. These products were never isolated cleanly or independently synthesised successfully *via* other methods to confirm the formation of them however Chatani *et al.* reported similar product formations in their C–H functionalisation of acetophenones substrates with arylboronates – stating the formation of the HB(OR)₂ as a by-product reduced their catalytic reaction.³² In addition, the ¹¹B{¹H} NMR spectra chemical shifts of related acetophenone compounds containing boronic ester (Bpin and Bnep) in the *meta* and *para* position of the arene ring were found between $\delta_B = 27 - 31$ ppm¹⁰⁹ and the ¹¹B{¹H} NMR spectra chemical shifts of hydroboration of related acetophenones substrates were found between $\delta_B = 22 - 23$ ppm.¹¹⁰ The same product formation, based on the ¹¹B{¹H} NMR spectrum, was also achieved when the reaction was performed with HBpin instead of B₂pin₂ which justified the formation of HBpin as an intermediate during the functionalisation reaction with B₂pin₂ and confirmed that HBpin could also act as the main group coupling partner. The analogous reaction was performed with 2-methoxyacetophenone with the same outcome of generation of the hydroboration product as well as the postulated formation of the expected C–X functionalisation product (**14**) (Figure 2.26).

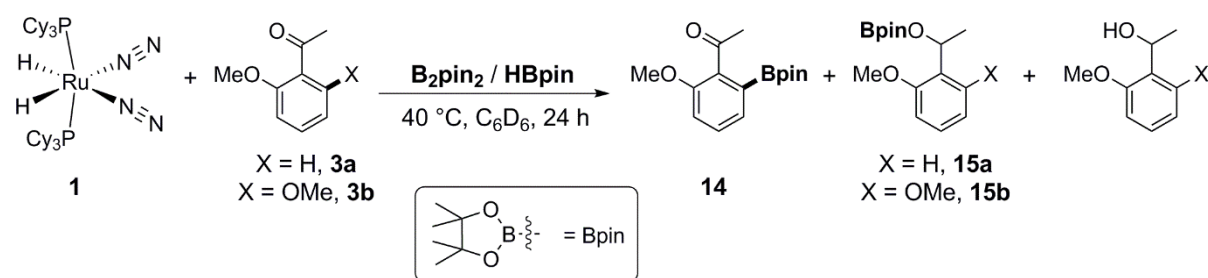


Figure 2.26. Speculated products from functionalisation of C–X bond

The viability of **4a** as a reactive intermediate in this functionalisation reaction was further investigated. The reaction of **4a** with B₂pin₂ at 50 °C resulted in the formation of one major species with signals in ¹H and ¹¹B{¹H} NMR spectra corresponding to signals assigned to the hydroboration product, **15a**. Repeating the reaction but using catalytic amounts of **4a** (10 mol %) and in the presence of 1 equivalent of 2,6-dimethoxyacetophenone as well as 1 equivalent of B₂pin₂ gave product peaks assigned to not only **15b** but notably **14** as well. These two results suggest there are two different pathways **4a** can take depending on the reaction conditions. In the presence of additional acetophenone substrate yields the postulated desired product however in the absence of the substrate, only hydroboration product was observed.

Sabo-Etienne has already reported the reaction of HBpin with **1-2H₂** to generate ruthenium σ -borane complexes [RuH[(μ -H)₂Bpin](σ -HBpin)(PCy₃)₂] and [Ru(H)₂(η^2 -HBpin)(η^2 -H₂)(PCy₃)₂].^{101,102} No control reaction was performed between **1** with B₂pin₂, however as HBpin was anticipated to

be generated from the functionalisation reaction, similar reactivity between HBpin and **1** was predicted. These σ -borane complexes were known to be active species in reduction of CO₂ to C₁ and C₂ containing molecules with HBpin¹¹¹ and therefore were not expected to prohibit turnover of the functionalisation reaction.

2.4 CONCLUSION

A comprehensive study of the organometallic products of the sp^2 C–O bond activation of aryl methyl and biaryl ethers bearing ketone directing groups by [Ru(H)₂(N₂)₂(PCy₃)₂] has been presented. Significant quantities of ruthenium-aryloxide (**6a**) or ruthenium-carbonyl (**5-N₂**) side-products are formed during C–O cleavage and their formation is rationalised based on the initial formation of alcohol by-products that react with [Ru(H)₂(N₂)₂(PCy₃)₂] at a faster rate than the ethers. In substrates where an *ortho*-C–H bond is available there is a kinetic preference for C–H over C–O bond activation.

DFT studies revealed that the lowest energy pathway for bond activation involves the oxidative addition of the C–X bond to Ru(II) to form Ru(IV) intermediates. In this pathway, the approach of the C–X bond to Ru is selectivity determining. Ligand dissociation (*i.e.* N₂ dissociation) occurs *en route* to the rate-determining step and that stationary points along the C–O cleavage pathway require large changes in the P–Ru–P angle. Alternative pathways for C–O bond activation were explored and shown to be marginally less favourable due to high energy transition states for either the bond activation step (S_NAr/hydrodeoxygenation) or the formation of the reactive intermediates required for bond activation (oxidative addition to Ru(0)).

The discovery of a ruthenium(II) complex capable of C–O bond activation under mild conditions (25 – 40 °C) and the new Ru(II)/Ru(IV) mechanism presented here for C–O bond cleavage may have broad implications for the development of new catalysts for chemical transformation of renewable resources.

2.5 FUTURE WORK

The expansion of the substrate scope and altering the directing group of these small aromatic molecules has only been briefly touched upon in this investigation. Changing the directing group from ketone to a hydrosilyl ether group has shown some promising results however isolation of the organometallic products was never achieved to confirm whether C–X bond activation occurred. Large scale reaction of **1** with **9** should provide a better opportunity to isolate either the intermediates or the final product.

The C–H activation of benzofuran was particularly interesting as it highlights the potentially different mechanisms in operation depending on the substrate. Further study into an array of cyclic ethers would add more information as to whether this ruthenium *bis*(dinitrogen) complex is able to

cleave just C–H bond of these cyclic ethers and whether the ring size and absence or presence of an unsaturated bond affects reactivity.

The low conversion of the reactions to form the cyclometallated intermediates in the C–O bond cleavage reactions prevented any meaningful kinetic experiments to be performed. However, the C–H activation of 2-methoxyacetophenone and 2-aryloxyacetophenone by **1** yielded > 50 % conversion to cyclometallated product in an 1 h and therefore performing kinetic analysis as well as kinetic isotope effect could provide evidence for the C–H mechanistic pathway.¹¹² Agreement of the kinetic data with the postulated mechanism operating in these reactions would allow greater confidence in the computational model of both the C–H and C–O activation pathways.

In addition, the functionalisation of the C–O bond was preliminarily investigated with HBpin and B₂pin₂ as the coupling partners. Expansion to see if other organoboranes could provide cleaner reactions would help to identify with more certainty the reaction products. As well as organoboranes, other heavier main group reagents were tested, and this exploratory investigation will be discussed in the next two chapters of this thesis with the formation of ruthenium main group (aluminium, magnesium and zinc) heterobimetallic hydride complexes.

2.6 REFERENCES

- 1 A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, 2006, **311**, 484–489.
- 2 Z. Sun, G. Bottari, A. Afanasenko, M. C. A. Stuart, P. J. Deuss, B. Fridrich and K. Barta, *Nat. Catal.*, 2018, **1**, 82–92.
- 3 E. Wenkert, E. L. Michelotti and C. S. Swindell, *J. Am. Chem. Soc.*, 1979, **101**, 2246–2247.
- 4 B.-T. Guan, S.-K. Xiang, B.-Q. Wang, Z.-P. Sun, Y. Wang, K.-Q. Zhao and Z.-J. Shi, *J. Am. Chem. Soc.*, 2008, **130**, 3268–3269.
- 5 B. T. Guan, Y. Wang, B. J. Li, D. G. Yu and Z. J. Shi, *J. Am. Chem. Soc.*, 2008, **130**, 14468–14470.
- 6 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457–2483.
- 7 L.-G. Xie and Z.-X. Wang, *Chem. - A Eur. J.*, 2011, **17**, 4972–4975.
- 8 L.-G. Xie and Z.-X. Wang, *Chem. - A Eur. J.*, 2010, **16**, 10332–10336.
- 9 Z. Li, S. L. Zhang, Y. Fu, Q. X. Guo and L. Liu, *J. Am. Chem. Soc.*, 2009, **131**, 8815–8823.
- 10 T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, 1979, **101**, 6319–6332.
- 11 H. Ogawa, H. Minami, T. Ozaki, S. Komagawa, C. Wang and M. Uchiyama, *Chemistry*, 2015, **21**, 13904–13908.
- 12 P. Kelley, S. Lin, G. Edouard, M. W. Day and T. Agapie, *J. Am. Chem. Soc.*, 2012, **134**, 5480–5483.
- 13 P. Álvarez-Bercedo and R. Martin, *J. Am. Chem. Soc.*, 2010, **132**, 17352–17353.
- 14 J. Cornella, E. Gómez-Bengoia and R. Martin, *J. Am. Chem. Soc.*, 2013, **135**, 1997–2009.
- 15 C. Zarate, M. Nakajima and R. Martin, *J. Am. Chem. Soc.*, 2017, **139**, 1191–1197.
- 16 B. Wang, Q. Zhang, J. Jiang, H. Yu and Y. Fu, *Chem. - A Eur. J.*, 2017, **23**, 17249–17256.
- 17 A. G. Sergeev and J. F. Hartwig, *Science*, 2011, **332**, 439–43.
- 18 J. Zakzeski, P. C. A. Bruijninx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552–3599.
- 19 Y.-R. Luo, in *Bond Dissociation Energies in Organic Compounds*, Boca Raton, FL: CRC Press, 1st edn., 2003, pp. 209–217.
- 20 K. Poppius, *Acta Chem. Scand.*, 1984, **38B**, 611–616.
- 21 J. Stein, L. N. Lewis, Y. Gao and R. A. Scott, *J. Am. Chem. Soc.*, 1999, **121**, 3693–3703.
- 22 N. M. Esfandiari and S. A. Blum, *J. Am. Chem. Soc.*, 2011, **133**, 18145–18147.
- 23 R. A. Jones, F. M. Real, G. Wilkinson, A. M. R. Galas and M. B. Hursthouse, *J. Chem. Soc. Dalt. Trans.*, 1981, 126–131.
- 24 A. G. Sergeev, J. D. Webb and J. F. Hartwig, *J. Am. Chem. Soc.*, 2012, **134**, 20226–20229.
- 25 F. Gao, J. D. Webb and J. F. Hartwig, *Angew. Chemie - Int. Ed.*, 2016, **55**, 1474–1478.
- 26 B. Sawatlon, T. Wititsuwannakul, Y. Tantirungrotechai and P. Surawatanawong, *Dalt. Trans.*, 2014, **43**, 18123–18133.
- 27 L. Xu, L. W. Chung and Y. D. Wu, *ACS Catal.*, 2016, **6**, 483–493.
- 28 M. Tobisu, T. Morioka, A. Ohtsuki and N. Chatani, *Chem. Sci.*, 2015, **6**, 3410–3414.
- 29 F. Kakiuchi, M. Usui, S. Ueno, N. Chatani and S. Murai, *J. Am. Chem. Soc.*, 2004, **126**, 2706–2707.
- 30 N. Chatani, H. Tatamidani, Y. Ie, F. Kakiuchi and S. Murai, *J. Am. Chem. Soc.*, 2001, **123**, 4849–4850.
- 31 F. Kakiuchi, S. Kan, K. Igi, N. Chatani and S. Murai, *J. Am. Chem. Soc.*, 2003, **125**, 1698–1699.
- 32 F. Kakiuchi, Y. Matsuura, S. Kan and N. Chatani, *J. Am. Chem. Soc.*, 2005, **127**, 5936–5945.
- 33 S. Ueno, E. Mizushima, N. Chatani and F. Kakiuchi, *J. Am. Chem. Soc.*, 2006, **128**, 16516–16517.
- 34 H. Kondo, N. Akiba, T. Kochi and F. Kakiuchi, *Angew. Chemie Int. Ed.*, 2015, **54**, 9293–9297.
- 35 T. Koreeda, T. Kochi and F. Kakiuchi, *J. Am. Chem. Soc.*, 2009, **131**, 7238–7239.
- 36 S. Ueno, N. Chatani and F. Kakiuchi, *J. Am. Chem. Soc.*, 2007, **129**, 6098–6099.
- 37 Y. Ogiwara, T. Kochi and F. Kakiuchi, *Org. Lett.*, 2011, **13**, 3254–3257.
- 38 Y. Zhao and V. Snieckus, *J. Am. Chem. Soc.*, 2014, **136**, 11224–11227.
- 39 Y. Zhao and V. Snieckus, *Org. Lett.*, 2015, **17**, 4674–4677.

- 40 Y. Zhao and V. Snieckus, *Chem. Commun.*, 2016, **52**, 1681–1684.
- 41 Z. Wang, Y. Zhou, W. H. Lam and Z. Lin, *Organometallics*, 2017, **36**, 2354–2363.
- 42 T. Matsubara, N. Koga, D. G. Musaev and K. Morokuma, *J. Am. Chem. Soc.*, 1998, **120**, 12692–12693.
- 43 T. Matsubara, N. Koga, D. G. Musaev and K. Morokuma, *Organometallics*, 2000, **19**, 2318–2329.
- 44 S. Ueno, T. Kochi, N. Chatani and F. Kakiuchi, *Org. Lett.*, 2009, **11**, 855–858.
- 45 U. Helmstedt and E. Clot, *Chemistry*, 2012, **18**, 11449–11458.
- 46 P. Lara, M. Paneque, M. L. Poveda, V. Salazar, L. L. Santos and E. Carmona, *J. Am. Chem. Soc.*, 2006, **128**, 3512–3513.
- 47 L. L. Santos, K. Mereiter and M. Paneque, *Organometallics*, 2013, **32**, 565–569.
- 48 J. Choi, Y. Choliy, X. Zhang, T. J. Emge, K. Krogh-Jespersen and A. S. Goldman, *J. Am. Chem. Soc.*, 2009, **131**, 15627–15629.
- 49 S. Kundu, J. Choi, D. Y. Wang, Y. Choliy, T. J. Emge, K. Krogh-Jespersen and A. S. Goldman, *J. Am. Chem. Soc.*, 2013, **135**, 5127–5143.
- 50 S. Sabo-Etienne and B. Chaudret, *Coord. Chem. Rev.*, 1998, **178–180**, 381–407.
- 51 D. E. Linn and J. Halpern, *J. Am. Chem. Soc.*, 1987, **109**, 2969–2974.
- 52 A. J. Toner, S. Gründemann, E. Clot, H.-H. H. Limbach, B. Donnadieu, S. Sabo-Etienne and B. Chaudret, *J. Am. Chem. Soc.*, 2000, **122**, 6777–6778.
- 53 Y. Guari, S. Sabo-Etienne and B. Chaudret, *J. Am. Chem. Soc.*, 1998, **120**, 4228–4229.
- 54 Y. Guari, A. Castellanos, S. Sabo-Etienne and B. Chaudret, *J. Mol. Catal. A Chem.*, 2004, **212**, 77–82.
- 55 M. L. Christ, S. Sabo-Etienne, G. Chung and B. Chaudret, *Inorg. Chem.*, 1994, **33**, 5316–5319.
- 56 P. D. Bolton, M. Grellier, N. Vautravers, L. Vendier and S. Sabo-Etienne, *Organometallics*, 2008, **27**, 5088–5093.
- 57 J. L. Snelgrove, J. C. Conrad, M. D. Eelman, M. M. Moriarty, G. P. A. Yap and D. E. Fogg, *Organometallics*, 2005, **24**, 103–109.
- 58 J. F. Hartwig, R. A. Andersen and R. G. Bergman, *Organometallics*, 1991, **10**, 1875–1887.
- 59 K. Osakada, K. Ohshiro and A. Yamamoto, *Organometallics*, 1991, **10**, 404–410.
- 60 D. J. Cole-Hamilton, R. J. Young and G. Wilkinson, *J. Chem. Soc., Dalt. Trans.*, 1976, 1995–2001.
- 61 Q. Major, A. J. Lough and D. G. Gusev, *Organometallics*, 2005, **24**, 2492–2501.
- 62 M. J. Camenzind, B. R. James, D. Dolphin, J. W. Sparapany and J. A. Ibers, *Inorg. Chem.*, 1988, **27**, 3054–3057.
- 63 M. E. Van Der Boom, S. Y. Liou, Y. Ben-David, L. J. W. Shimon and D. Milstein, *J. Am. Chem. Soc.*, 1998, **120**, 6531–6541.
- 64 J. Alós, M. A. Esteruelas, M. Oliván, E. Oñate and P. Puylaert, *Organometallics*, 2015, **34**, 4908–4921.
- 65 J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822–8824.
- 66 J. P. Perdew, *Phys. Rev. B*, 1986, **34**, 7406–7406.
- 67 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100.
- 68 H. T. Andrae, D.; Häußermann, U.; Dolg, M.; Stoll, H.; Preuß, *Theor. Chim. Acta*, 1990, **77**, 123–141.
- 69 J. M. L. Martin and A. Sundermann, *J. Chem. Phys.*, 2001, **114**, 3408–3420.
- 70 A. Bergner, M. Dolg, W. Küchle, H. Stoll and H. Preuß, *Mol. Phys.*, 1993, **80**, 1431–1441.
- 71 A. Höllwarth, M. Böhme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.*, 1993, **208**, 237–240.
- 72 W. J. Hehre, K. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261.
- 73 T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294–301.
- 74 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213–222.
- 75 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.
- 76 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999–3093.
- 77 J. A. Panetier, S. A. MacGregor and M. K. Whittlesey, *Angew. Chemie Int. Ed.*, 2011, **50**, 2783–2786.

- 78 S. A. Macgregor, D. McKay, J. A. Panetier and M. K. Whittlesey, *Dalt. Trans.*, 2013, **42**, 7386–7395.
- 79 M. K. Cybulski, D. McKay, S. A. Macgregor, M. F. Mahon and M. K. Whittlesey, *Angew. Chemie Int. Ed.*, 2017, **56**, 1515–1519.
- 80 R. N. Perutz and S. Sabo-Etienne, *Angew. Chemie - Int. Ed.*, 2007, **46**, 2578–2592.
- 81 C. Grünwald, O. Gevert, J. Wolf, P. González-Herrero and H. Werner, *Organometallics*, 1996, **15**, 1960–1962.
- 82 V. Rodriguez, S. Sabo-Etienne, B. Chaudret, J. Thoburn, S. Ulrich, H.-H. Limbach, J. Eckert, J.-C. Barthelat, K. Hussein and C. J. Marsden, *Inorg. Chem.*, 1998, **37**, 3475–3485.
- 83 M. Grellier, T. Ayed, J. C. Barthelat, A. Albinati, S. Mason, L. Vendier, Y. Coppel and S. Sabo-Etienne, *J. Am. Chem. Soc.*, 2009, **131**, 7633–7640.
- 84 I. M. Riddlestone, N. A. Rajabi, J. P. Lowe, M. F. Mahon, S. A. Macgregor and M. K. Whittlesey, *J. Am. Chem. Soc.*, 2016, **138**, 11081–11084.
- 85 D. S. Van Lori S., J. Eckert, O. Eisenstein, J. H. Hall, J. C. Huffman, S. A. Jackson, T. F. Koetzle, G. J. Kubas, P. J. Vergamini and K. G. Caulton, *J. Am. Chem. Soc.*, 1990, **112**, 4831–4841.
- 86 T. R. Cundari, T. V. Grimes and T. B. Gunnoe, *J. Am. Chem. Soc.*, 2007, **129**, 13172–13182.
- 87 D. Conner, K. N. Jayaprakash, T. R. Cundari and T. B. Gunnoe, *Organometallics*, 2004, **23**, 2724–2733.
- 88 N. Sieffert and M. Bühl, *J. Am. Chem. Soc.*, 2010, **132**, 8056–8070.
- 89 A. J. Johansson, E. Zuidema and C. Bolm, *Chem. - A Eur. J.*, 2010, **16**, 13487–13499.
- 90 I. Atheaux, F. Delpech, B. Donnadieu, S. Sabo-Etienne, B. Chaudret, K. Hussein, J.-C. Barthelat, T. Braun, S. B. Duckett and R. N. Perutz, *Organometallics*, 2002, **21**, 5347–5357.
- 91 K. Hussein, C. J. Marsden, J.-C. Barthelat, V. Rodriguez, S. Conejero, S. Sabo-Etienne, B. Donnadieu and B. Chaudret, *Chem. Commun.*, 1999, 1315–1316.
- 92 F. Delpech, S. Sabo-Etienne, J.-C. Daran, B. Chaudret, K. Hussein, C. J. Marsden and J.-C. Barthelat, *J. Am. Chem. Soc.*, 1999, **121**, 6668–6682.
- 93 F. Delpech, S. Sabo-Etienne, B. Chaudret and J.-C. Daran, *J. Am. Chem. Soc.*, 1997, **119**, 3167–3168.
- 94 D. G. Hamilton and R. H. Crabtree, *J. Am. Chem. Soc.*, 1988, **110**, 4126–4133.
- 95 G. Collin and H. Höke, *Ullmann's Encycl. Ind. Chem.*, 2007.
- 96 S. Yow, A. E. Nako, L. Neveu, A. J. P. White and M. R. Crimmin, *Organometallics*, 2013, **32**, 5260–5262.
- 97 X. Zhang, E. J. Watson, C. A. Dullaghan, S. M. Gorun and D. A. Sweigart, *Angew. Chemie - Int. Ed.*, 1999, **38**, 2206–2208.
- 98 D. J. Paymode and C. V. Ramana, *J. Org. Chem.*, 2015, **80**, 11551–11558.
- 99 T. Ueyama, S. Mochida, T. Fukutani, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2011, **13**, 706–708.
- 100 M. Ayoub and A. Z. Abdullah, *Renew. Sustain. Energy Rev.*, 2012, **16**, 2671–2686.
- 101 V. Montiel-Palma, M. Lumbierres, B. Donnadieu, S. Sabo-Etienne and B. Chaudret, *J. Am. Chem. Soc.*, 2002, **124**, 5624–5625.
- 102 S. Lachaize, K. Essalah, V. Montiel-Palma, L. Vendier, B. Chaudret, J.-C. Barthelat and S. Sabo-Etienne, *Organometallics*, 2005, **24**, 2935–2943.
- 103 Y. Gloaguen, G. Alcaraz, L. Vendier and S. Sabo-Etienne, *J. Organomet. Chem.*, 2009, **694**, 2839–2841.
- 104 G. Alcaraz, E. Clot, U. Helmstedt, L. Vendier and S. Sabo-Etienne, *J. Am. Chem. Soc.*, 2007, **129**, 8704–8705.
- 105 S. Lachaize, S. Sabo-Etienne, B. Donnadieu and B. Chaudret, *Chem. Commun. (Camb.)*, 2003, **24**, 214–215.
- 106 R. Ben Said, K. Hussein, J.-C. Barthelat, I. Atheaux, S. Sabo-Etienne, M. Grellier, B. Donnadieu and B. Chaudret, *Dalt. Trans.*, 2003, 4139–4146.
- 107 R. Ben Said, K. Hussein, B. Tangour, S. Sabo-Etienne and J.-C. Barthelat, *New J. Chem.*, 2003, **27**, 1385–1391.
- 108 A. Suzuki, *Chem. Commun.*, 2005, 4759–4763.
- 109 L. H. Andrade and T. Barcellos, *Org. Lett.*, 2009, **11**, 3052–3055.
- 110 W. Wang, X. Shen, F. Zhao, H. Jiang, W. Yao, S. A. Pullarkat, L. Xu and M. Ma, *J. Org. Chem.*,

- 2018, **83**, 69–74.
- 111 S. Bontemps, L. Vendier and S. Sabo-Etienne, *Angew. Chemie Int. Ed.*, 2012, **51**, 1671–1674.
- 112 E. M. Simmons and J. F. Hartwig, *Angew. Chemie Int. Ed.*, 2012, **51**, 3066–3072.

3 CHAPTER THREE – FORMATION OF A SERIES OF $M\cdot Ru$ ($M = Al, Zn, Mg$) HETEROBIMETALLIC HYDRIDE COMPLEXES

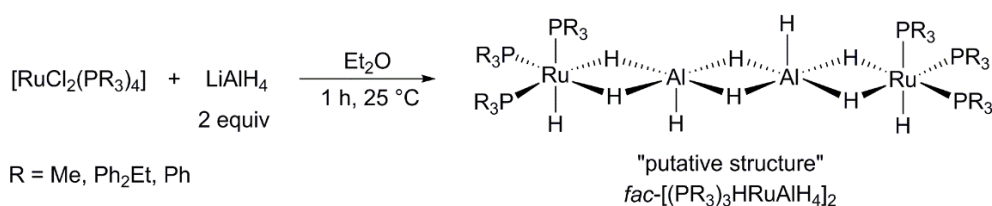
3.1 INTRODUCTION

The reactions of $[Ru(H)_2(\eta^2-H_2)_2(PCy_3)_2]$ with molecules containing E–H bonds ($E = B$ and Si) have been studied extensively by Chaudret's and Sabo-Etienne's group's respectively (CHAPTER ONE), however extension to include heavier main group hydrides have so far been limited.^{1,2} The use of heavier metallic main group hydrides complements the reactivity shown by silicon with access to expanding the coordination sphere around the main group metal and therefore provides the opportunity to form additional bonding motifs between the main group metal and ruthenium centre.

In terms of existing $M\cdot Ru$ heterobimetallic complexes ($M = Al, Zn, Mg$) there have only been a handful of publications to date. These heterobimetallic complexes have been studied due to their structure and bonding, the spectroscopic properties they exhibit and the role they can play in further reactions. Below is a summary of the literature of these $M\cdot Ru$ heterobimetallic complexes.

3.1.1 $Al\cdot Ru$ heterobimetallic complexes

In 1986 Wilkinson *et al.* reported the synthesis of 3 different aluminohydride complexes of ruthenium(II) from the reaction of $[RuCl_2(PR_3)_4]$ ($R = Me, Ph_2Et$ and Ph) with 2 equivalents of $LiAlH_4$ (Scheme 3.1).³ IR spectra for all 3 complexes exhibited strong absorbances between $1800 - 1650\text{ cm}^{-1}$ for the bridging and terminal hydrides (no exact assignment of the absorbance was made for the terminal or bridging hydrides although it was anticipated the terminal hydrides should exhibit a higher frequency absorbance).



Scheme 3.1 Synthesis of dimeric aluminohydride complexes of $Ru(II)$

Isolation of these 3 complexes for X-ray crystallography was not possible however the structure of these complexes was postulated to be similar to the known dimeric variants of these aluminohydride complexes with other transition metal centres (manganese, rhenium and tungsten) (Figure 3.1).⁴⁻⁷ In the ^1H NMR spectra a broad quartet was observed due to both the terminal $Ru-H$ and bridging $Ru-H-Al$

environments ($R = \text{Me}$, $\delta_{\text{H}} = -10.76$ ppm, $J_{\text{PH}} = 20.4$ Hz; $R = \text{Ph}_2\text{Et}$, $\delta_{\text{H}} = -10.90$ ppm, $J_{\text{PH}} = 20.0$ Hz; $R = \text{Ph}$, $\delta_{\text{H}} = -10.90$ ppm, $J_{\text{PH}} = 20.0$ Hz) and a broad singlet was observed due to the terminal Al–H and bridging Al–H–Al environments ($R = \text{Me}$, $\delta_{\text{H}} = 4.60$ ppm; $R = \text{Ph}_2\text{Et}$, $\delta_{\text{H}} = 4.51$ ppm; $R = \text{Ph}$, $\delta_{\text{H}} = 4.50$ ppm). Low temperature NMR spectroscopy only managed to decoalesce the signal for the terminal Al–H and bridging Al–H–Al hydrides with the activation energy of this process calculated to be $\Delta G^\ddagger = 10.5 \pm 0.2$ kcal mol⁻¹. The facile exchange process of the terminal and bridging Ru–H hydrides, even at low temperatures, was noted to deviate from the behaviour of the similar manganese,^{4,5} tungsten⁶ and rhenium⁷ systems. This facile exchange was postulated to derive from the *facial*-configuration of the PR₃ groups around ruthenium allowing easy rotation of the hydrides without rearrangement around the metal. The *facial*-isomer of these ruthenium aluminohydride complexes were further confirmed by the single phosphorous environment exhibited in each respective spectrum ($R = \text{Me}$, $\delta_{\text{P}} = -2.5$ ppm; $R = \text{Ph}_2\text{Et}$, $\delta_{\text{H}} = 46.7$ ppm; $R = \text{Ph}$, $\delta_{\text{H}} = 47.2$ ppm) along with the quartet coupling pattern of the terminal and bridging Ru–H signal in the ¹H NMR spectra. ²⁷Al{¹H} NMR spectroscopy was also performed on these samples giving values indicative of 5 coordinate aluminium centres ($R = \text{Me}$, $\delta_{\text{Al}} = 74$ ppm; $R = \text{Ph}_2\text{Et}$, $\delta_{\text{Al}} = 71$ ppm; $R = \text{Ph}$, $\delta_{\text{Al}} = 68$ ppm).

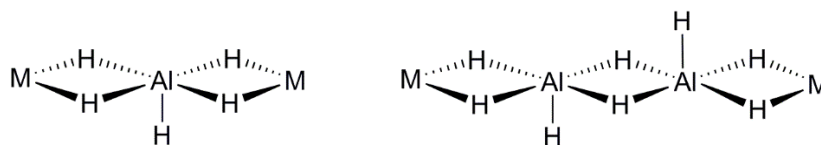
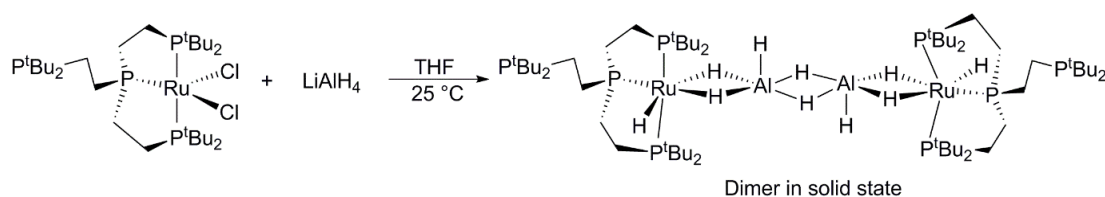


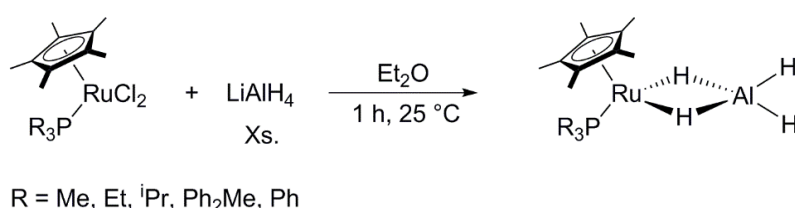
Figure 3.1 Motifs of the bridging and terminal aluminium hydrides in heterobimetallic complexes ($M = \text{transition metal}$)

It would not be till 2014 that Field *et al.* obtained the first crystallographic evidence of a ruthenium complex coordinated to a tetrahydridoaluminate ligand with the $(\text{Al}_2\text{H}_8)^{2-}$ unit motif (Figure 3.1).⁸ The crystal structure represented the dimeric form of this complex however the solution state data was ambiguous as to whether the complex existed as a monomer or dimer (Scheme 3.2). The geometry around the ruthenium centres was distorted octahedral with the average bridging Ru–H bond lengths of 1.66 Å, the average terminal Ru–H bond lengths of 1.58 Å, the average bridging Al–H bond lengths in Ru–H–Al unit of 1.81 Å and the average terminal Al–H bond lengths of 1.54 Å. In the ¹H NMR spectrum 4 distinct resonances were observed for the 4 different hydride environments: a doublet of triplets of doublets was observed at $\delta_{\text{H}} = -13.54$ ppm ($J_{\text{HP}} = 22$ and 22 Hz, $J_{\text{HH}} = 6.6$ Hz) for the terminal Ru–H, a broad singlet at $\delta_{\text{H}} = -10.20$ ppm for the bridging hydrides in the Al–H–Al unit, a doublet of triplets at $\delta_{\text{H}} = -10.13$ ppm ($J_{\text{HP}} = 53$ and 14 Hz) for the bridging hydrides in the Ru–H–Al unit, and finally a broad resonance at $\delta_{\text{H}} = 2.81$ ppm for the terminal Al–H. Only additional multinuclear NMR spectroscopy data was provided for this complex.



Scheme 3.2 Formation of first isolated ruthenium tetrahydridoaluminate complex with $(\text{Al}_2\text{H}_8)^{2-}$ unit

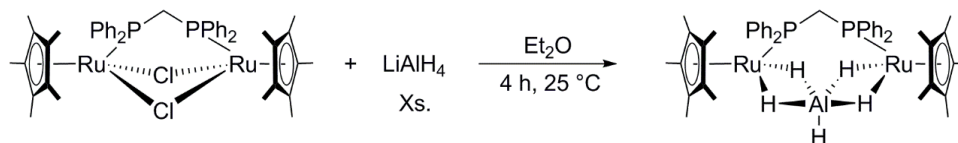
In 1987, Suzuki *et al.* reported the novel synthesis of 5 monomeric aluminohydride complexes of ruthenium(II) from the reaction of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{Cl})_2(\text{PR}_3)]$ ($\text{R} = \text{Me}, \text{Et}, ^i\text{Pr}, \text{Ph}_2\text{Me}$ and Ph) with an excess of LiAlH_4 (Scheme 3.3).⁹ These 5 complexes were characterised by ^1H , ^{13}C NMR, and IR spectroscopy. The key feature of these complexes was the upfield chemical shifts of the bridging hydrides found as broad resonances in the ^1H NMR spectra ($\delta_{\text{H}} = -13.01 - -13.87$ ppm, $\text{fwhm} = \text{ca. } 75$ Hz) relative to the terminal aluminium hydrides ($\delta_{\text{H}} = 3.57 - 4.55$ ppm). At low temperature (-20 °C) the signal for the terminal aluminium hydrides of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{AlH}_4)(\text{PMe}_3)]$ decoalesced into two broad singlets $\delta_{\text{H}} = 3.86$ (fwhm = 21 Hz) and 5.36 ppm (fwhm = 33 Hz) however no decoalescence was observed for the bridging hydrides. This result highlighted that no exchange between the bridging and terminal aluminium hydrides occurred at ambient temperatures. IR absorbance for both the bridging and terminal aluminium hydrides for all 5 complexes were found within the region of $1718 - 1875 \text{ cm}^{-1}$ as sharp peaks. The assignment of these ruthenium aluminohydride complexes as monomeric in solution was further evidenced from microanalysis measurement of the molecular weight of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{AlH}_4)(\text{PMe}_3)]$ as 374 g mol^{-1} at low temperatures in benzene under 1 atm of argon, however no X-ray crystallography was obtained, although the solid state structure may differ from solution state.



Scheme 3.3 Synthesis of novel monomeric aluminohydride complexes of Ru(II)

Continuing with the use of LiAlH_4 as the aluminium source, the reaction of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ru}_2(\mu\text{-dppm})\text{Cl}_2]$ ($\text{dppm} = 1,1\text{-bis(diphenylphosphino)methane}$) with an excess of LiAlH_4 resulted in the formation of yellow crystals identified as $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\mu\text{-AlH}_5)]$ (Scheme 3.4).¹⁰ This ruthenium aluminohydride complex displayed diagnostic strong absorbance bands in the IR spectrum at 1779 and 1728 cm^{-1} for the bridging and terminal hydrides respectively. Upon forming the deuteride analogue of this complex using LiAlD_4 , the absorbance bands for the hydrides shifted down

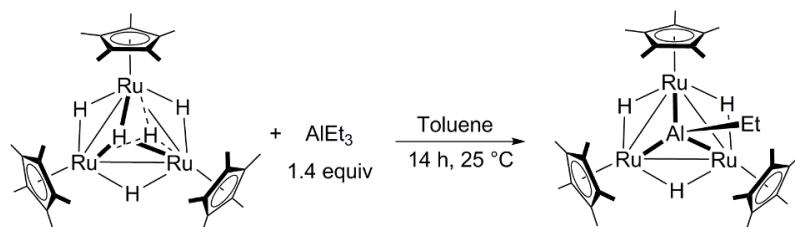
to 1275 and 1255 cm^{-1} respectively as expected. Only one resonance was observed in the ^1H NMR spectrum for the bridging hydrides, $\delta_{\text{H}} = -13.96$ ppm (d, $J_{\text{PH}} = 22.8$ Hz) which failed to decoalesce at low temperatures. No resonance was observed for the terminal Al–H environment, even at low temperature, however the resonance was postulated to be incredibly broad and lost in the baseline of the spectrum due to coupling with the quadrupolar aluminium nucleus. A single resonance at $\delta_{\text{P}} = 58.4$ ppm was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum which suggested a highly symmetric complex. The structure of this complex was confirmed by single crystal X-ray crystallography. The geometry of the AlH_5 unit adopted a distorted square based pyramid with the H–Al–H bond angle of the 4 basal hydrides measured as $77(1)^\circ$, $84(1)^\circ$, $78(1)^\circ$ and $86(1)^\circ$ respectively. The average bond angle between the 4 basal hydrides with the axial hydride was measured to be 113° . The 4 bridging Al–H bond lengths were identical, measured to be $1.88(2)$ Å with corresponding shorter bridging Ru–H bonds at $1.55(3)$ Å. For comparison the axial Al–H bond length was measured to be $1.49(5)$ Å. No Ru---Ru interaction was expected as the Ru–Ru distance exceeded 4 Å however the Ru–Al bond lengths were both within the sum of the single bond radii¹¹ at $2.445(2)$ and $2.464(2)$ Å respectively. Girolami *et al.* stipulated that the aluminium was best described as an $[(\mu\text{-H})_2\text{AlH}(\mu\text{-H})_2]^{2-}$ unit stabilised by two Ru(II) centres however beyond analysing the X-ray data, no further information about the bonding description of this complex was ascertained.



Scheme 3.4 Formation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\mu\text{-AlH}_5)]$

In 2003 Suzuki *et al.* published the reactions of a trinuclear ruthenium polyhydride precursor, $[\{\eta^5\text{-C}_5\text{Me}_5\}\text{Ru}]_3(\mu\text{-H})_3(\mu_3\text{-H})_2]$, with MeLi, ZnEt₂, MgⁱPr₂, GaMe₃ and AlEt₃ to generate a number of new bimetallic polyhydride complexes.¹² No X-ray crystallographic data was obtained for the aluminium ruthenium polyhydride complexes however X-ray data were collected for the Li, Zn, Mg and Ga analogues which allowed for confidence in the assignment of the structure of the aluminium ruthenium complex with the formula $[\{\eta^5\text{-C}_5\text{Me}_5\}\text{Ru}]_3(\mu\text{-H})_3(\mu_3\text{-AlEt})$ (Scheme 3.5). A single resonance was observed at $\delta_{\text{H}} = -3.84$ ppm in the ^1H NMR spectrum for the 3 bridging hydrides. Aside from cyclic voltammetry measurements of this complex and some ^{13}C NMR spectrum data, no further examination was made on the characterisation of this complex as the lack of X-ray crystallography data prevented any comparison with the other main group polyhydride complexes. It would be interesting to perform ^{27}Al NMR spectroscopy to see if the aluminium does sit in a 4 coordinate environment as postulated. Suzuki *et al.* also noted that only 1 equivalent of the main group substrate was required to cap only one face of the Ru_3 plane to allow for substrate binding on the vacant side of the Ru_3 plane.

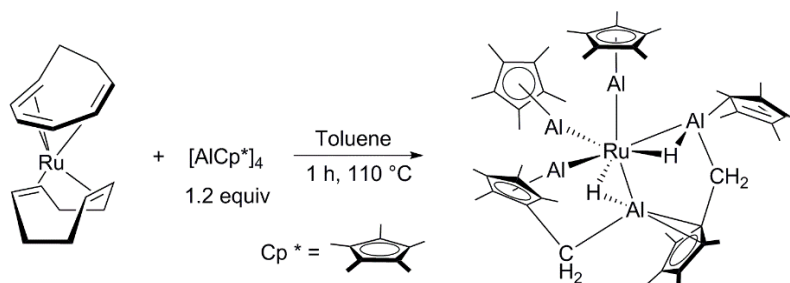
Strict control of stoichiometry was required to achieve this single capping and when 1.4 equivalents of AlEt_3 was used, further reaction led to 2 aluminium centres capping the 2 sides of the Ru_3 plane. Therefore, purposely forming the double capped aluminium ruthenium polyhydride complex would allow for certainty that only one side of the Ru_3 plane was indeed capped by only one of the aluminium substrate.



Scheme 3.5 Formation of $[\{\eta^5\text{-C}_5\text{Me}_5\}\text{Ru}\}_3(\mu\text{-H})_3(\mu_3\text{-AlEt})_2]$

The C–H activation of the methyl groups in C_5Me_5 ligand of $[\text{Al}(\eta^5\text{-C}_5\text{Me}_5)]_4$ was achieved upon reacting with $[\text{Ru}(\eta^4\text{-COD})(\eta^6\text{-COT})]$ at 110 °C in toluene (Scheme 3.6).¹³ The X-ray crystallography data was obtained of this aluminium ruthenium complex with 5 aluminium centres surrounding one ruthenium centre and 2 bridging hydrides located from the electron density map. Ru–Al bond lengths between 2.294(2) – 2.49(3) Å were measured which were within the sum of the single bond radii.¹¹ The bridging Ru–H bond lengths were measured to be 1.7164 and 1.6498 Å with the corresponding Al–H bond lengths measured to be 1.914 and 2.038 Å respectively (no estimated standard deviation (*esd*) values were found for these values). This solid state structure suggested the presence of a bridging hydride and a terminal Ru–H hydride motif as opposed to two bridging hydrides. The bond angles around ruthenium suggested a structure between distorted pentagonal bipyramidal and distorted trigonal prismatic geometry. This aluminium ruthenium complex was also characterised by multinuclear NMR spectroscopy data, however the assignment made of the resonances to the corresponding environment was sparse. A resonance was observed in the ^1H NMR spectrum at $\delta_{\text{H}} = -15.84$ ppm and was characterised as a singlet with an integration of 1H. This resonance was most likely due to the bridging hydride as the iron analogue was found at $\delta_{\text{H}} = -19.00$ ppm however the latter resonance integrated to 2H for both hydrides (solid state data also supported two bridging hydrides). The ^1H NMR spectrum resonance of the remaining hydride was not mentioned in the paper. Performing low temperature NMR spectroscopy could have revealed the identity of this hydride resonance if it was lost in the baseline or could have decoalesced the singlet at $\delta_{\text{H}} = -15.84$ ppm if this was incorrectly integrated as 1H originally. IR spectroscopy could also have provided another handle as to whether there were bridging and terminal Al–H motifs in the structure. Nevertheless, ^{27}Al NMR spectroscopy was performed with only one resonance observed, $\delta_{\text{Al}} = -5.4$ ppm which was indicative of either 4 or 6 coordinate aluminium centres however having only one signal was surprising considering there were

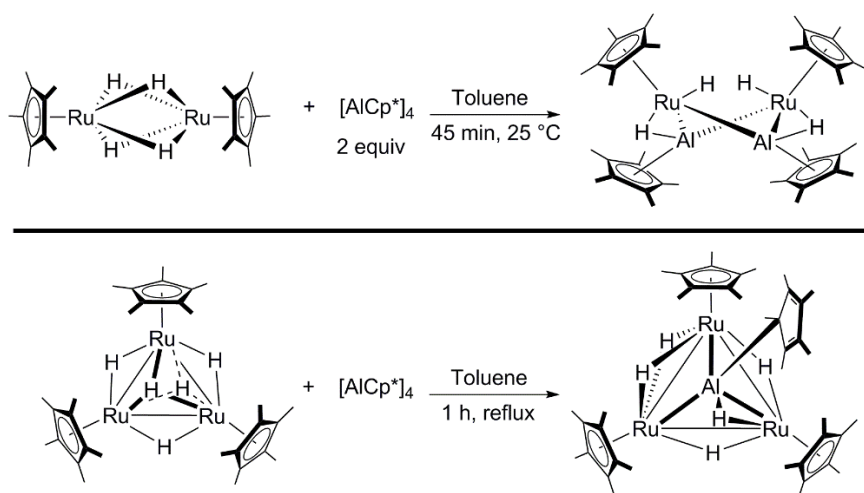
inequivalent aluminium environments in this complex though it was not clear if solid or solution state ^{27}Al NMR spectroscopy was performed. Analysis of this ruthenium aluminium complex and comparison to the iron analogue was not covered in detail as the iron analogue was the main focus of the paper.



Scheme 3.6 C–H activation of methyl groups in $[\text{AlCp}^*]_4$

In 2009 Fischer *et al.* expanded on the work by Suzuki *et al.*¹² by reacting the dimeric $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_2(\mu\text{-H})_4]$ and trimeric $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_3(\mu\text{-H})_3(\mu_3\text{-H})_2]$ ruthenium polyhydrides with $[\text{Al}(\eta^5\text{-C}_5\text{Me}_5)]_4$ to generate the corresponding polyhydride complexes (Scheme 3.7).¹⁴ The product from the reaction with the dimeric ruthenium polyhydride (Scheme 3.7 – Top) displayed a single resonance in ^1H NMR spectrum at $\delta_{\text{H}} = -16.30$ ppm for all 4 hydrides at room temperature. Low temperature ^1H NMR spectroscopy failed to decoalesce the signal to separate the terminal and bridging hydrides. This facile exchange process was exemplified in the IR spectrum with only one broad absorption observed at 1820 cm^{-1} for both the terminal and bridging hydrides and not a single sharp absorbance. X-ray crystallographic data was also obtained for this complex with long Ru---Ru distance ($3.142(5)\text{ \AA}$), long Al---Al distance ($2.86(3)\text{ \AA}$) and short Ru–Al bond distances of $2.263(9)$ and $2.377(11)\text{ \AA}$ however the data set was heavily disordered with both metals statistically distributed over all positions of the Ru_2Al_2 core and, of course, hydride positions were not located in this instance to confirm the assignment of terminal and bridging hydrides in this structure.

The product $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_3(\mu\text{-H})_5(\mu_3\text{Al}(\eta^1\text{-C}_5\text{Me}_5))]$ from the reaction with the trimeric ruthenium polyhydride (Scheme 3.7 – Bottom) displayed a single resonance in ^1H NMR spectrum at $\delta_{\text{H}} = -13.61$ ppm for all 5 hydrides at room temperature and again low temperature failed to decoalesce this signal. In the IR spectrum 3 strong absorbance were observed at 2051 , 1948 and 1747 cm^{-1} for the 3 different hydride environments in the complex. X-ray crystallographic data was obtained to confirm the configuration of the complex bearing 5 bridging hydrides in 3 different environments and the aluminium ligated in an η^1 -fashion to one C_5Me_5 ligand. The Ru–H bond lengths in the Ru–H–Ru unit averaged to $1.73\text{ \AA}$ whereas the Al–H bond lengths in the Al–H–Ru averaged to $1.78\text{ \AA}$. These reactions deviate from the reactivity observed using $[\text{Ru}(\eta^4\text{-COD})(\eta^6\text{-COT})]$ ¹³ with no C–H activation of the methyl group of the C_5Me_5 ligand observed.



Scheme 3.7 (Top) Reaction of $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_2(\mu\text{-H})_4]$ with $[\text{AlCp}^*]_4$. (Bottom) Reaction of $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_3(\mu\text{-H})_3(\mu_3\text{-H})_2]$ with $[\text{AlCp}^*]_4$ to give $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_3(\mu\text{-H})_5(\mu_3\text{Al}(\eta^1\text{-C}_5\text{Me}_5))]$

In 2012, Wolf *et al.* published evidence of a new bonding motif for aluminohydride ruthenium complexes which was identified in the product from the reaction between $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{Cl})]_4$ and LiAlH_4 (Figure 3.2 – A).¹⁵ This anionic tetrahydroaluminate complex (A) was isolated with the X-ray crystallography data showing a mixture of the expected product as well as minor hydroxide contamination, nevertheless the hydrides were located on the Fourier difference map with the new bridging $(\text{AlH}_4)^-$ motif characterised with a $\mu, \eta^1: \eta^1$ co-ordination mode. Multinuclear NMR spectroscopy analysis was performed on this complex. In ^1H NMR spectrum, complex A was identified by a singlet at $\delta_{\text{H}} = -15.44$ ppm for the bridging Ru–H–Al hydrides, a singlet at $\delta_{\text{H}} = -15.22$ ppm for the bridging Ru–H–Ru hydride and 2 separate broad resonances at $\delta_{\text{H}} = 3.06$ and 4.39 ppm for the terminal Al–H hydrides. ^{27}Al NMR spectrum revealed a quintet at $\delta_{\text{Al}} = 98.8$ ppm ($J_{\text{AlH}} = 167$ Hz) which was consistent with 4 coordinate aluminium centre coupling to 4 equivalent hydrides, this would suggest on the ^{27}Al NMR spectroscopy acquisition time the terminal and bridging Al–H were in fast exchange regime. IR spectroscopy revealed a single broad absorbance at 1690 cm^{-1} for the Ru–H stretches.

Additional 4 alkylaluminate caged complexes were reported in this paper from the reaction of the anionic aluminohydride ruthenium complex with RLi ($\text{R} = \text{Et}, ^i\text{Pr}, ^n\text{Bu}$) (Figure 3.2). These unusual caged systems were characterised by X-ray, multinuclear solid and solution state NMR and IR spectroscopy as well as microanalysis to give the expected data set of ruthenium(II) aluminohydride complexes.¹⁶ Low temperature ^1H and ^7Li NMR spectroscopy of complex E revealed that this caged structure was retained in solution state.

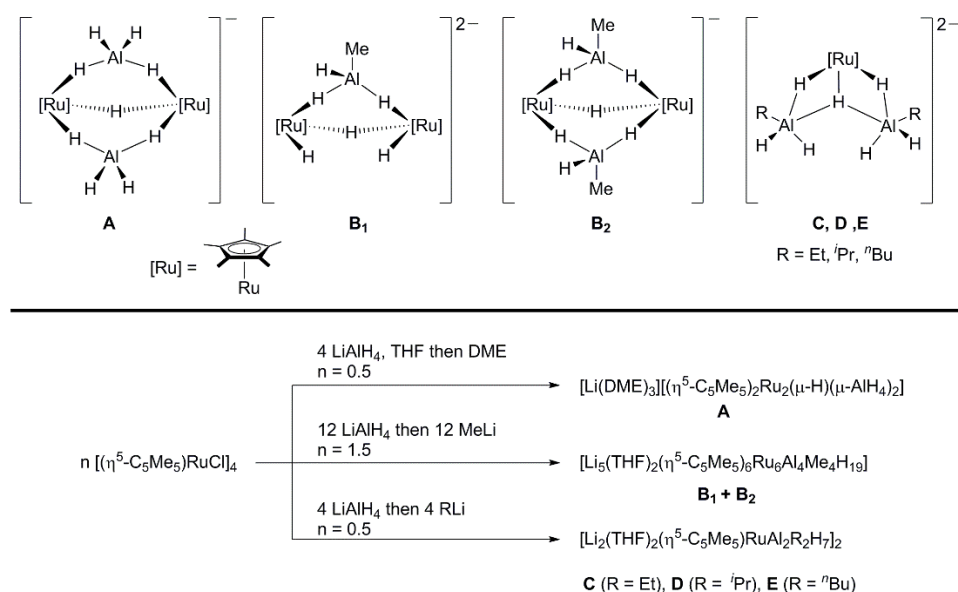
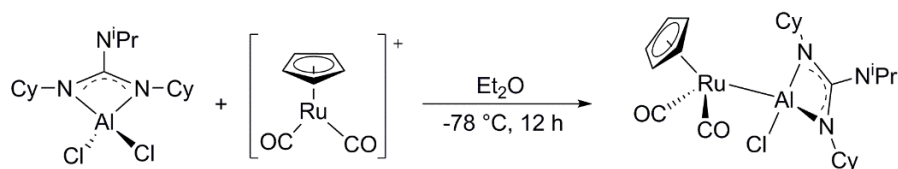


Figure 3.2 (Top) Framework of the ruthenium aluminohydride complexes. (Bottom) Synthesis of the cage structures

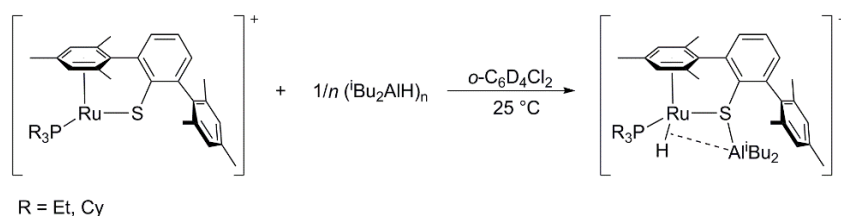
Aldridge *et al.* synthesised a new aluminium ruthenium heterobimetallic complex containing the Ru–Al bond motif unsupported by any bridging or terminal hydrides (Scheme 3.8).¹⁷ This aluminium ruthenium heterobimetallic complex was characterised by IR and multinuclear NMR spectroscopy including solution state ^{27}Al NMR spectroscopy. In ^{27}Al NMR spectrum a resonance was observed at $\delta_{\text{Al}} = 154$ ppm (shift of *ca.* 60 ppm from the parent guanidinato stabilised aluminium dichloride complex) which was indicative of generating a new metal–aluminium bond based on their research into analogous aluminium iron heterobimetallic complexes.¹⁷ Single crystal of this aluminium ruthenium heterobimetallic complex suitable for X-ray crystallography was obtained to confirm the structural assignment of the complex. The geometry around the aluminium centre was a distorted tetrahedral to accommodate the constrained guanidinato ligand (N–Al–N 69.65(9) °) and the Ru–Al bond length was measured to be 2.4412(8) Å which fell into the range of Ru–Al bond lengths with and without bridging hydrides (*vide supra*).



Scheme 3.8 Formation of guanidinato stabilised Al–Ru heterobimetallic complex

The products from Al–H bond activation of $^i\text{Bu}_2\text{AlH}$ by ruthenium complexes¹⁸ were isolated and characterised by multinuclear NMR spectroscopy and X-ray crystallography.¹⁹ In the ^1H NMR

spectra the Ru–H signals were found as doublets upfield (R = Et, $\delta_{\text{H}} = -12.4$ ppm, $J_{\text{HP}} = 26.1$ Hz; R = Cy, $\delta_{\text{H}} = -12.7$ ppm, $J_{\text{HP}} = 26.4$ Hz). ^{27}Al NMR spectroscopy failed due to the high line width as a result of the quadrupolar aluminium nuclei. Instead, Oestreich *et al.* turned to DFT calculations and a chemical shift of $\delta_{\text{Al}} = 178$ ppm was predicted in the ^{27}Al NMR spectrum which was noted as only slightly shifted from the parent aluminium substrate ($\delta_{\text{Al}} = 158$ ppm). X-ray crystallography confirmed the structure of the complexes. When the phosphine ligand was PEt_3 short Ru–H bond was measured (1.65(3) Å) with corresponding longer Al–H bond (1.98(3) Å) however when the phosphine ligand was PCy_3 the Ru–H bond was measured as 1.53(4) Å with a much longer Al–H distance of 2.16 Å. In both complexes, long Ru---Al distances were measured (R = Et, 2.81 Å; R = Cy, 2.83 Å). Further DFT calculations were also performed on $[(\text{DmpS})\text{Ru}(\text{PEt}_3)(^i\text{Bu}_2\text{AlH})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (DmpS = 2,6-dimesitylphenyl) and the Mayer bond orders revealed that despite the long Ru---Al there were partial covalent bond characters between the Ru–H, Al–H and Ru–Al bonds which suggested delocalised bonding. Additional natural localised molecular orbital analysis (NLMO) and electron localisation function (ELF) calculations suggested the bonding was best described as a 3-centre,2-electron interaction whereby the main interaction was donation from $\sigma(\text{Ru}-\text{H})$ orbital to the empty hybridised $\text{Al}(\text{sp}^3)$ orbital. Only the DFT data were reported for $[(\text{DmpS})\text{Ru}(\text{PR}_3)(^i\text{Bu}_2\text{AlH})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ where R = Et however the shorter Al–H bond distance in the crystal structure relative to the R = Cy analogue would have suggested some delocalisation in the Ru–H–Al motif anyway and therefore it would be interesting to compare the data with $[(\text{DmpS})\text{Ru}(\text{PR}_3)(^i\text{Bu}_2\text{AlH})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ where the Al---H distance was much longer to see if this 3-centre,2-electron interaction existed in this complex. These complexes were also found to be capable catalysts for hydrodefluorinative Friedel-Crafts alkylation chemistry.



Scheme 3.9 Formation of $[(\text{DmpS})\text{Ru}(\text{PR}_3)(^i\text{Bu}_2\text{AlH})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (R = Et or Cy)

3.1.2 Zn•Ru heterobimetallic complexes

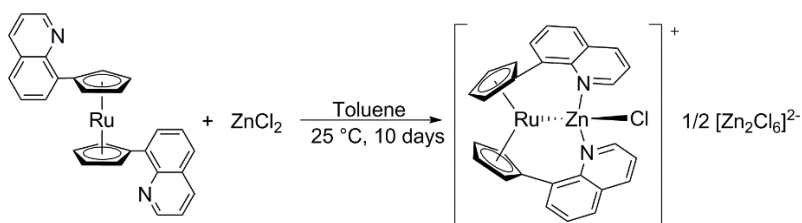
The reaction of *trans*- $\{\text{Ru}(\text{Ph}_2\text{PC}_5\text{H}_4\text{N})_2(\text{CO})_3\}^{20}$ with ZnCl_2 resulted in the formation of the first binuclear zinc ruthenium heterobimetallic complex characterised by single crystal X-ray crystallography.²¹ This complex was also characterised by IR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and elemental analysis. A single ν_{CO} absorbance was observed in the IR spectrum at 2041 cm^{-1} which was a higher wavenumber than the parent ruthenium compound ($\nu_{\text{CO}} = 1897\text{ cm}^{-1}$). This indicated a decrease in π back-donation from the ruthenium to CO ligand due to the formation of the Ru–Zn bond and change

in the local stereochemistry around ruthenium from D_{3h} to C_{2v} . This change in geometry from trigonal bipyramidal to octahedral around ruthenium was confirmed by the X-ray crystallography data. A long Ru–Zn bond length was measured (2.659(1) Å) which was greater than the sum of the single bond radii of Ru and Zn¹¹ and suggested a weak interaction between the two metals. Comparison with analogous Cd and Hg complexes in the paper confirmed the trend observed whereby the stronger the Ru–M (M = Cd, Hg and Zn) interaction, the lower the π back-donation from the ruthenium to CO, and therefore the higher the ν_{CO} wavenumber observed in IR spectrum.



Scheme 3.10 Formation of $[RuZn(\mu\text{-}2\text{-PhPC}_5\text{H}_4\text{N})_2(\text{CO})_3\text{Cl}_2]\cdot\text{MeOH}$

In 2002, Enders *et al.* reported the synthesis of a novel zinc ruthenocene complex (Scheme 3.11).²² Again, the use of a chelating ligand around the ruthenium helped to tether the Lewis acid to form a new Ru–Zn bond. This complex was characterised by multinuclear NMR spectroscopy and X-ray crystallography. The Ru–Zn bond length was measured to be 2.561(1) Å which was slightly shorter than the Ru–Zn bond length reported in $[RuZn(\mu\text{-}2\text{-PhPC}_5\text{H}_4\text{N})_2(\text{CO})_3\text{Cl}_2]\cdot\text{MeOH}$ but still larger than the sum of the single bond radii.¹¹ No further reactivity of this complex was reported but as the metal---metal interaction of this complex and the one reported by Che *et al.*²¹ (Scheme 3.10) were both quite weak, but forced into the geometry due to the rigid ligand framework, it would be interesting to see if any bond activation or small molecule activation could be achieved at the site of these two metal centres.

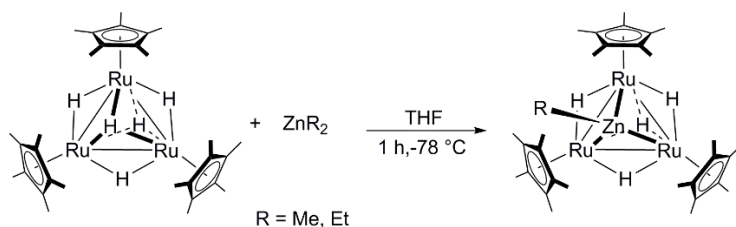


Scheme 3.11 Formation of novel zinc ruthenocene complex

As well as the aluminium ruthenium polyhydride complex synthesised by Suzuki *et al.* (Scheme 3.5), a zinc ruthenium polyhydride complex, $[\{\eta^5\text{-C}_5\text{Me}_5\}\text{Ru}]_3(\mu\text{-H})_3(\mu_3\text{-ZnEt})(\mu_3\text{-H})]$ was also isolated under strict stoichiometry control to generate the mono-capped complex (Scheme 3.12).¹² This complex

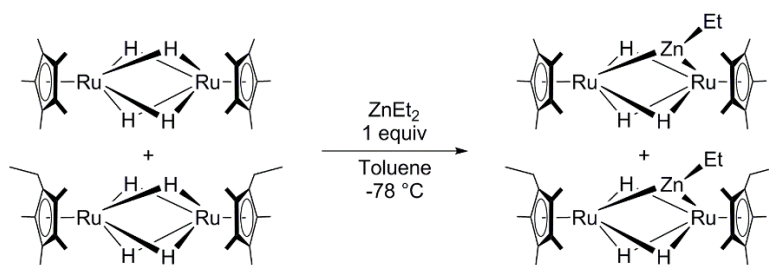
was characterised by multinuclear NMR spectroscopy with the resonances for the μ_3 -H motif observed at $\delta_{\text{H}} = -26.97$ ppm and the μ -H at $\delta = 2.56$ ppm in the ^1H NMR spectrum. Suitable crystals were grown for X-ray crystallography to confirm the formation of this complex. Long Ru---Ru distances (2.7450(6) Å and 2.7371(8) Å) and elongated Ru–Zn bond distances (2.6747(10) Å and 2.6561(8) Å) were measured from the X-ray data. The Ru–Zn bond distances were within the values found for non-bridged Ru–Zn bonds (*vide supra*). The Ru–H $_{\mu}$ bond lengths averaged to 1.69 Å and the Ru–H $_{\mu_3}$ bond lengths averaged to 1.87 Å. No further examination beyond some cyclic voltammetry measurements was taken of this complex however formation of the bi-capped zinc ruthenium polyhydride complex, $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_3(\mu\text{-H})_3(\mu^3\text{-ZnEt})_2]$, was probed to confirm formation of the mono-capped polyhydride complex. The resonance for the single bridging hydride resonance was observed downfield at $\delta_{\text{H}} = 8.08$ ppm. The huge difference between these hydride chemical shifts were not discussed in the paper but this would point towards a massive difference in reactivity of the hydrides which would be interesting to further examine.

In 2007, Suzuki *et al.* reported a follow-up study in the generation of the dimethyl zinc analogues of these polyhydride complexes (Scheme 3.12).²³ The paper was an expansion on the multinuclear NMR spectroscopic data with emphasis on understanding the mechanism of the exchange between the bridging hydrides as observed on the ^1H NMR spectroscopy time scale. Variable temperature ^1H NMR spectroscopy allowed for thermodynamic parameters to be calculated for this exchange process with the conclusion that it was most likely through an intramolecular site-exchange process due to the $\Delta S^\ddagger$ value calculated for both complexes being close to 0 cal mol⁻¹ K⁻¹.



Scheme 3.12 Formation of $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_3(\mu\text{-H})_3(\mu_3\text{-ZnR})(\mu_3\text{-H})]$ (R = Me, Et)

Suzuki *et al.* also synthesised novel dinuclear ruthenium zinc complexes $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_2(\mu\text{-H})_3(\mu\text{-ZnR})]$ and $[\{\eta^5\text{-C}_5\text{Me}_4\text{EtRu}\}_2(\mu\text{-H})_3(\mu\text{-ZnR})]$ (R = Me and Et).²³ A crossover experiment was performed using $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_2(\mu\text{-H})_4]$ and $[\{\eta^5\text{-C}_5\text{Me}_4\text{EtRu}\}_2(\mu\text{-H})_4]$ as the starting ruthenium hydride source which resulted in no exchange in the ligands in the final product and therefore suggested these dinuclear systems do not fragment then recombine in solution (Scheme 3.13). These dinuclear ruthenium zinc complexes were only characterised by multinuclear NMR spectroscopy with the bridging hydride signals all observed as a broad resonance between $\delta_{\text{H}} = -15.04$ - -15.09 ppm.



Scheme 3.13 Crossover experiment using $[\{\eta^5\text{-C}_5\text{Me}_5\}\text{Ru}\}_2(\mu\text{-H})_3(\mu\text{-ZnEt})$ and $[\{\eta^5\text{-C}_5\text{Me}_4\text{Et}\}\text{Ru}\}_2(\mu\text{-H})_3(\mu\text{-ZnEt})$

Fischer *et al.* reported the preparation, characterisation and bond analysis of a number of organozinc rich compounds which included closed shell 18-valence electron compounds of ruthenium, $[\text{Ru}(\text{Zn}(\eta^5\text{-C}_5\text{Me}_5)_4)(\text{ZnMe})_6]$ and $[\text{Ru}(\text{Zn}(\eta^5\text{-C}_5\text{Me}_5)_4)(\text{ZnMe})_4(\text{H})_2]$ (Figure 3.3).^{24–26} These complexes were characterised by X-ray crystallography with the range for the Ru–Zn($\eta^5\text{-C}_5\text{Me}_5$) bond lengths in the “RuZn₁₀” complex measured as 2.545(1) – 2.567(1) Å and in the “RuZn₈” complex as 2.469(1) – 2.488(1) Å and the range for the Ru–Zn(Me) bond length in “RuZn₁₀” complex was measured as 2.489(1) – 2.503(1) Å and in the “RuZn₈” complex as 2.438(1) – 2.492(1) Å. DFT calculations on these complexes revealed no significant attraction between the zinc atoms and therefore these organozinc rich compounds were best described as more like classical complexes rather than cluster complexes.²⁷

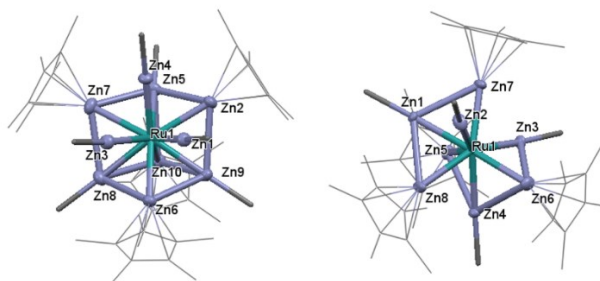
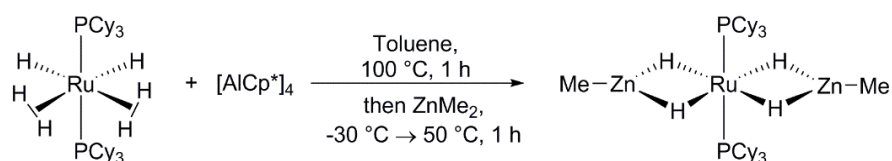


Figure 3.3 X-ray crystal structures of $[\text{Ru}(\text{Zn}(\eta^5\text{-C}_5\text{Me}_5)_4)(\text{ZnMe})_6]$ (left) and $[\text{Ru}(\text{Zn}(\eta^5\text{-C}_5\text{Me}_5)_4)(\text{ZnMe})_4(\text{H})_2]$ (right). Hydrogens omitted for clarity

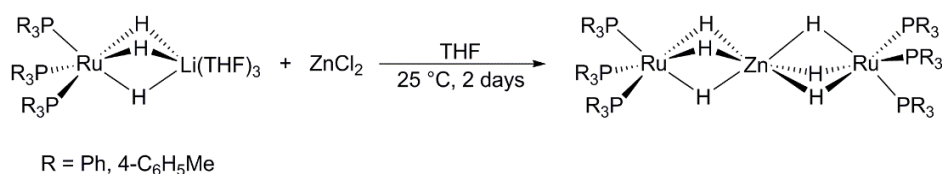
In addition to organozinc rich ruthenium complexes Fischer *et al.* also synthesised and isolated one of the first zinc ruthenium heterobimetallic containing unambiguous Ru–H–Zn bridging hydride motifs in 2013 (Scheme 3.14).²⁶ In the ^1H NMR spectrum a diagnostic broad resonance was observed at $\delta_{\text{H}} = -9.94$ ppm representing all 4 bridging hydrides. The T_1 relaxation time for this resonance was 470 ms which was closer to classical hydride behaviour²⁸ however it was not clear if this was the T_1 minimum time or what temperature this value was obtained at and therefore the behaviour as to whether these hydrides are classical or non-classical was debateable based on this measurement. Low temperature NMR spectroscopy was also not performed but would have provided a more complete

picture for the T_1 measurements and whether any decoalescence of the broad hydride signal occurred at lower temperatures. Nevertheless, the $\nu_{\text{Ru-H}}$ vibration was observed at 1592 and 1444 cm^{-1} in the IR spectrum which was consistent with a bridging Ru-H than a terminal Ru-H stretch. X-ray crystallography data of this complex unambiguously indicated the presence of the Ru-H-Zn motif. The average Ru-H $_{\mu}$ and Zn-H $_{\mu}$ bond lengths were measured to be 1.63 and 1.78 Å respectively. The Ru-Zn bond lengths were short at 2.436(1) Å which was within the sum of the single bond radii of both Ru and Zn¹¹. No DFT calculations were performed on this molecule but would be interesting to analyse the bonding within the Ru-H-Zn motif to confirm the assignment of this complex as a Ru(II) 18 valence electron compound.



Scheme 3.14 Formation of $[\text{Ru}(\text{PCy}_3)_2(\text{ZnMe})_2(\mu\text{-H})_4]$

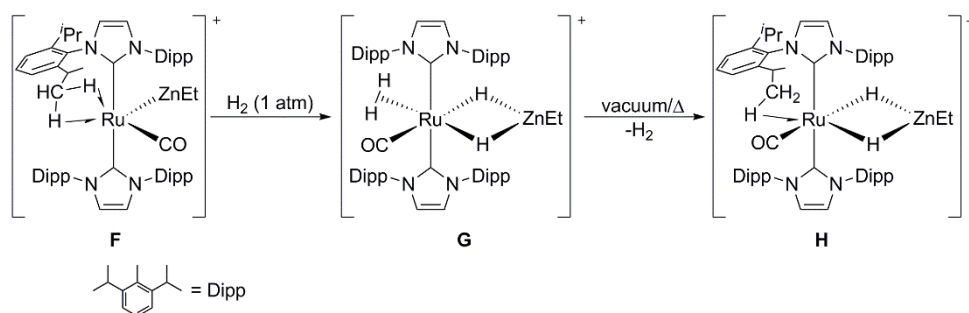
In the same year, Wolf *et al.* also isolated and characterised two zinc ruthenium polyhydride complexes containing the Ru-H-Zn motif as identified by X-ray crystallography (Scheme 3.15).^{29,30} In these complexes the Zn centre was sandwiched by 2 Ru centres; so an inverse of the complex isolated by Fischer *et al.*²⁶ (Scheme 3.14). For $[\text{Zn}\{\text{Ru}(\mu\text{-H})_3(\text{PPh}_3)_3\}_2]$ a diagnostic multiplet signal for the bridging hydrides was observed at $\delta_{\text{H}} = -9.68$ ppm in the ^1H NMR spectrum alongside a singlet at $\delta_{\text{P}} = 55.3$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum which became a multiplet upon proton coupling. Similar values and characteristics were obtained for the multinuclear NMR spectra for $[\text{Zn}\{\text{Ru}(\mu\text{-H})_3(\text{P}(4\text{-C}_6\text{H}_5\text{Me})_3)_3\}_2]$ complex except for the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum whereby the $\delta_{\text{P}} = -53.3$ ppm. No explanation was given for this vastly different chemical shift in the phosphorus NMR spectra. Vibrational frequencies at 1782 and 1777 cm^{-1} were recorded for the $\nu_{\text{Ru-H}}$ stretches for $[\text{Zn}\{\text{Ru}(\mu\text{-H})_3(\text{PPh}_3)_3\}_2]$ and $[\text{Zn}\{\text{Ru}(\mu\text{-H})_3(\text{P}(4\text{-C}_6\text{H}_5\text{Me})_3)_3\}_2]$ respectively. For both complexes shorter Ru-H $_{\mu}$ bond lengths (1.58(3) – 1.80(4) Å) were measured compared to longer Zn-H $_{\mu}$ bond lengths (2.02(3) – 2.09(4) Å) by X-ray crystallography. NBO calculations were performed on $[\text{Zn}\{\text{Ru}(\mu\text{-H})_3(\text{P}(4\text{-C}_6\text{H}_5\text{Me})_3)_3\}_2]$ complex revealing small Wiberg bond indices for Ru-Zn and Zn-H $_{\mu}$ (>0.03) and large Wiberg bond index for Ru-H $_{\mu}$ (0.80). The WBI suggested a bonding description whereby there was a stronger bond order between Ru-H $_{\mu}$ than Zn-H $_{\mu}$ – in agreement with X-ray data. Complementary QTAIM calculations were not given to provide a more complete bonding description of these complexes and not just the covalent description given by the NBO calculations.



Scheme 3.15 Formation of $[Zn\{Ru(\mu-H)_3(PR_3)_3\}_2]$ ($R = Ph$ or $4-C_6H_5Me$)

In 2016, Whittlesey *et al.* published the formation of a zinc ruthenium heterobimetallic capable of activating H₂ across the Ru–Zn to generate a new heterobimetallic complex with bridging hydrides (Scheme 3.16).³¹ ¹H NMR spectroscopy and X-ray crystallography confirmed complex **F** contained an unsupported Ru–Zn bond and 2 agostic C–H interactions from one of the ⁱPr groups from the Dipp (2,6-diisopropylphenyl) ligand. Exposure of **F** to H₂ (1 atm.) led to the generation of complex **G**. Complex **G** was characterised by X-ray crystallography and ¹H NMR spectroscopy demonstrating 2 hydride resonances at $\delta_H = -5.33$ (3H, br) and -12.13 (1H, s) ppm. Low temperature ¹H NMR spectroscopy resolved the broad resonance at $\delta_H = -5.33$ ppm into two signals at $\delta_H = -5.09$ (2H, $T_1 = 31$ ms) and -7.79 (1H, $T_1 = 72$ ms) ppm and was therefore assigned as the η^2 -H₂ environment and Ru–H–Zn (*trans* to CO) respectively. It was interesting that exchange spectroscopy (EXSY) and magnetisation transfer experiments showed that no exchange occurred between the Ru–H–Zn hydride (*trans* to η^2 -H₂) and the other 3 hydride environments. The $T_1(\text{min})$ value calculated for the Ru–H–Zn hydride *trans* to η^2 -H₂ was 683 ms, indicative of classical hydride behaviour. However, bizarrely, D₂ labelling experiment actually disagreed with this conclusion showing all the hydrides underwent H/D exchange.

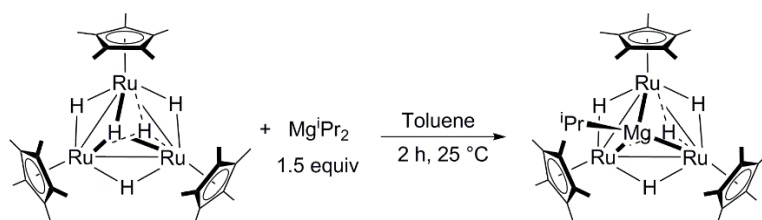
Subjecting complex **G** to a vacuum at 50 °C resulted in formation of complex **H**. Complex **H** was characterised by X-ray crystallography and ¹H NMR spectroscopy demonstrating 2 resonances at $\delta_H = -27.06$ and -3.75 ppm for the bridging hydrides. NBO calculations provided additional analysis in the bonding within these complexes with no direct Ru–Zn interaction found in either complex **G** and **H** despite the normal Ru–Zn bond distances (2.5125(3) and 2.4896(4) Å respectively) (*vide supra*). In both complexes, NPA charges on the H _{μ} *trans* to CO ligand were more negative compared to the NPA charged on the H _{μ} *trans* to η^2 -H₂ ligand and therefore the hydrides *trans* to η^2 -H₂ ligand were more terminal hydride in behaviour which was in agreement with the analysis from ¹H NMR spectroscopy and the bond lengths from X-ray crystallography.



Scheme 3.16 Formation and reactivity of zinc ruthenium heterobimetallic complexes

3.1.3 Mg•Ru heterobimetallic complexes

As well as the aluminium and zinc ruthenium polyhydride complex synthesised by Suzuki *et al.* (Scheme 3.5 and Scheme 3.12), a magnesium ruthenium polyhydride complex, $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_3(\mu\text{-H})_3(\mu_3\text{-Mg}^i\text{Pr})(\mu_3\text{-H})]$, was also isolated and characterised. The formation of this polyhydride complex was confirmed by ^1H NMR spectroscopy with two resonances observed at $\delta_{\text{H}} = -24.70$ (1H) and -5.25 (3H) ppm for the $\mu_3\text{-H}$ and $\mu\text{-H}$ hydrides respectively. X-ray crystallography confirmed the formation of this trinuclear ruthenium polyhydride complex mono-capped by an alkyl magnesium unit with long Ru---Mg distances of 2.787(13), 2.8007(12) and 2.7715(13) Å and long Ru---Ru distances of 2.7516(6), 2.7500(4) and 2.7548(6) Å measured. The Ru–H $_{\mu}$ bond lengths measured ranged from 1.57(3) – 1.86 (3) Å and the Ru–H $_{\mu_3}$ bond lengths measured ranged from 1.94(4) – 1.98(4) Å. It is worth noting that the longer Ru–H $_{\mu}$ bond lengths do overlap with the Ru–H $_{\mu_3}$ bond lengths within the *esd* of these hydrides. Nevertheless, the X-ray crystallography would point towards a heterobimetallic system whereby the Ru---Mg interaction was supported through bridging hydrides. Again, DFT calculations were not performed to confirm this lack of Ru---Mg interaction. This complex represented the first magnesium ruthenium heterobimetallic system isolated by X-ray crystallography.



Scheme 3.17 Formation of $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ru}\}_3(\mu\text{-H})_3(\mu_3\text{-Mg}^i\text{Pr})(\mu_3\text{-H})]$

In the following work, this author presents the synthesis, characterisation and reactivity of a number of new **M•Ru** heterobimetallics hydride complexes (M = Al, Zn, Mg) with either dihydrogen ligated in an η^2 fashion or dinitrogen ligated in an end-on fashion at the ruthenium centre. The important bonding interactions within these heterobimetallic complexes were analysed by computational methods

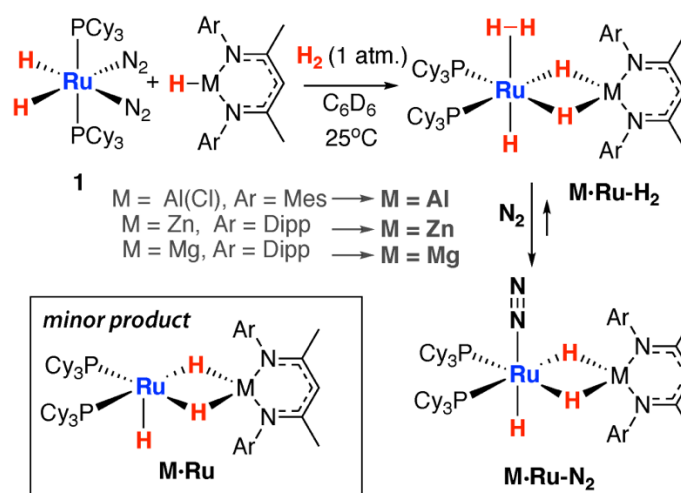
to give a bonding description whereby there was minimal M---Ru interaction and instead these complexes were supported by bridging hydride interactions.

3.2 RESULTS AND DISCUSSIONS

3.2.1 Synthesis and characterisation

1.1.1.8 M•Ru-H₂

Reacting 1 equivalent of [Ru(H)₂(N₂)₂(PCy₃)₂] (**1**) with 1 equivalent of the β-diketiminate stabilised hydrides of aluminium, zinc and magnesium under an atmosphere of H₂ proceeded at 25 °C over the course of 24 h and resulted in generation of a series of new heterobimetallic dihydrogen complexes **M•Ru-H₂** (M = Al, Zn, Mg, Scheme 3.18). No reactivity was observed between the reaction of **1** with ^{Dipp}BDICaH•THF, even after heating the reaction to 80 °C with only the decomposition of **1** detected by NMR spectroscopy.



Scheme 3.18 Preparation of dihydrogen and dinitrogen complexes of a series of heterobimetallic hydrides

These heterobimetallic dihydrogen complexes were characterised by a single broad resonance, integrating to five protons, in the hydride region of the ¹H NMR spectrum (**Al**, δ_H = −10.85 ppm; **Zn**, δ_H = −10.71 ppm; **Mg**, δ_H = −10.32 ppm). While low temperature ¹H NMR spectroscopy data acquired at 193 K failed to resolve the fluxional process that interconverted the hydride and dihydrogen ligands of **M•Ru-H₂**, the formulation of these complexes was supported by T₁-relaxation times, DFT calculations (Figure 3.4) and D₂ exchange reactions. T₁ measurements were taken across a 193 - 293 K temperature range at 400 MHz and all three complexes exhibited short T₁(min) times (**Al**, 36 ms; **Zn**, 35 ms; **Mg**, 52 ms) indicative of non-classical hydride behaviour. Due to the fluxional processes in operation these data likely represent a time-average of dihydrogen, bridging hydride and terminal hydride ligands and as such may be longer than the true T₁(min) values of the H₂ ligand. Isolation of

M•Ru-H₂ for X-ray crystallography failed however the geometry of these heterobimetallic dihydrogen complexes were examined by computation studies.

All computational studies in this chapter were conducted using Gaussian 09. The ω B97x-D functional was employed.³² Ru, Al, Mg and Zn centres were described with Stuttgart RECPs and associated basis sets,^{33–35} the 6-31++G(d,3pd) basis set was used for all hydrides, 6-31G* basis set was used to describe C and H atoms and 6-311+G* basis set was used to describe N, P and Cl atoms.^{36–38}

DFT calculations pointed towards the heterobimetallic dihydrogen complexes having a near octahedral geometry at ruthenium, possessed by a *cis*-relation between the two phosphine ligands. In addition, five hydrogens in total surrounding the ruthenium, one as a terminal hydride, two as bridging hydrides and the remaining two hydrogens as dihydrogen ligated in an η^2 -fashion on ruthenium centre, as the most favoured geometry (Figure 3.4). The plausibility of the geometry for these heterobimetallic dihydrogen complexes was further corroborated from inference of the **M•Ru-N₂** complexes (*vide infra*).

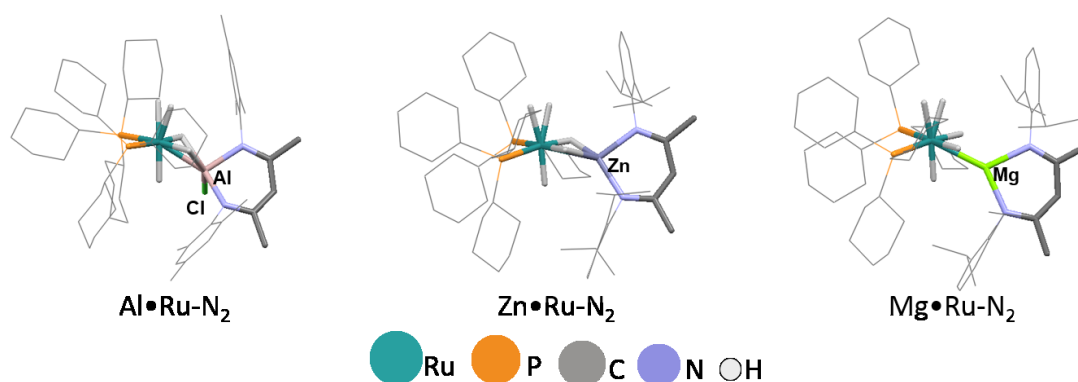


Figure 3.4 Optimised structures of **M•Ru-H₂** complexes from DFT calculations

	Al	Zn	Mg
H–H	0.87 Å	0.87 Å	0.88 Å
Ru–η^2H₂	1.71 Å	1.75 Å	1.73 Å
	1.72 Å	1.74 Å	1.71 Å
Ru–H_t	1.65 Å	1.62 Å	1.66 Å
Ru–H_{μ}	1.65 Å	1.67 Å	1.66 Å
	1.65 Å	1.70 Å	1.69 Å
Ru–M	2.41 Å	2.47 Å	2.53 Å
	2.489 Å ^a	2.480 Å ^a	2.680 Å ^a
P–Ru–P	103.1 °	106.4 °	107.1 °

Table 3.1 Selected bond lengths (Å) and bond angles (°) from optimised DFT models of the dihydrogen heterobimetallic complexes. ^aSum of single bond radii (Ru + M)¹¹

Even though DFT calculations were used to confirm the thermodynamic plausibility of these dihydrogen heterobimetallic hydrides, the actual bond lengths ascertained for the light atoms cannot be scrutinised in great depths due to inherent approximation in the method and so the degree of dihydrogen activation cannot be analysed accurately. Nevertheless, the calculated values of the Ru–H bond lengths in Table 3.1 for each respective heterobimetallic complex showed very similar short Ru–H bond lengths between the bridging and terminal hydride and longer M–H_μ bonds which corroborated with the weak interaction of the main group metal to the bridging hydrides from NBO and QTAIM calculations (Figure S 5.49 and Figure S 5.50). The metal---metal bond distance measured from DFT are within the sum of the single bond radii as described by Pauling¹¹ however the bonding description given by the NBO and QTAIM calculations suggested an alternative picture whereby we have weak interactions between the two metal centres. For example, small Wiberg bond indices were calculated by NBO analysis: **Al**, 0.15; **Zn**, 0.07; **Mg**, 0.02 and small ρ values were calculated for the bond critical paths between the two metal centres: **Al**, 0.05; **Zn**, 0.05; **Mg**, 0.03. The small ρ values indicated that a majority of the electron density did not reside between the two metal centres but was most likely residing on the actual metal centres. This localised electron density on the metal centres was further exemplified by the NPA charges calculated where in all the **M•Ru-H₂** complexes we have an extremely negative ruthenium centre balanced by a highly positive main group metal (Figure S 5.49).

1.1.1.9 **M•Ru intermediate**

Exposure of **M•Ru-H₂** to a N₂ atmosphere resulted in gradual formation of **M•Ru-N₂** (Scheme 3.18). While ruthenium dinitrogen complexes are well known,^{39,40} and include [Ru(NH₃)₅(N₂)]⁺² the first isolated dinitrogen complex,^{41,42} those incorporating main group metals are rare. Despite conducting reactions at modest pressures of N₂ (4 atm.) and also bubbling N₂ through a solution of **M•Ru-H₂**, in all cases a mixture was formed, and the position of the equilibrium was not forced entirely toward the dinitrogen complexes. Moreover, for the **Mg•Ru-H₂** complex, pressures of N₂ above 1 atm. actually hinders formation of the **Mg•Ru-N₂** complex. The ratio of the H₂ : N₂ complexes after addition of N₂ (4 atm.) was calculated to be 6 : 1 and 5 : 1 for the Zn and Mg heterobimetallic complexes respectively. The direct reaction of **1** with the β-diketiminato stabilised hydrides, in N₂ atmosphere, also resulted in the formation of a mixture of **M•Ru-N₂** and **M•Ru-H₂** and this result was ascribed to unavoidable trace decomposition of the main group hydride species leading to the generation of H₂ *in situ*.

A third species was observed in these reactions at low concentration which was tentatively assigned as **M•Ru**. The apical ruthenium site of **M•Ru** was not occupied by a diatomic ligand and this was the expected intermediate in a dissociative exchange mechanism between **M•Ru-H₂** and **M•Ru-N₂**. A further reaction of mixtures of **Al•Ru-N₂** and **Al•Ru-H₂** with CO provided additional evidence for ligand exchange occurring primarily at the apical site on ruthenium (Figure 3.5). Placing a sample containing both **Al•Ru-H₂** and **Al•Ru-N₂** under an atmosphere of CO resulted in complete conversion

into the **Al•Ru-CO** heterobimetallic complex. **Al•Ru-CO** displayed diagnostic hydride resonances at 298 K for both bridging hydrides $\delta_{\text{H}} = -12.16$ ppm, fwhm = 106 Hz and terminal hydride $\delta_{\text{H}} = -9.05$ ppm, fwhm = 35 Hz. Isolation of **Al•Ru-CO** was not possible as a further substitution reaction occurred over 24 h with a second CO ligand replacing a PCy₃ ligand, with free PCy₃ observed in ³¹P{¹H} NMR spectrum, to give a new complex postulated as **Al•Ru-(CO)₂**. This complex displayed diagnostic hydride resonances at 298 K for both bridging hydrides $\delta_{\text{H}} = -9.93$ ppm and terminal hydride $\delta_{\text{H}} = -9.39$ ppm. Isolation of **Al•Ru-(CO)₂** as single crystals was not successful to confirm this assignment through X-ray crystallography.

Further substitution reactions were carried out with both the zinc and magnesium heterobimetallic with CO (and CNAr, Ar = 2,6-xylyl, 5.4 CHAPTER THREE: EXPERIMENTAL) with multinuclear NMR spectra showing a similar outcome with the conversion of **M•Ru-N₂** into **M•Ru-CO** and **M•Ru-(CO)₂** however the dihydrogen species, **M•Ru-H₂** remained present in solution in both these cases, which was remarkable considering the lability of the dihydrogen ligand. Furthermore, no breaking up of the heterobimetallic species was observed through variable temperature ¹H NMR spectroscopy with no formation of the free parent main group hydride or ruthenium carbonyl species observed by multinuclear NMR spectroscopy.^{43,44}

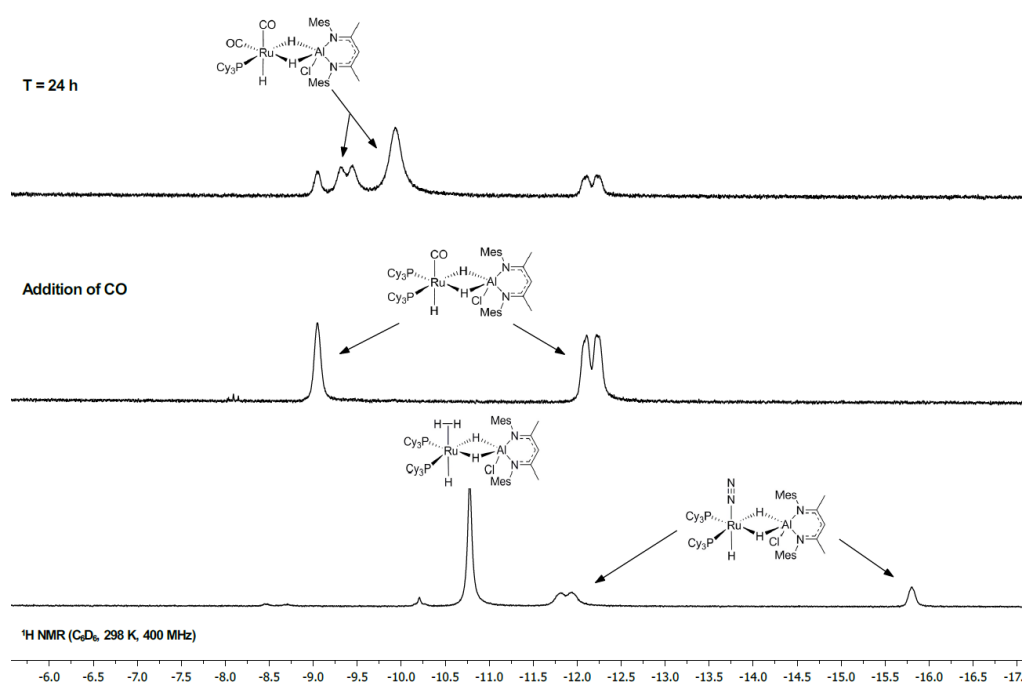
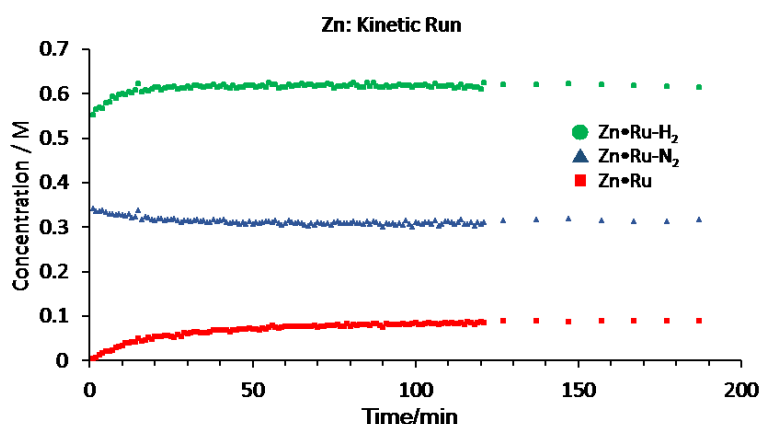


Figure 3.5 ¹H-NMR spectra stack plot of the addition of CO to a sample containing a mixture of **Al•Ru-H₂** and **Al•Ru-N₂**

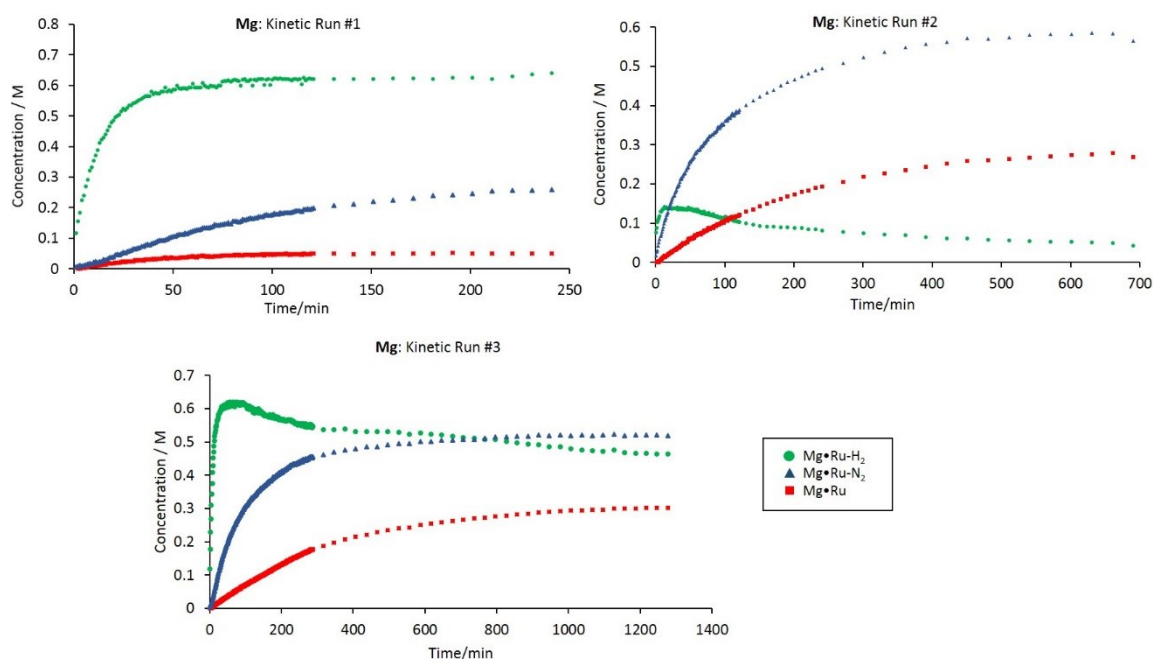
Kinetic measurements were also performed on these reaction, *via* ¹H NMR spectroscopy, between **1** and the zinc and magnesium hydride respectively under an atmosphere of N₂ at 25 °C. The

reaction for the zinc heterobimetallic hydride complexes was complete within 5 minutes of the acquired data. No change in the ratio between the three heterobimetallic hydride complexes was observed after total consumption of starting material and the initial rate data was not possible to interpret as the reaction was too fast (Graph 3.1). Low temperature kinetic measurements were not taken but would have provided a slower rate of reaction to allow for more information to be ascertained about the initial reactivity.



Graph 3.1 Kinetic experiment of reaction of **1** with *DippBDIZnH*

The reaction for the magnesium heterobimetallic hydride complexes required multiple measurements as the results were not reproducible across 2 runs. Although efforts were taken to use the same conditions for each kinetic experiment, slight alterations in the mixing and diffusion of the sample as the sample thawed in the spectrometer resulted in different reaction rates as well as time taken for complete consumption of starting materials. Therefore, no quantitative information could be ascertained from these experiments however qualitative data in all 3 runs showed that **Mg•Ru-H₂** was formed initially and then converted into **Mg•Ru-N₂** via the intermediate **Mg•Ru**.



Graph 3.2 Kinetic experiments of reaction of **1** with *DippBDIMgH*

3.2.2 M•Ru-N₂

These heterobimetallic dinitrogen complexes, **M•Ru-N₂**, displayed diagnostic hydride resonances for both bridging (**Al**, $\delta_{\text{H}} = -11.95$ ppm, fwhm = 113 Hz; **Zn**, $\delta_{\text{H}} = -11.40$ ppm; **Mg**, $\delta_{\text{H}} = -11.36$ ppm) and terminal (**Al**, $\delta_{\text{H}} = -15.81$ ppm, fwhm = 37 Hz; **Zn**, $\delta_{\text{H}} = -15.20$ ppm; **Mg**, $\delta_{\text{H}} = -15.69$ ppm) hydrides. Assignment of these hydrides was confirmed by calculation of the NMR spectra by DFT methods. The larger fwhm value for the resonance assigned to the bridging hydride, relative to the terminal hydride, in **Al•Ru-N₂** was consistent with the bridging hydride coupling to the quadrupolar ²⁷Al nucleus (*I* = 5/2). The unusual chemical shift of the terminal hydrides being further upfield relative to the bridging hydrides (*c.f.* **Al•Ru-CO**) can be postulated as the result of the weaker *trans* influence from the dinitrogen ligand resulting in greater contribution of the electron density from ruthenium to the terminal hydride and therefore experience a greater ‘shielding’ effect to give this upfield signal.

The T₁(min) relaxation times for all three heterobimetallic dinitrogen complexes were all long (0.2 – 0.5 s), as would be expected in the absence of the dihydrogen ligand. The terminal hydride resonance of **M•Ru-N₂** (M = Zn and Mg) were sharp enough to resolve the *cis* couplings from the ¹H NMR spectra at 298 K (**Zn**, ²*J*_{H-H} = 7.7 Hz; ²*J*_{P-H} = 21.1 Hz; **Mg**, ²*J*_{H-H} = 9.4 Hz; ²*J*_{P-H} = 17.9 Hz). In addition, the resonances for the bridging hydrides of **M•Ru-N₂** showed a classical AA’XX’ second order coupling pattern indicative of *cis*-relation between the phosphine ligands.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectra collected on $\text{M}\cdot\text{Ru}\cdot\text{N}_2$ provided support for the *cis*-relation between the large PCy_3 ligands. At room temperature in toluene- d_8 two ^{31}P resonances were observed in $\text{Al}\cdot\text{Ru}\cdot\text{N}_2$ ($\delta_{\text{P}} = 51.8$ and 38.5 ppm at 298 K). The two ^{31}P resonances were attributed to the additional steric bulk of the chlorine atom on the aluminium centre leading to magnetic and chemical inequivalence of the phosphine ligands due to hindered rotation about the $\text{N}-\text{C}_{\text{Ar}}$ bond of the diisopropylphenyl groups of the β -diketiminato ligand. At the same temperature, $\text{M}\cdot\text{Ru}\cdot\text{N}_2$ ($\text{M} = \text{Zn}, \text{Mg}$) displayed a single ^{31}P NMR spectra resonance (**Zn**, $\delta_{\text{P}} = 46.6$ ppm; **Mg**, $\delta_{\text{P}} = 45.6$ ppm). The three-coordinate Zn- and Mg-parent hydrides imparted a higher degree of freedom of rotation around the $\text{N}-\text{C}_{\text{Ar}}$ bond of the diisopropylphenyl groups within these heterobimetallic complexes and therefore the *cis*-phosphine ligands were chemically equivalent but magnetically inequivalent at room temperature. However, at lower temperature the ^{31}P resonance of $\text{M}\cdot\text{Ru}\cdot\text{N}_2$ decoalesced into two resonances (**Zn**, $\delta_{\text{P}} = 47.5$ and 43.8 ppm at 253 K; **Mg**, $\delta_{\text{P}} = 45.5$ and 42.8 ppm at 233 K), consistent with a further fluxional process that renders the phosphine ligands chemically inequivalent. Over the same temperature range the methyl and methine ^1H resonances of the isopropyl groups of the main group fragment decoalesced into a complex series of resonances (Figure 3.6). While the data cannot unambiguously rule out the formation of isomers that differ in the coordination environment about ruthenium, the data were consistent with $\text{M}\cdot\text{Ru}\cdot\text{N}_2$ retaining *cis*-phosphine ligands but adopting a low symmetry due to a locked conformation of the β -diketiminato ligand. Hindered rotation about the $\text{N}-\text{C}_{\text{Ar}}$ bond of these β -diketiminato ligand systems is common (Figure 3.6). The main group fragments in these complexes appeared tightly bound across $193 - 353$ K and no data have been collected that support bimetallic dissociation into the monometallic components.^{45,46}

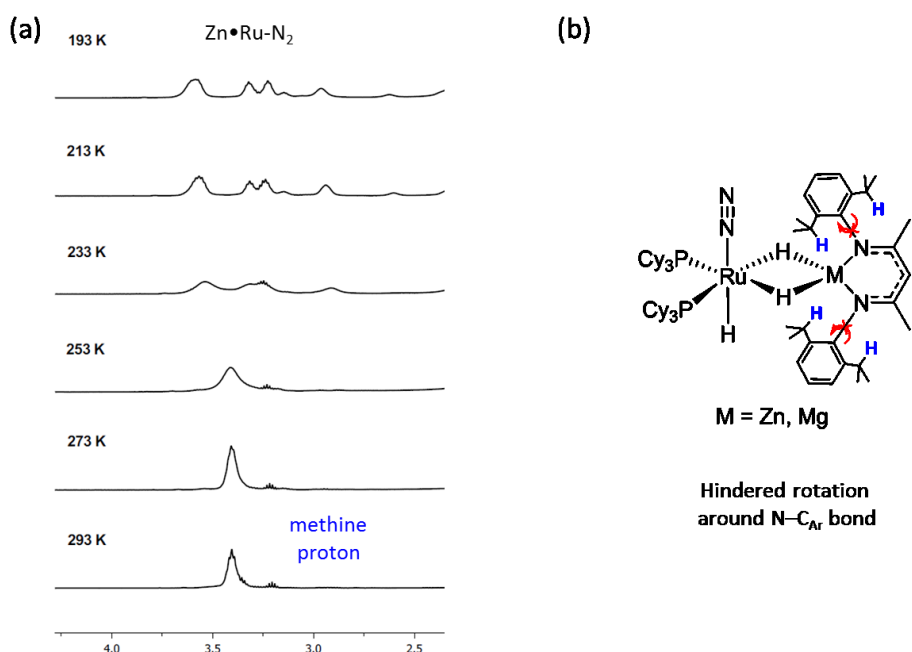


Figure 3.6 (a) VT ^1H NMR of $\text{Zn}\cdot\text{Ru}\cdot\text{N}_2$ showing just the methine proton of isopropyl groups. (b) Hindered rotation about $\text{N}-\text{C}_{\text{Ar}}$ bond of β -diketiminato ligand at low temperature

The dinitrogen ligands of these **M•Ru-N₂** complexes were found to display strong $\nu_{\text{N}=\text{N}}$ stretching frequencies (**Al**, 2160 cm⁻¹; **Zn**, 2135 cm⁻¹, **Mg**, 2130 cm⁻¹) acquired on solid samples of **M•Ru-N₂**. These vibrational frequencies were consistent with that reported for **1** (CHAPTER 2), in addition their assignment as N₂ and not H₂ stretches was confirmed by preparation of **M•Ru-D₂**, an isotopomer of **M•Ru-H₂**. For comparison the Raman stretch of free N₂ is 2331 cm⁻¹.

M•Ru-N₂ crystallised upon storage of concentrated hydrocarbon solutions under an N₂ atmosphere at -35 °C (Figure 3.7). The solid-state structures reflected the solution characterisation data and in the case of **Zn•Ru-N₂** the data were of sufficient quality to locate the terminal and bridging hydride ligands from the electron density difference map. The geometry at ruthenium was a heavily distorted octahedron with the main group metal sitting in the secondary coordination sphere attached by bridging hydride ligands and 3-centre,2-electron interactions. In the equatorial plane, the P-Ru-P angles were obtuse (X-ray = 104 – 107 °; DFT = 104 – 106 °) and the H_{eq}-Ru-H_{eq} angles were close to 90 ° (X-ray; DFT = 92 – 94 °). The length of the terminal Ru-H_{ax} bond of **Zn•Ru-N₂** (1.45(3) Å) was shorter than both the bridging Ru-H_{eq} (1.62(3) and 1.70(2) Å) and bridging Zn-H bonds (1.82(3) and 1.88(3) Å). The Ru---M distances were short (**Al**, 2.443(2) Å; **Zn**, 2.4957(3) Å; **Mg**, 2.581(3) Å) and could be interpreted as an indication of a metal---metal interaction.

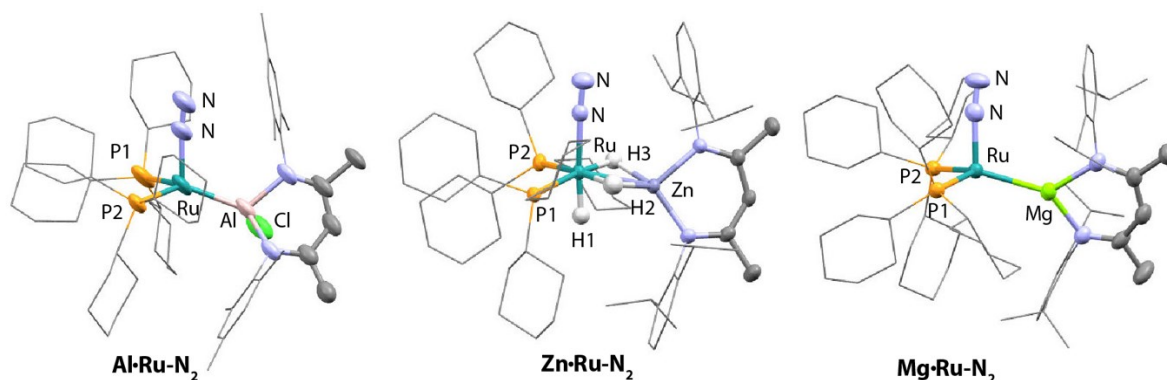


Figure 3.7 Crystal structures of **M•Ru-N₂** (**M** = **Al**, **Zn**, **Mg**)

The metal---metal distances in **M•Ru-N₂** were all close to the sum of the single bond radii as defined by Pauling¹¹ and only the Ru---Zn distance was longer than the sum of the covalent radii defined by Pyykkö.⁴⁷ The *formal shortness ratio* (*fsr*) was used as a crude metric to interrogate the nature of metal---metal bonds by normalising the metal---metal bond distances.^{48–51} The *fsr* of **M•Ru-N₂** determined using the Pauling radii were all ~1 and could be an indicator of a metal-metal bond (**Al**, 0.99; **Zn**, 1.00; **Mg**, 0.99). The presence of multiple bridging ligands is well known to contract metal--metal separations, however, to a point that the true nature of the bonding can become opaque. The *fsr* has previously been used in our group as an indicator of metal-metal bonding, but only in combination

with detailed spectroscopic (NMR, Infrared) and computational analysis (DFT, QTAIM) to support the conclusion.

The DFT calculations reproduced the position of the heavy atoms in **M•Ru-N₂** and confirmed the location and bond lengths of the hydride ligands in **Zn•Ru-N₂**. The bridging hydride ligands of **M•Ru-N₂** were located in the equatorial plane of ruthenium and co-ordinate to the main group metal in a κ^2 -binding mode through short Ru-H_{eq} (DFT = 1.6–1.7 Å) and long M-H_{eq} distances (DFT = 1.8–1.95 Å). The location of the main group metal was not perfectly within the equatorial plane and slippage toward the axial hydride on ruthenium and the resulting κ^3 -binding mode was observed for the whole series. The effect was quantified by considering both the M---H_{ax} distance from the DFT calculations (**Al**, 2.1 Å; **Zn**, 2.55 Å; **Mg**, 2.4 Å) and the N–Ru–M angle from the X-ray data (**Al**, 112.15(18)°; **Zn**, 95.64(8)°; **Mg**, 107.32(16)°) and was most pronounced for the aluminium analogue. For comparison, the Al---H_{ax} distance was on the upper limit of the range suggested for a significant bonding interaction in analysis of σ -complexes of aluminium,¹² and was slightly longer than Al–H distances (1.9–2.0 Å) in a related rhodium---aluminium heterobimetallic hydride that has been formulated with a κ^3 -binding mode (Figure 3.8).⁵²

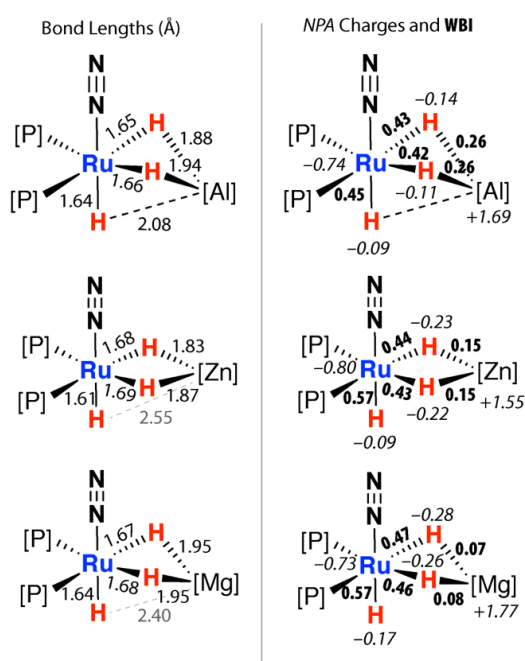


Figure 3.8 Calculated bond lengths in **M•Ru-N₂** along with selected NPA charges and WBI

NBO analysis in combination with QTAIM calculations revealed that, despite the short distances, metal–metal bonding in **M•Ru-N₂** was nominal at best. The Wiberg bond indices (WBI) of the Ru---M interactions were small and decrease across the series **Al** (0.15) > **Zn** (0.07) > **Mg** (0.02). The WBIs of the Ru–H_{ax} bonds were similar to the Ru–H_{eq} bonds suggestive of a similar covalent

character despite the bridging interaction. The $M-H_{eq}$ WBIs were much smaller and decrease across the series **Al** > **Zn** > **Mg** suggestive of decreasing covalent character as the main group metal becomes more electropositive. NPA charges on both these hydrides and ruthenium were negative while the main group metal was, expectedly, highly positive. The combined NPA charge on the ruthenium, hydride and dinitrogen moieties becomes more negative across the series **Mg** ~ **Zn** > **Al**. In combination the analysis was consistent with a large ionic component to the bonding and in the extreme these complexes can be formulated as $[M(Dipp)]^+[RuH_3(N_2)]^-$ adducts in which the key interaction between the two fragments was *via* the bridging hydride ligands (Figure 3.9). Furthermore, the use of covalent bond classification (CBC) and half-arrow notations to depict 3-centre,2-electron interactions of the bridging hydrides can be used to describe these heterobimetallic hydride complexes as a $Ru(L_4X_2)$ system. The 3-centre,2-electron interactions satisfy the 18 valence electron configuration of the transition metal centre without requiring a metal–metal bond (Figure 3.10).

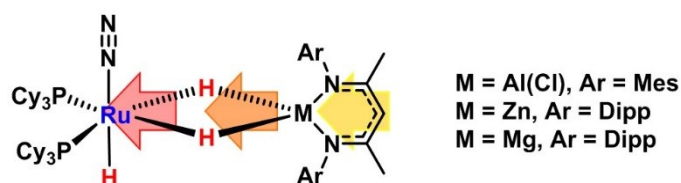


Figure 3.9 Proximity effect of the main group metal through the bridging hydrides on the ruthenium centre

For comparison, in 2015 our group reported a series of rhodium hydride complexes which possess similar *fsr* to those reported herein but with defined Rh–M bonds.⁴⁹ The metal–metal bonding was supported by both calculations and spectroscopic data and crucially these complexes possessed a four-legged piano-stool geometry at rhodium and long $M\cdots H$ distances ($> 2.0 \text{ \AA}$) that were conserved across a series ($M = B, Si, Al, Zn, Mg$). These rhodium complexes were described as $Rh(L_2X_5)$ using the CBC method (Figure 3.10).^{53,54} More recently Whittlesey *et al.* isolated a heterobimetallic complex in which Ru and Zn sites were bridged by two hydride ligands in a κ^2 -fashion (Scheme 3.16).³¹ The bonding mode and computational analysis were near identical to that found for **Zn•Ru-N₂** and the authors of this study also concluded that no significant direct $Ru\cdots Zn$ interaction was found in this species.

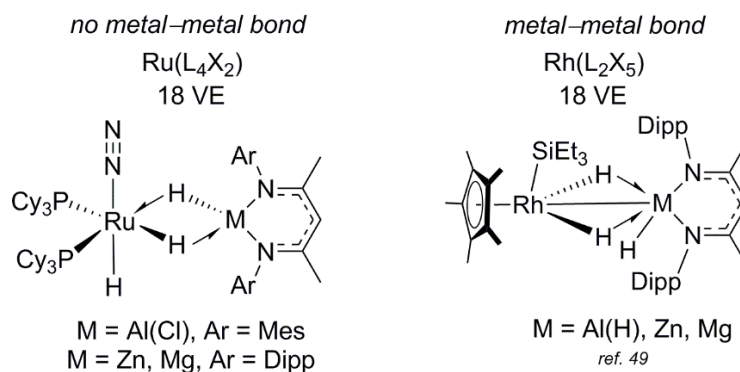


Figure 3.10 CBC and half-arrow notation of heterobimetallic complexes

3.2.3 Tuneable N_2 activation

Detailed understanding of the coordination of N_2 at transition metal centres has paved the way for countless discoveries in dinitrogen fixation.^{55–58} End-on N_2 binding can be considered within the Dewar-Chatt-Duncanson model (Figure 3.11). Donation of electron-density from the filled bonding σ -orbital into a vacant orbital of suitable symmetry on the transition metal is accompanied by back-donation from the transition metal to the $1\pi_g^*$ anti-bonding orbitals of the diatomic. The back-donation is synonymous with lowering of the $\nu_{\text{N}=\text{N}}$ stretching frequency and is often associated with activation of N_2 and catalytic methods for its transformation to NH_3 (or related nitrogen containing molecules at the amine or hydrazine oxidation level).^{59,60}

The extent of back-donation is a tuneable property. It can be regulated by the judicious control of the ligand environment at the transition metal. Modification of the oxidation state, coordination number, or geometry of the transition metal or the electronic or steric properties of the ligands all affect the symmetry and energy of the frontier molecular orbitals (fMOs) of the transition metal fragment and influence the extent of back-donation. For example, as part of detailed investigations into N_2 fixation with carefully designed trigonal bipyramidal group 8 complexes, Peters *et al.* have shown that the extent of back-donation to N_2 , is a function of both the metal⁶¹ and the σ -donating properties of the ligand *trans* to the N_2 coordination site.

More recently bimetallic complexes have been explored in dinitrogen fixation. For example, Lu *et al.* have reported a [Co–Co] bimetallic complex as a catalyst for the reductive silylation of N_2 with Me_3SiCl .⁶² As part of these studies, it has been shown that N_2 binding to [Co–M] bimetallics can be subtly modulated by the choice of the second metal, with $\nu_{\text{N}=\text{N}}$ decreasing across the first row period $\text{M} = \text{V} > \text{Cr} > \text{Co}$ ($\Delta\nu = 25 \text{ cm}^{-1}$).⁶³ In related studies, Thomas *et al.* have shown that modification of the early transition metal in [Co–M] complexes from $\text{M} = \text{Ti}$ to Zr has an impact on N_2 binding to the late transition metal, again reported by the change in the N_2 stretching vibrational spectroscopy ($\Delta\nu =$

39 cm⁻¹).^{64,65} Both these systems contain defined and quantifiable metal–metal bonds and N₂ coordination occurs at a site in line with the metal–metal bond maximising the prospect for bimetallic cooperation.

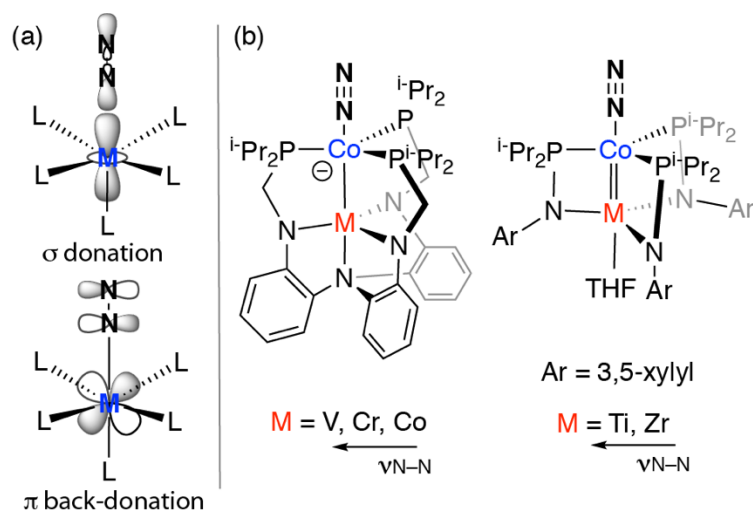


Figure 3.11 (a) Dewar-Chatt-Duncanson Model for N₂ binding and (b) Tuneable N₂ binding to heterobimetallic complexes

In this work, experimentally determined $\nu_{\text{N}\equiv\text{N}}$ stretches for **M•Ru-N₂** decreased across the series Al > Zn > Mg. The calculated vibrational modes also followed this trend, and while the absolute values were systematically over-estimated compared to experiment, the differences relative to $\nu_{\text{N}\equiv\text{N}}$ of Al, $\Delta\nu$, matched closely (Table 3.2). It is worth noting that the differences in the experimental N $\equiv$ N and Ru–N bond lengths were very small and were well within the measurement error of the X-ray diffraction data.

	Al	Zn	Mg
Ru–N (X-ray)	2.007(7) Å	2.022(2) Å	2.011(6) Å
N–N (X-ray)	1.086(7) Å	1.107(3) Å	1.101(9) Å
N–N (DFT)	1.104 Å	1.106 Å	1.107 Å
WBI (DFT)	2.76	2.75	2.74
$\nu_{\text{N}\equiv\text{N}}$ (IR)	2160 cm ⁻¹	2135 cm ⁻¹	2130 cm ⁻¹
$\nu_{\text{N}\equiv\text{N}}$ (DFT)^[a]	2342 cm ⁻¹	2320 cm ⁻¹	2311 cm ⁻¹
$\Delta\nu$ (IR)	0 cm ⁻¹	25 cm ⁻¹	30 cm ⁻¹
$\Delta\nu$ (DFT)	0 cm ⁻¹	21 cm ⁻¹	30 cm ⁻¹

[a] Uncorrected values.

Table 3.2 Experimental and computation data on N₂ binding to **M•Ru-N₂**

The molecular orbital analysis of some simplified models delivered an explanation for the tuneable N₂ activation and the trend disclosed above. The frontier molecular orbitals (fMOs) of the square-based pyramidal transition metal fragment, *cis*-[Ru(H)₃(PMe₃)₂][−] were represented in Figure 3.12a. The LUMO was preferentially orientated to accept electron density from the 3σ_g orbital of N₂ while the HOMO and HOMO-2 were orientated in a fashion to back-donate to the degenerate and orthogonal 1π_g orbitals. The model was expanded to include the main group fragment and similar symmetry fMOs were calculated for model heterobimetallic complexes in which peripheral groups on the ligands were truncated Figure 3.12b.

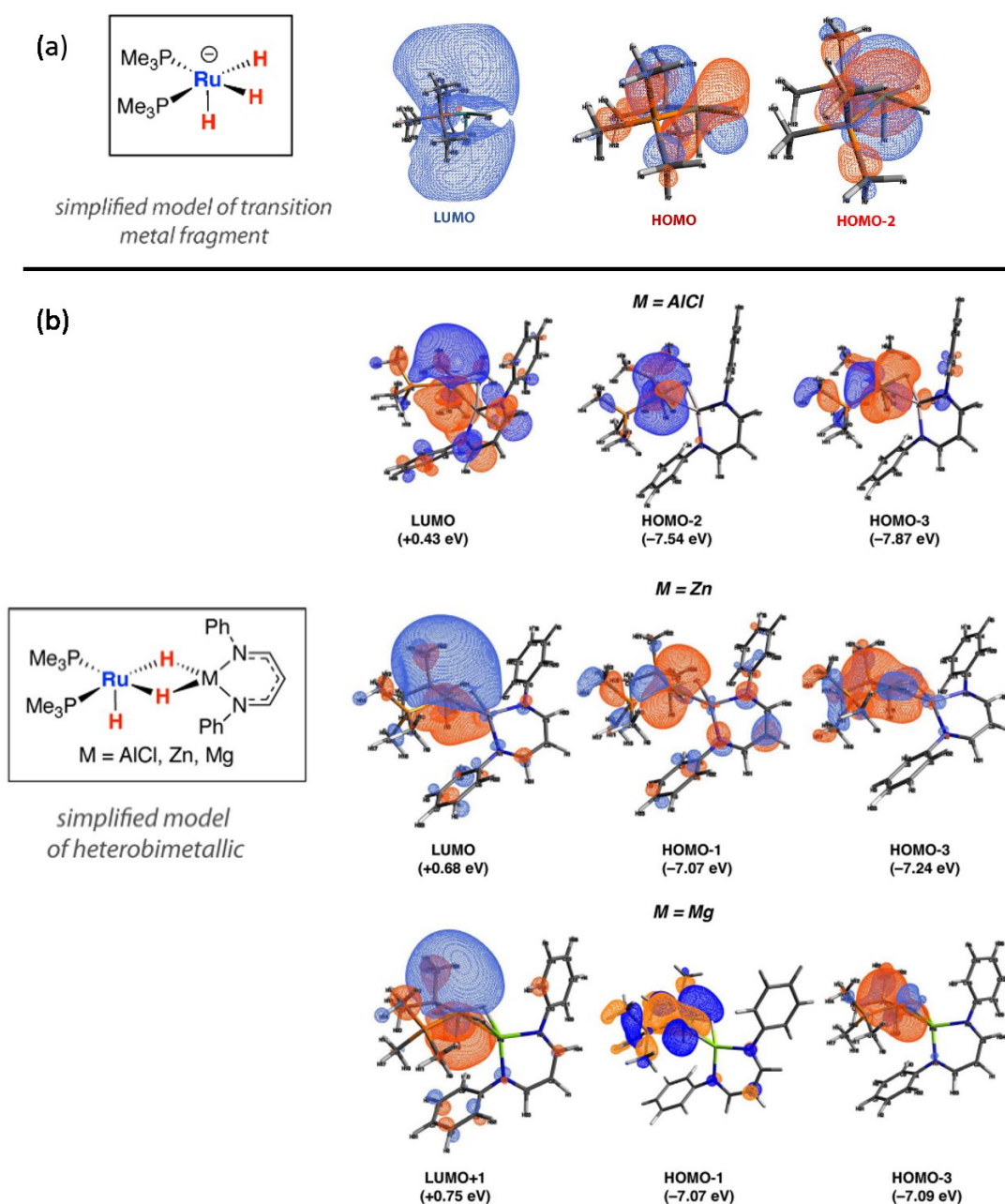


Figure 3.12 (a) Selected fMOs of *cis*-[Ru(H)₃(PMe₃)₂][−] of relevance for N₂ binding, (b) Selected fMOs and energies of the model heterobimetallic complexes

Inspection of the energies of the fMOs of suitable symmetry for N₂ binding revealed that on decreasing the electronegativity of the main group metal (χ_m Al = 1.61 > Zn = 1.59 > Mg = 1.29) all the molecular orbitals of the model heterobimetallic complex were destabilised to a small extent (Figure 3.13). The orbital destabilisation was a direct effect of the second metal on the ruthenium centre. This effect was not exerted through a metal–metal bond nor did it require a *trans* relationship between the second metal and the binding site, it occurred due to modulation of the degree of ionicity of the metal–hydride bonding and charge localisation on transition metal centre (Figure 3.8).

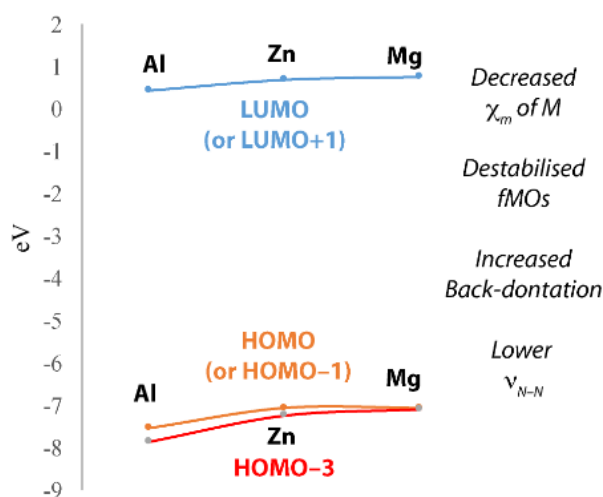


Figure 3.13 Energies of selected fMOs of model heterobimetallic complex.

The heterobimetallic complex with the least electronegative main group metal, Mg, had the lowest covalent character to the bonding and the largest charge localisation on the transition metal fragment and hence the most destabilised fMOs. Destabilisation of the occupied frontier molecular orbitals on ruthenium raised their energy and therefore allowed increased back-donation into N₂ anti-bonding bonding orbital resulting in a reduction of the N–N bonding order and the observed lowering of the N₂ stretching frequency. The degree of back-donation from ruthenium into N₂ was further examined by looking at the values obtained from second-order perturbation calculations on the **M•Ru-N₂** complexes. The most significant donor-acceptor contribution from Ru(4d) → $\pi^*(\text{N-N})$ increased from Al = 20.0 kcal mol⁻¹ < Zn = 23.5 kcal mol⁻¹ < Mg = 24.6 kcal mol⁻¹ which mirrored the observed trend in the degree activation of N₂ in these heterobimetallic complexes.

The values from second-order perturbation calculations for the parallel donation of the $\sigma(\text{N-N})$ into an empty Ru(4d) orbital of the correct symmetry can be scrutinised further. The values obtained for all three **M•Ru-N₂** complexes were small (< 10 kcal mol⁻¹) which was in agreement with N₂ being a poor σ -donor and justified the labile nature of the dinitrogen on the ruthenium centre and the ease at which these complexes undergo substitution reactions with CO.

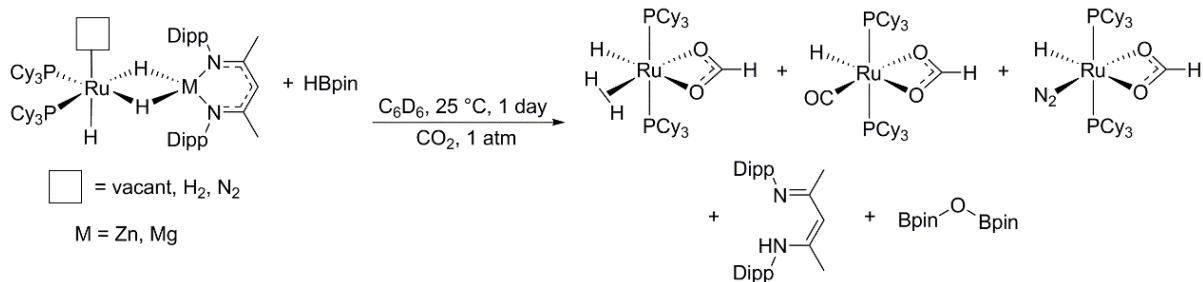
Overall the Ru---M (M = Al, Zn, Mg) heterobimetallic hydride complexes synthesised here demonstrated N₂ (and H₂) binding.⁴⁸ These complexes possessed weak metal---metal interactions at best. The main group metal sits in the secondary coordination sphere of a pseudo-octahedral ruthenium complex. A combination of characterisation techniques (single crystal X-ray diffraction and infrared spectroscopy) and DFT and QTAIM calculations indicated that the variation of main group metal has an effect on N₂ activation with the more electropositive ligands resulting in a subtle but measurable increase in back-donation to the diatomic. The results were rationalised through detailed DFT calculations which ultimately show that the electronegativity of the main group metal impacts the energy of fMOs on ruthenium and, hence, dinitrogen binding.

The ability for this apical site on the ruthenium, in these heterobimetallic complexes, to co-ordinate N₂ and H₂ (as well as CO) allowed for further examination into reactivity with other small molecules.

3.2.4 Reactivity with CO₂ and HBpin

Research into the use of CO₂ as a C₁ source has been pursued as a method to help combat the rising levels of CO₂ in the atmosphere⁶⁶ but also as an alternative abundant, cheap non-toxic resource.⁶⁷ The activation and functionalisation of CO₂ with borane substrates mediated by [Ru(H)₂(η^2 -H₂)₂(PCy₃)₂], **1-2H₂**, has been explored by Sabo-Etienne *et al.*^{44,68} (CHAPTER 1). Comparison of the reduction of CO₂ with HBpin by the monometallic ruthenium species *versus* the heterobimetallic **M•Ru** species will be of interest to see (i) if the heterobimetallic species can also perform the same transformation and if yes (ii) is there any difference in the product distribution?

Due to the inability to isolate large amounts of one of the heterobimetallic cleanly, the heterobimetallic species were generated *in situ* and used directly in these reactions. Complete conversion of the starting materials into the **M•Ru** heterobimetallic species (M = Zn and Mg) was ensured before addition of 1 equivalent of HBpin to observe if any reactivity occurred prior to CO₂ addition. Slight broadening of the hydride region in ¹H NMR spectrum was observed however no evidence of reactivity or dissociation of the heterobimetallic species was shown by multinuclear NMR spectroscopy. Upon addition of CO₂ (1 atm.) the major products observed in both the zinc and magnesium systems were formation of the free β -diketiminato ligand, [RuH(η^2 -H₂)(κ^2 -O₂CH)(PCy₃)₂], [RuH(CO)(κ^2 -O₂CH)(PCy₃)₂] and B₂pin₂O (Scheme 3.19).^{44,69}

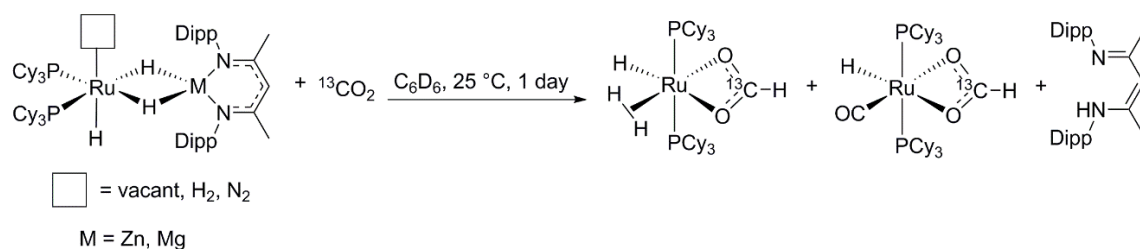


Scheme 3.19 Reaction of **M•Ru** (M = Zn, Mg) hydride complexes with HBpin and CO₂

For the magnesium reaction some additional unidentified resonances ($\delta_{\text{H}} = 16.38$ and 16.17 ppm) were observed in the proton and phosphorous NMR spectra ($\delta_{\text{P}} = 51.8$ ppm). One of the unidentified species was postulated as the dinitrogen analogue of the formate complex, $[\text{RuH}(\text{N}_2)(\kappa^2\text{-O}_2\text{CH})(\text{PCy}_3)_2]$, which demonstrated a triplet at $\delta_{\text{H}} = -13.82$ ppm ($J_{\text{HP}} = 14.3$ Hz) for the Ru–H environment with the corresponding formate peak as a broad signal $\delta_{\text{H}} = 8.58$ ppm. However why these signals for the postulated dinitrogen analogue would not be seen in the zinc system would raise doubts about this assignment as the main group hydride should be independent of the formation of $[\text{RuH}(\text{N}_2)(\kappa^2\text{-O}_2\text{CH})(\text{PCy}_3)_2]$.

The formation of these monometallic ruthenium formate species in combination with free β -diketiminate showed that upon addition of CO₂ dissociation of the heterobimetallic species occurred. Therefore, it was likely the monometallic ruthenium species were actually performing the reduction to form B₂pin₂O and not the heterobimetallic species (B₂pin₂O was identified from the indicative peaks in the ¹H and ¹¹B{¹H} NMR spectra). Also, both HBpin and the ^{Dipp}BDIMH (M = Zn, Mg) (generated after dissociation of the heterobimetallic) could act as the reducing reagent in this reaction which could explain why the presence of the main group hydride was not observed by ¹H NMR spectroscopy during the reaction. It is also worth noting that ^{Dipp}BDIMgH was known to catalyse the reduction of CO₂ with HBpin in presence of B(C₆F₅)₃.⁷⁰

This result indicated that these heterobimetallic species were susceptible to dissociation under CO₂. To confirm this conclusion and to try and identify the other unknown species observed during the reduction reactions the heterobimetallic species were reacted with ¹³C-labelled CO₂ (1 atm.) at 25 °C (Scheme 3.20). Again, in both the zinc and magnesium systems $[\text{RuH}(\eta^2\text{-H}_2)(\kappa^2\text{-O}_2\text{CH})(\text{PCy}_3)_2]$ and $[\text{RuH}(\text{CO})(\kappa^2\text{-O}_2\text{CH})(\text{PCy}_3)_2]$ were formed with the expected two doublets for the formate peaks due to coupling to the enriched ¹³C environment. Free ligand was also detected in the reaction confirming the competency of the main group hydride as the reducing agent in both the systems. Only in the reaction with the magnesium heterobimetallics was the triplet at $\delta_{\text{H}} = -13.82$ ppm, postulated as $[\text{RuH}(\text{N}_2)(\kappa^2\text{-O}_2\text{CH})(\text{PCy}_3)_2]$, observed along with the corresponding formate peak, now a sharp doublet due to coupling to the ¹³C labelled atom, at $\delta_{\text{H}} = 8.64$ ppm, detected in the proton NMR spectrum.



Scheme 3.20 Reaction of $M\bullet Ru$ ($M = Zn, Mg$) hydride complexes with $^{13}CO_2$

Importantly, the unidentified singlets downfield at $\delta_H = 16.38$ and 16.17 ppm were again observed but only in the reaction with **Mg•Ru**. These resonances remained singlets in this reaction and indicated no participation of the $^{13}CO_2$ in their formation. The identity of these peaks remained elusive however its formation, though not directly involving CO_2 was only formed in the presence of the gas as well the ruthenium and main group hydride. The discriminate nature of using either the Zn- or Mg-main group hydride to form these two downfield resonances would point towards some reactivity at backbone of the β -diketiminato ligand only accessible for the magnesium hydride⁷⁰ however no substantive evidences has been collected to confirm this.

3.3 CONCLUSION

In summary, the synthesis and characterisation of a series of ruthenium main group heterobimetallic complexes with X-ray structures obtained for the **M•Ru-N₂** complexes ($M = Al, Zn$ and Mg) was achieved. The bonding characteristics of these heterobimetallic complexes were probed using experimental data in combination with computational methods.

A small decrease in the $\nu_{N\equiv N}$ stretch, corresponding to weakening of the N–N bond, was observed from changing the main group metal of the heterobimetallic from $Al < Zn < Mg$. This trend was rationalised due to the greater ionic character of the metal–hydride bonding within the **M•Ru-N₂** complex which was more pronounced with the less electronegative metal. The increased ionic character resulted in greater destabilisation of the fMOs of ruthenium which in turn allowed for increased back-donation from $Ru(4d) \rightarrow \pi^*(N-N)$ and consequently longer N–N bond lengths. Importantly, differing to the *status quo*, there was no significant metal---metal bond to influence this degree of N₂ activation. Instead the main group fragment altered the electron density of the bridging hydrides which in turn affected the energetics of the orbital contributions around the ruthenium metal. While the net effect on the N₂ stretching frequency for the series of complexes reported herein was subtle, it clearly represents an example of a growing number of phenomena in which the binding and reactivity of small molecules at a transition metal centre can be modified by the proximity of a second metal.^{71–74}

In addition, initial investigation into the reactivity of these heterobimetallic hydride complexes in the reduction of CO_2 with HBpin showed that dissociation of the heterobimetallic hydride into their parent complexes was, instead, observed.

3.4 FUTURE WORK

Further inspection into this proximity effect of the second metal would allow for deeper analysis into the N₂ tuneability of these heterobimetallic hydride complexes. This could include altering the electronics of the main group metal by simply changing the aryl groups on the β -diketiminate ligand or even the methyl group of the backbone of these ligands. As **Mg•Ru-N₂** had the greatest “activation” of the dinitrogen ligand, by making the bonding description of the heterobimetallic complex even more extreme in terms of the ionic character this should amplify the proximity effect by destabilising the relevant fMOs further.

Beyond understanding the bonding of these heterobimetallic hydride complexes, more research is required on the application of these heterobimetallic hydride complexes in synthesis and/or catalysis. The co-ordination of small molecules in the apical site of ruthenium was possible (CO, CNAr where Ar = 2,6-xylyl) however the “Goldilocks effect” seemed to be in play as to whether co-ordination of the small molecule led to dissociation of the complex or formation of a stable heterobimetallic complex. Again, altering the β -diketiminate ligand around the main group or the phosphine around the ruthenium may lead to success however this would be a long and potential unfruitful process. Instead looking into literature, comparing the **M•Ru-H₂** complex, which potentially contains 5 hydrogens in total around ruthenium, with **1-2H₂** which contains 6 hydrogens in total, there are similarities. The area of hydrogenation chemistry by **1-2H₂** is incredibly vast (CHAPTER 1) and again comparison with how these heterobimetallic hydride complexes perform under similar hydrogenation chemistry would be interesting *i.e.* does the inclusion of a second metal component have any benefit?

As mentioned at the end of Chapter 2, the research into these heterobimetallic hydride complexes stemmed from the initial research into using these heavier main group complexes as alternative options to organoborane substrates in the conversion of an unreactive bond into a reactive intermediate *i.e.* C–X bond (X = H or O) into a C–E bond (E = Al, Zn, or Mg). This area is still very much work in progress and initial reactivity of **1** with 2-methoxyacetophenone and the main group hydrides has not led to the desired outcome – no formation of a new C–E (E = Zn or Mg) bonds. Instead, Chapter 4 will be a continuation of the formation of these heterobimetallic hydride complexes but instead using solely aluminium dihydride complexes as the main group partner and the divergence from these mono hydride complexes.

3.5 REFERENCES

- 1 S. Sabo-Etienne, M. Muñoz-Hernández, G. Chung and B. Chaudret, *New J. Chem.*, 1994, **18**, 175–177.
- 2 R. Ben Said, K. Hussein, B. Tangour, S. Sabo-Etienne and J.-C. Barthelat, *New J. Chem.*, 2003, **27**, 1385–1391.
- 3 A. R. Barron and G. Wilkinson, *J. Chem. Soc. Dalt. Trans.*, 1986, 287–289.
- 4 G. S. Girolami, G. Wilkinson, M. Thornton-Pett and M. B. Hursthouse, *J. Am. Chem. Soc.*, 1983, **105**, 6752–6753.
- 5 G. S. Girolami, C. G. Howard, G. Wilkinson, H. M. Dawes, M. Thornton-Pett, M. Motevalli and M. B. Hursthouse, *J. Chem. Soc. Dalt. Trans.*, 1985, 921–929.
- 6 A. R. Barron, M. B. Hursthouse, M. Motevalli and G. Wilkinson, *J. Chem. Soc. Chem. Commun.*, 1985, 664–665.
- 7 A. R. Barron, D. Lyons, G. Wilkinson, M. Motevalli, A. J. Howes and M. B. Hursthouse, *J. Chem. Soc., Dalt. Trans.*, 1986, 279–285.
- 8 R. Gilbert-Wilson, L. D. Field and M. Bhadbhade, *Inorg. Chem.*, 2014, **53**, 12469–12479.
- 9 D. Hwan Lee, H. Suzuki and Y. Moro-oka, *J. Organomet. Chem.*, 1987, **330**, C20–C22.
- 10 W. Lin, S. R. Wilson and G. S. Girolami, *Organometallics*, 1997, **16**, 2987–2994.
- 11 L. Pauling, *J. Am. Chem. Soc.*, 1947, **69**, 542–553.
- 12 M. Ohashi, K. Matsubara, T. Iizuka and H. Suzuki, *Angew. Chemie Int. Ed.*, 2003, **42**, 937–940.
- 13 T. Steinke, M. Cokoja, C. Gemel, A. Kempter, A. Krapp, G. Frenking, U. Zenneck and R. A. Fischer, *Angew. Chemie Int. Ed.*, 2005, **44**, 2943–2946.
- 14 T. Cadenbach, T. Bollermann, C. Gemel and R. A. Fischer, *Dalt. Trans.*, 2009, **127**, 322–329.
- 15 M. Plois, T. Wiegand and R. Wolf, *Organometallics*, 2012, **31**, 8469–8477.
- 16 A. R. Barron and G. Wilkinson, *Polyhedron*, 1986, **5**, 1897–1915.
- 17 I. M. Riddlestone, J. Urbano, N. Phillips, M. J. Kelly, D. Vidovic, J. I. Bates, R. Taylor and S. Aldridge, *Dalt. Trans.*, 2013, **42**, 249–258.
- 18 Y. Ohki, Y. Takikawa, H. Sadohara, C. Kesenheimer, B. Engendahl, E. Kapatina and K. Tatsumi, *Chem. - An Asian J.*, 2008, **3**, 1625–1635.
- 19 F. Forster, T. T. Metsänen, E. Irran, P. Hrobárik and M. Oestreich, *J. Am. Chem. Soc.*, 2017, **139**, 16334–16342.
- 20 A. Maisonne, J. P. Farr, M. M. Olmstead, C. T. Hunt and A. L. Balch, *Inorg. Chem.*, 1982, **21**, 3961–3967.
- 21 W.-H. Chan, Z.-Z. Zhang, T. C. W. Mak and C.-M. Che, *J. Chem. Soc. Dalt. Trans.*, 1998, **41**, 803–810.
- 22 M. Enders, G. Kohl and H. Pritzkow, *Organometallics*, 2002, **21**, 1111–1117.
- 23 M. Ohashi, K. Matsubara and H. Suzuki, *Organometallics*, 2007, **26**, 2330–2339.
- 24 T. Cadenbach, T. Bollermann, C. Gemel, M. Tombul, I. Fernandez, M. von Hopffgarten, G. Frenking and R. A. Fischer, *J. Am. Chem. Soc.*, 2009, **131**, 16063–16077.
- 25 M. Molon, C. Gemel, R. W. Seidel, P. Jerabek, G. Frenking and R. A. Fischer, *Inorg. Chem.*, 2013, **52**, 7152–7160.
- 26 M. Molon, C. Gemel and R. A. Fischer, *Eur. J. Inorg. Chem.*, 2013, **2013**, 3616–3622.
- 27 A. D. McNaught and A. Wilkinson, in *IUPAC Compendium of Chemical Terminology*, IUPAC, Research Triangle Park, NC, 2nd edn., 1997, p. 1265.
- 28 D. G. Hamilton and R. H. Crabtree, *J. Am. Chem. Soc.*, 1988, **110**, 4126–4133.
- 29 M. Plois, R. Wolf, W. Hujo and S. Grimme, *Eur. J. Inorg. Chem.*, 2013, **2013**, 3039–3048.
- 30 M. Plois, W. Hujo, S. Grimme, C. Schwickert, E. Bill, B. De Bruin, R. Pöttgen and R. Wolf, *Angew. Chemie Int. Ed.*, 2013, **52**, 1314–1318.
- 31 I. M. Riddlestone, N. A. Rajabi, J. P. Lowe, M. F. Mahon, S. A. Macgregor and M. K. Whittlesey, *J. Am. Chem. Soc.*, 2016, **138**, 11081–11084.
- 32 J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615–6620.
- 33 D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123–141.
- 34 A. Bergner, M. Dolg, W. Küchle, H. Stoll and H. Preuß, *Mol. Phys.*, 1993, **80**, 1431–1441.
- 35 J. M. L. Martin and A. Sundermann, *J. Chem. Phys.*, 2001, **114**, 3408–3420.

- 36 W. J. Hehre, K. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261.
- 37 T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294–301.
- 38 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213–222.
- 39 L. D. Field, R. W. Guest, K. Q. Vuong, S. J. Dalgarno and P. Jensen, *Inorg. Chem.*, 2009, **48**, 2246–2253.
- 40 D. G. Gusev, F. M. Dolgushin and M. Y. Antipin, *Organometallics*, 2000, **19**, 3429–3434.
- 41 A. D. Allen and C. V. Senoff, *Chem. Commun.*, 1965, 621–622.
- 42 C. V. Senoff, *J. Chem. Educ.*, 1990, **67**, 368–370.
- 43 M. L. Christ, S. Sabo-Etienne and B. Chaudret, *Organometallics*, 1994, **13**, 3800–3804.
- 44 S. Bontemps, L. Vendier and S. Sabo-Etienne, *Angew. Chemie Int. Ed.*, 2012, **51**, 1671–1674.
- 45 A. E. Nako, Q. W. Tan, A. J. P. White and M. R. Crimmin, *Organometallics*, 2014, **33**, 2685–2688.
- 46 A. Hicken, A. J. P. White and M. R. Crimmin, *Inorg. Chem.*, 2017, **56**, 8669–8682.
- 47 P. Pyykkö and M. Atsumi, *Chem. - A Eur. J.*, 2009, **15**, 186–197.
- 48 M. J. Butler and M. R. Crimmin, *Chem. Commun.*, 2017, **53**, 1348–1365.
- 49 O. Ekkert, A. J. P. White, H. Toms and M. R. Crimmin, *Chem. Sci.*, 2015, **6**, 5617–5622.
- 50 O. Ekkert, A. J. P. White and M. R. Crimmin, *Angew. Chemie Int. Ed.*, 2016, **55**, 16031–16034.
- 51 R. J. Eisenhart, L. J. Clouston and C. C. Lu, *Acc. Chem. Res.*, 2015, **48**, 2885–2894.
- 52 O. Ekkert, S. D. A. Strudley, A. Rozenfeld, A. J. P. White and M. R. Crimmin, *Organometallics*, 2014, **33**, 7027–7030.
- 53 M. L. H. Green, *J. Organomet. Chem.*, 1995, **500**, 127–148.
- 54 J. C. Green, M. L. H. Green and G. Parkin, *Chem. Commun.*, 2012, **48**, 11481–11503.
- 55 M. D. Fryzuk, *Chem. Commun.*, 2013, **49**, 4866–4868.
- 56 J. Chatt, *J. Organomet. Chem.*, 1975, **100**, 17–28.
- 57 M. Hidai and Y. Mizobe, *Chem. Rev.*, 1995, **95**, 1115–1133.
- 58 B. A. MacKay and M. D. Fryzuk, *Chem. Rev.*, 2004, **104**, 385–401.
- 59 K. C. MacLeod and P. L. Holland, *Nat. Chem.*, 2013, **5**, 559–565.
- 60 N. Hazari, *Chem. Soc. Rev.*, 2010, **39**, 4044–4056.
- 61 J. Fajardo and J. C. Peters, *J. Am. Chem. Soc.*, 2017, **139**, 16105–16108.
- 62 R. B. Siedschlag, V. Bernales, K. D. Vogiatzis, N. Planas, L. J. Clouston, E. Bill, L. Gagliardi and C. C. Lu, *J. Am. Chem. Soc.*, 2015, **137**, 4638–4641.
- 63 L. J. Clouston, V. Bernales, R. K. Carlson, L. Gagliardi and C. C. Lu, *Inorg. Chem.*, 2015, **54**, 9263–9270.
- 64 W. Zhou, N. I. Saper, J. P. Krogman, B. M. Foxman and C. M. Thomas, *Dalt. Trans.*, 2014, **43**, 1984–1989.
- 65 B. Wu, K. M. Gramigna, M. W. Bezpalko, B. M. Foxman and C. M. Thomas, *Inorg. Chem.*, 2015, **54**, 10909–10917.
- 66 M. Aresta and A. Dibenedetto, *Dalt. Trans.*, 2007, 2975–2992.
- 67 T. Sakakura, J. C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387.
- 68 S. Bontemps, L. Vendier and S. Sabo-Etienne, *J. Am. Chem. Soc.*, 2014, **136**, 4419–4425.
- 69 J. Feldman, S. J. McLain, A. Parthasarathy, W. J. Marshall, J. C. Calabrese and S. D. Arthur, *Organometallics*, 1997, **16**, 1514–1516.
- 70 M. D. Anker, M. Arrowsmith, P. Bellham, M. S. Hill, G. Kociok-Köhn, D. J. Liptrot, M. F. Mahon and C. Weetman, *Chem. Sci.*, 2014, **5**, 2826–2830.
- 71 M. V. Vollmer, J. Xie and C. C. Lu, *J. Am. Chem. Soc.*, 2017, **139**, 6570–6573.
- 72 J. Takaya and N. Iwasawa, *J. Am. Chem. Soc.*, 2017, **139**, 6074–6077.
- 73 R. C. Cammarota and C. C. Lu, *J. Am. Chem. Soc.*, 2015, **137**, 12486–12489.
- 74 M. J. Butler, A. J. P. White and M. R. Crimmin, *Angew. Chemie Int. Ed.*, 2016, **55**, 6951–6953.

4 CHAPTER FOUR – REACTIONS OF β -DIKETIMINATE STABILISED ALUMINIUM DIHYDRIDE COMPLEXES WITH RUTHENIUM(II) *BIS*(DINITROGEN) COMPLEX

4.1 INTRODUCTION

Aluminium is the most abundant metal in the Earth's crust however its use in synthetic chemistry has been limited to modest scales namely LiAlH_4 as a reducing reagent and AlX_3 (X = halide) as Lewis acid reagents. Beyond the cheaper cost associated with using aluminium as a synthon, aluminium also offers diverse reactivity associated with its low electronegativity ($\chi_{\text{m}} = 1.61$) and ability to have a range of coordination geometries (3.1.1 $\text{Al}\cdot\text{Ru}$ heterobimetallic complexes).¹ Understanding the bonding within these novel molecular aluminium containing complexes through spectroscopic techniques in combination with computational methods have been under explored relative to the heterogeneous family of aluminium containing complexes.

One area of contention is assigning the oxidation state of aluminium within novel heterobimetallic complexes which can become more ambiguous with unconventional bond motifs. Aluminium most commonly exists in the +3 oxidation state in inorganic compounds with +1 oxidation state normally associated with aluminium in the gaseous phase trapped in a noble gas matrix² or tetrameric aluminium compounds.³ However, in 2000 Roesky *et al.* isolated the first monomeric Al(I) complex in the solid state, $\text{Dipp}^{\text{BDI}}\text{Al(I)}$.⁴ The sterically demanding β -diketiminato ligand supporting the aluminium centre prevented dimerization of the molecule and has paved the way for alternative routes to the accessibility of low valent main group complexes.^{5–7} Below is a short summary of the characterisation data obtained on a handful of aluminium compounds in the +1 oxidation state in various states of matter.

4.1.1 Tetrameric Aluminium(I) Compounds

Formation of molecular aluminium(I) compounds such as AlH , Al_2O , Al_2Se , and AlX (X = halide ion) had been evidenced under extreme reaction conditions requiring high temperatures ($> 1000^\circ\text{C}$) and sometimes reduced pressures.^{3,8,9} Stabilisation of aluminium(I) compounds has historically been troublesome as disproportionation into metallic aluminium and aluminium(III) compounds were normally the outcome. Nevertheless, there were a number of reports on the successful stabilisation of aluminium(I) compounds for characterisation by X-ray crystallography which have yielded the tetrameric form of the aluminium(I) compounds as opposed to the monomeric form.

In 1991, Schnöckel *et al.* reported the X-ray crystallographic evidence of a stable tetrameric aluminium(I) complex under standard conditions, $[(\text{Cp}^*\text{Al})_4]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) (Figure 4.1, complex

4.1).¹⁰ The X-ray crystallographic data confirmed the tetrahedron arrangement of the aluminium sites with each aluminium coordinated to Cp* ligand. The average measured Al–Al bond distance was 2.77 Å which was comparable to metallic aluminium (2.86 Å). Complex **4.1** exhibited a sharp resonance at $\delta_{\text{Al}} = -81$ ppm (fwhm = 170 Hz) in the solution state ²⁷Al NMR spectrum in benzene.

In 1994, Schnöckel *et al.* also stabilised “AlBr” in a NEt₃/toluene solvent mixture to yield an adduct of NEt₃ with AlBr, [Al₄Br₄(NEt₃)₄] (Figure 4.1, complex **4.7**). The X-ray crystallographic data of complex **4.7** showed the four aluminium sites bound in a square ring arrangement with bromine groups coordinated to the aluminium in alternating fashion above and below the plane of the ring. The average measured Al–Al bond distance was 2.64 Å which was shorter than the tetrameric aluminium(I) compounds but still in the expected range of single Al–Al bonds. Although DFT was performed to calculate the favourability of the tetramerisation of “AlBr” into [Al₄Br₄(NEt₃)₄], it would be interesting to compare the energy compensation of [Al₄Br₄(NEt₃)₄] going from the square ring geometry to a tetrahedron geometry in order to justify why [Al₄Br₄(NEt₃)₄] adopted the square ring geometry. Since these two publications Schnöckel’s group and Roesky’s group have led the research and characterisation into these tetrameric aluminium(I) compounds (Figure 4.1).^{11–16}

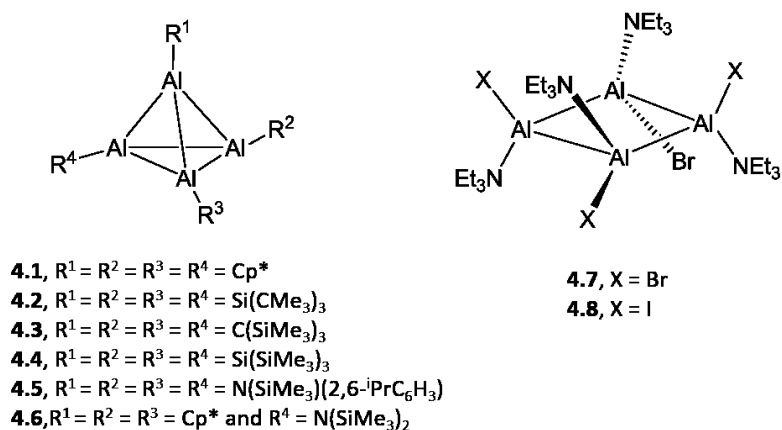
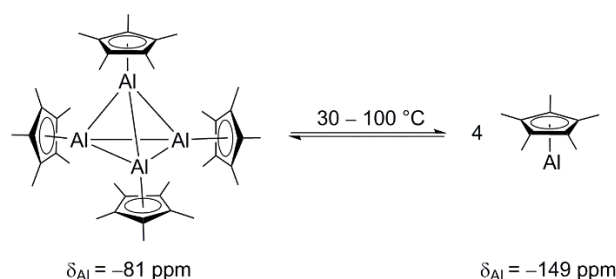


Figure 4.1 Aluminium(I) tetramers that have been characterised by X-ray crystallography

One of the major question in this area of chemistry was identifying whether the aluminium(I) compounds existed as a tetramer in solution state as well as solid state. ²⁷Al NMR spectroscopy provided a solution as the coordination number of the aluminium site in question affected the chemical shift value and therefore the difference between the monomeric and tetrameric aluminium(I) compounds should yield indicative chemical shifts. Research into AlCp* and [AlCp*]₄ had been the most extensive especially with the successfully characterisation of the tetrameric form by X-ray crystallography. Solution state ²⁷Al NMR spectroscopy was performed on [AlCp*]₄ across –80 – 25 °C temperature range in toluene with only one resonance observed at $\delta_{\text{Al}} = -81$ ppm (fwhm = 140 Hz) as reported in the original paper by Schnöckel *et al.*¹⁰ Increasing the temperature to 30 °C resulted in the formation of a second resonance at $\delta_{\text{Al}} = -149$ ppm which was assigned to the monomeric AlCp* complex (Scheme

4.1).¹⁷ The ratio of the resonances at $\delta_{\text{Al}} = -81$ and -149 ppm altered depending on the temperature and was reversible up to $100\text{ }^{\circ}\text{C}$ whereupon decomposition of the Al(I) complex occurred to give metallic aluminium, Cp^*H and unidentified organometallic Al(III) compounds. The incredibly shielded chemical shifts of “AlCp*” was attributed to the ring current induced by the Cp^* ligand being against the direction of the external magnetic field. It was pertinent to mention that Roesky *et al.* also performed variable temperature solution state ^{27}Al NMR spectroscopy on a sample of $[\text{AlCp}^*]_4$ however only detected one resonance at $\delta_{\text{Al}} = -78$ ppm and no resonance was observed around $\delta_{\text{Al}} = -149$ ppm even upon heating beyond $30\text{ }^{\circ}\text{C}$.¹⁸



Scheme 4.1 Equilibrium between tetrameric and monomeric form of “AlCp*”

Nevertheless, the equilibrium behaviour of the chemical shifts in ^{27}Al NMR spectra of “AlCp*” gave confidence that the two resonances corresponded to the tetrameric and monomeric form of “AlCp*” and therefore at low temperatures “AlCp*” existed as a tetramer in solution. In addition, in 1995 Schnöckel *et al.* reported the gas phase electron diffraction data of AlCp* and the data pointed towards a monomeric unit.¹⁹ It is worth mentioning that the findings acknowledged that the data collected also contained other products besides the AlCp* unit and therefore refinement to the data had to be made with assumption of known decomposition products at the elevated temperature this gas-phase data had to be collected at. However, formation and existence of the monomeric AlCp* at temperatures beyond $30\text{ }^{\circ}\text{C}$ was indirectly corroborated by this gas-phase electron diffraction data.

The use of ^{27}Al NMR spectroscopy to distinguish between tetrameric and monomeric forms of Al(I) compounds in solution was further investigated by Schnöckel *et al.*¹⁷ ^{27}Al NMR spectra data of a small number of aluminium(I) compounds were acquired and compared to values obtained from simulated ^{27}Al NMR spectra of both monomeric and tetrameric aluminium(I) compounds from computational calculations (Table 4.1).

AlCp* and $[\text{AlCp}^*]_4$ gave comparable chemical shifts from the experimental and calculated ^{27}Al NMR spectroscopy. However, the massive divergence between the experimental and calculated chemical shift of AlCl was attributed to solvent effects. The experimentally acquired chemical shift was measured in toluene and Et_2O at $-80\text{ }^{\circ}\text{C}$ ²⁰ (non-coordinating solvents like pentane resulted in disproportionation) and therefore the chemical shift of $\delta_{\text{Al}} = 15$ ppm represented monomeric AlCl stabilised by Et_2O . On the other hand, the chemical shift acquired through calculations were simulated

in gaseous state and therefore unrepresentative of the experimental conditions. Repeating the calculation with the addition of two and three dimethyl ether molecules resulted in a calculated chemical shift closer to the experimental value ($\delta_{\text{Al}} = -50$ and -65 ppm respectively). The computed values were still not great and asked the question why solvent effects were not in play for AlCp^* where the values are comparable from computation and experimental results.

More experimental data was required in order to improve upon the computational method however the use of computational technique to complement the experimental result was helpful in deciphering chemical shifts of these aluminium(I) compounds and providing, at minimum, qualitative information concerning solvent effects on chemical shifts.

Complex	T / °C	Solvent	Fwhm / Hz	Chemical Shift	
				Experimental	Calculated
AlCl	-80	Tol/ Et_2O (3:1)	1800	+15 ²⁰	+150
$[\text{AlCp}^*]_4$	-80	Tol	1225	-81	-85
	25	Tol	140	-81 ¹⁰	
AlCp^*	100	Tol	100	-150	-143
$[\text{AlCp}]_4$	-80	Tol/ Et_2O (3:1)	1250	-111	-105

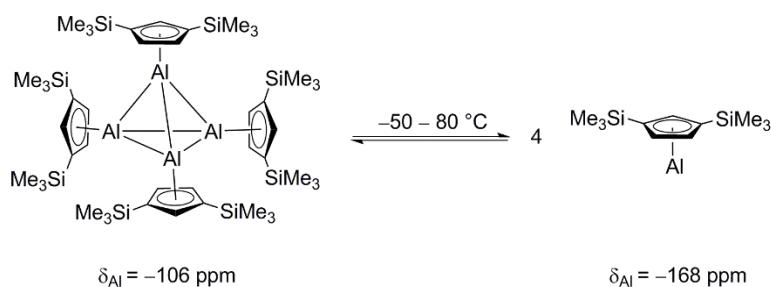
²⁷Al NMR (70.4 MHz, external standard $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. Calculations at SCF and MP2 theory level

Table 4.1 Experimental and Calculated ²⁷Al NMR spectra chemical shifts of Al(I) compounds

A follow up paper was published by Schnöckel *et al.* reporting solution state ²⁷Al NMR spectroscopic data on a number of new aluminium(I) compounds¹⁴ however characterisation by X-ray crystallography was not achieved on these new compounds except for complex **4.6**, $[(\text{Cp}^*\text{Al})_3\text{AlN}(\text{SiMe}_3)_2]$ (Figure 4.1). This complex exhibited a resonance at $\delta_{\text{Al}} = -62$ ppm (fwhm = 300 Hz) which was assigned to the Cp^*Al site however no resonance was reported for the $\text{AlN}(\text{SiMe}_3)_2$ site which was attributed to the large fwhm and the lower intensity due to the presence of only one $\text{AlN}(\text{SiMe}_3)_2$ site compared to three Cp^*Al sites in complex **4.6** and therefore the signal was most likely lost in the baseline of the spectrum. The observed resonance at $\delta_{\text{Al}} = -62$ ppm was also assigned to the tetramer as no free AlCp^* was observed by ²⁷Al NMR spectroscopy, even upon heating to 80 °C no dissociation of the tetramer to the monomeric form was observed.

Only one other aluminium(I) compound synthesised, but not fully characterised, demonstrated two resonances at low temperatures (-50 °C) for the tetrameric form $[(\text{C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Al}]_4$ ($\delta_{\text{Al}} = -106$ ppm, fwhm = 520 Hz) and monomeric form $(\text{C}_5\text{H}_3(\text{SiMe}_3)_2)\text{Al}$ ($\delta_{\text{Al}} = -168$ ppm, fwhm = 950 Hz) of the complex (Scheme 4.2). The data from this complex in combination with the data from AlCp^* complex

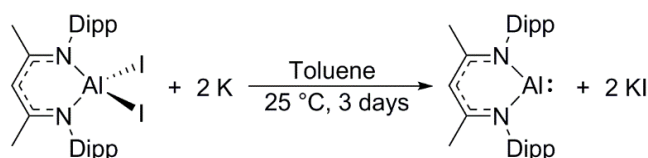
led to the conclusion that ^{27}Al NMR spectroscopy can be used to determine whether these aluminium(I) compounds existed as tetramers or monomers in solution with the more upfield resonance assigned to the monomer relative to the tetramer. This was explained as the result of the tetramerisation process and therefore formation of Al–Al bonds which in turn weakened the π -interaction between the aluminium and the aryl ligand and therefore less shielding was observed by the aluminium centre which resulted in the more downfield resonance of the tetrameric aluminium(I) compound relative to the monomer.



Scheme 4.2 Equilibrium between tetrameric and monomeric form of " $(\text{C}_5\text{H}_3(\text{SiMe}_3)_2)\text{AlI}$ "

4.1.2 Molecular Aluminium(I) Compounds

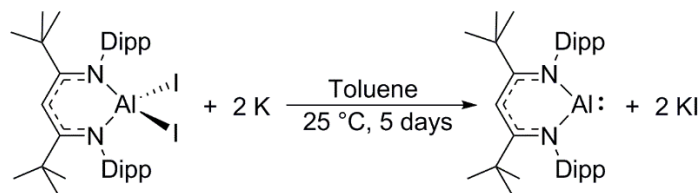
In 2000, Roesky *et al.* reported the synthesis and full characterisation, including X-ray crystallography data, of the first stable monomeric aluminium(I) compound at standard conditions (Scheme 4.3).⁴ The thermodynamic instability of a monomeric aluminium(I) complex was remedied by the use of a bulky β -diketiminato ligand with 2,6-diisopropylphenyl groups on the nitrogen atom of the ligand to stabilise the aluminium centre and prevent dimerization of the monomer. DFT calculations were performed agreeing with the unusual 2 coordinate aluminium site with the presence of a nonbonded lone pair of electrons characterised as having singlet carbene-like character. The Lewis base character of the $^{\text{Dipp}}\text{BDIAL(I)}$ complex was further demonstrated by the reactivity this complex displayed in reactions.^{3,21–23} The solid state structure of $^{\text{Dipp}}\text{BDIAL(I)}$ confirmed this compound was monomeric however no ^1H DOSY (diffusion ordered spectroscopy) measurements were performed to confirm $^{\text{Dipp}}\text{BDIAL(I)}$ was still monomeric in solution. In addition, Roesky *et al.* noted that no solution state ^{27}Al NMR spectroscopy resonance was detected for this compound to confirm the 2 coordinate geometry around the aluminium site rather than the 3 coordinate geometry if dimerization occurred.



Scheme 4.3 Synthesis of $^{\text{Dipp}}\text{BDIAL(I)}$

Comparison of the spectroscopic data of $^{Dipp}BDIAI(I)$ and $^{Dipp}BDIAI(H)_2$ unambiguously confirmed the differences between these two product.²⁴ In 2015 Arnold *et al.* published a paper on using polarised K-edge X-ray absorption near edge structure (XANES) spectroscopy in order to probe whether there was a difference in the electronic structure in a series of β -diketiminato stabilised aluminium(III) complexes and $^{Dipp}BDIAI(I)$ complex.²⁵ The conclusion from the Al K-edge XANES spectroscopy was that both $^{Dipp}BDIAI(H)_2$ and $^{Dipp}BDIAI(I)$ exhibit nearly identical energies for the transitions to final excited state orbitals of similar compositions and symmetries. However, the presence of an additional low-energy feature in the XANES spectrum of $^{Dipp}BDIAI(I)$, which was not there for $^{Dipp}BDIAI(H)_2$, was attributed to a transition into a low lying unoccupied p -orbital on aluminium which was orthogonal to the β -diketiminato ligand. This low lying unoccupied p -orbital was indicative of the coordination number around aluminium *i.e.* not trivalent and therefore the difference in the oxidation state of the aluminium compound was arguably *not* the cause of this additional feature in the XANES spectrum but a consequence of the coordination number of aluminium.

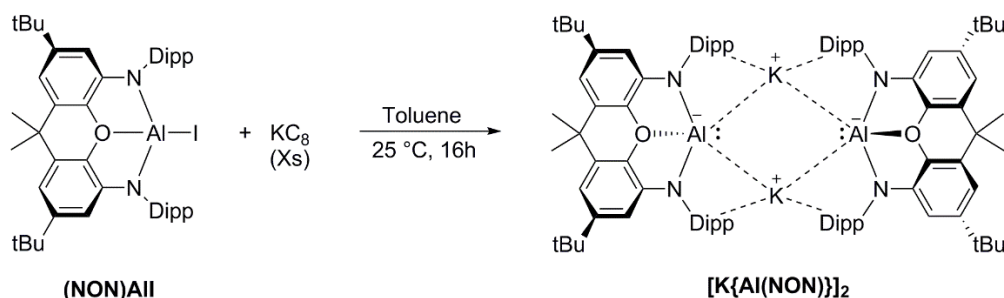
Cui *et al.* also synthesised and characterised by multinuclear NMR, IR and UV-vis spectroscopy, and X-ray crystallography the analogue of $^{Dipp}BDIAI(I)$ whereby the groups on the backbone of the β -diketiminato ligand were *tert*butyl groups instead of methyl groups (Scheme 4.4).²⁶ No ^{27}Al NMR spectroscopy data was reported.



Scheme 4.4 Synthesis of analogue of $^{Dipp}BDIAI(I)$

In 2018, Aldridge *et al.* reported the synthesis and full characterisation of a dimeric nucleophilic alumanyl anion, $[K\{Al(NON)\}]_2$ ($NON = 4,5$ -bis(2,6-diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene) (Scheme 4.5).²⁷ X-ray crystallography of $[K\{Al(NON)\}]_2$ revealed a centrosymmetric dimer with two $[Al(NON)]^-$ units stabilised by potassium-arene contacts. The measured Al---Al distance by X-ray diffraction was long at 6.627(1) Å. Independent synthesis of the dihydrogen aluminate, $[K\{H_2Al(NON)\}]_2$ and comparison of spectroscopic data (including X-ray crystallographic data) with $[K\{Al(NON)\}]_2$ confirmed unambiguously the formation of $[K\{Al(NON)\}]_2$ as a ‘true’ aluminium(I) compound. ^1H DOSY measurements were undertaken with the hydrodynamic radius determined as 9.7 Å which was larger than the monomeric $(NON)AlI$ starting precursor (7.7 Å) and indicated $[K\{H_2Al(NON)\}]_2$ remained dimeric in solution. The nucleophilic

behaviour of $[\text{K}\{\text{H}_2\text{Al}(\text{NON})\}]_2$ was demonstrated by its reactivity with electrophilic substrates to form new aluminium–element bonds.²⁷



Scheme 4.5 Synthesis of an anionic aluminium(I) nucleophile, $[\text{K}\{\text{Al}(\text{NON})\}]_2$

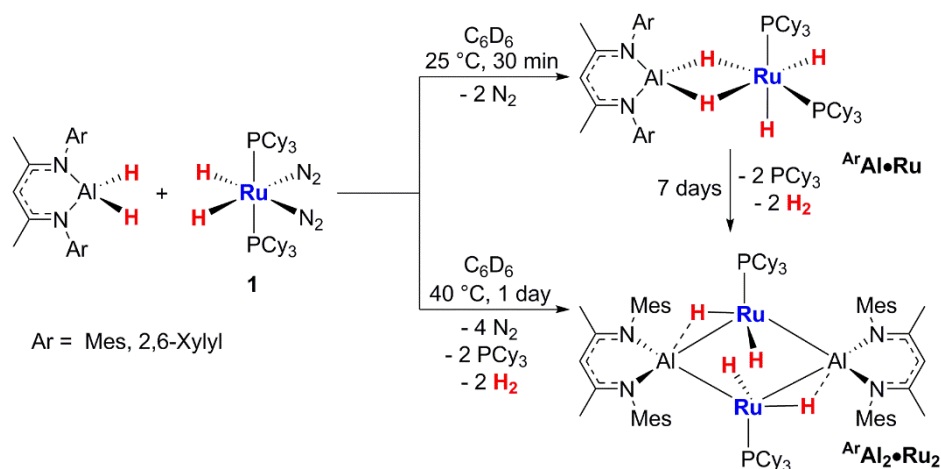
Chapter 3 explored the formation of new **M•Ru** heterobimetallic hydride complexes ($\text{M} = \text{Al}, \text{Zn}, \text{Mg}$) from the reaction of **1** with main group monohydride complexes. In this chapter the author of this thesis will present the formation of a number of new **Al•Ru** heterobimetallic complexes derived from the reaction of **1** with β -diketiminate stabilised aluminium dihydride reagents and the application of solid state ^{27}Al NMR spectroscopy to help characterise these new complexes.

4.2 RESULTS AND DISCUSSIONS

4.2.1 Synthesis and characterisation

4.2.1.1 Ar = Mes or 2,6-Xylyl

The reactions of 1 equivalent of $[\text{Ru}(\text{H})_2(\text{N}_2)_2(\text{PCy}_3)_2]$ (**1**) with 1 equivalent of $^{\text{Ar}}\text{BDIAL}(\text{H})_2$ ($\text{Ar} = \text{Mes}, 2,6\text{-Xylyl}$) proceeded cleanly at 25 °C to generate the aluminium ruthenium heterobimetallic hydride complexes $^{\text{Ar}}\text{Al}\bullet\text{Ru}$ ($\text{Ar} = \text{Mes}, 2,6\text{-Xylyl}$) (Scheme 4.6).



Scheme 4.6 Preparation of $^{\text{Ar}}\text{Al}\bullet\text{Ru}$ heterobimetallic hydride complexes ($\text{Ar} = \text{Mes}, 2,6\text{-Xylyl}$)

The ^{Mes}Al•Ru complex was characterised by an indicative broad peak at $\delta_H = -11.77$ ppm (fwhm = 1021 Hz) for all 4 hydrides in the ¹H NMR spectrum at 293 K (Figure 4.2). Upon cooling the reaction to 273 K the broad peak decoalesced into 2 broad peaks at $\delta_H = -9.69$ (fwhm = 77 Hz) and -13.49 (fwhm = 101 Hz) ppm for the terminal and bridging hydrides respectively. A second fluxional process was further resolved at 213 K with 4 broad peaks observed at $\delta_H = -9.32$ (H_t, fwhm = 84 Hz), -9.91 (H_t, fwhm = 77 Hz), -12.45 (H_μ, fwhm = 217 Hz) and -13.86 (H_μ, fwhm = 198 Hz) ppm in the ¹H NMR spectrum for the 4 magnetically inequivalent hydrides. Long T₁(min) = 247 ms were measured for the hydride resonances at 313 K at 400 MHz (all 4 hydrides were recorded as one resonance at this temperature) indicative of classical hydride behaviour.²⁸ At 293 K only one resonance was observed in ³¹P{¹H} NMR at $\delta_P = 69.9$ ppm which upon cooling the reaction to 213 K decoalesced into 2 broad peaks observed at $\delta_P = 70.7$ and 66.2 ppm.

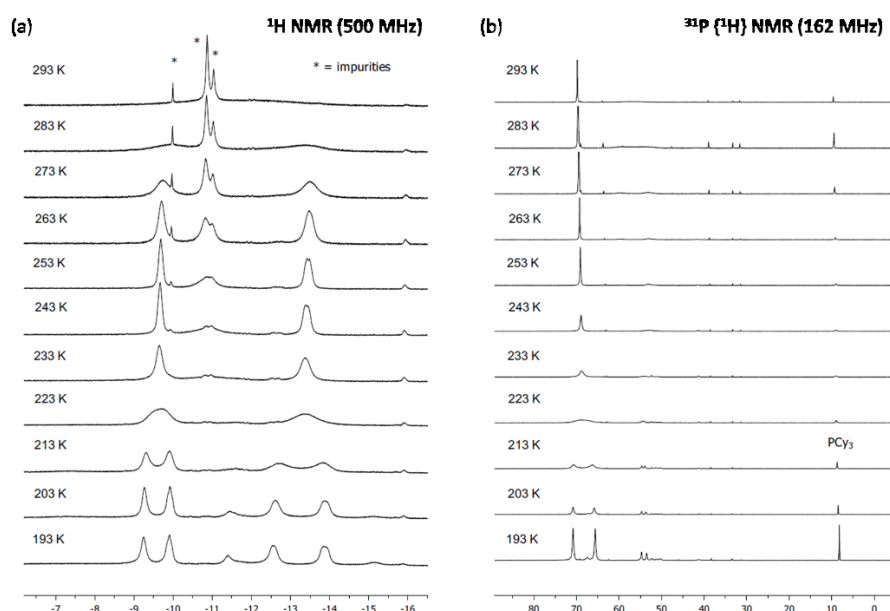


Figure 4.2 VT NMR spectra of ^{Mes}Al•Ru. Only Ru–H region shown in ¹H NMR spectrum for clarity

The low temperature NMR spectroscopy data agreed with the assignment of the structure of ^{Mes}Al•Ru whereby the PCy₃ ligands were in a *cis*-arrangement around the ruthenium, one in the axial and one in the equatorial position to give magnetically inequivalent phosphines. The activation parameters for the exchange process between the axial and equatorial PCy₃ ligands was calculated to give $\Delta G^\ddagger_{298K} = 37 \pm 11$ kJ mol⁻¹, $\Delta H^\ddagger = 45 \pm 4.8$ kJ mol⁻¹ and $\Delta S^\ddagger = +26 \pm 30$ J K⁻¹ mol⁻¹ and similar values were calculated based on the ¹H NMR spectra data. The positive entropy of activation (with the caveat of the error associated with the Eyring analysis) potentially suggests that the mechanism of exchange was through a dissociative process whereby the heterobimetallic complex could break apart to give just the aluminium and ruthenium fragments to allow for the rearrangement of the ligands around the ruthenium centre *via* C₃ rotation (Figure 4.3). No coupling between the hydrides and phosphines

were observed due to the proximity of the hydrides to the quadrupolar aluminium nuclei and the facile exchange process of the hydrides within the NMR spectroscopy acquisition time. Similar multinuclear NMR spectroscopy characterisation was observed for the analogous reaction of **1** with ^{2,6-Xylyl}BDIAL(H)₂ however no variable temperature NMR spectroscopy was performed on this complex.

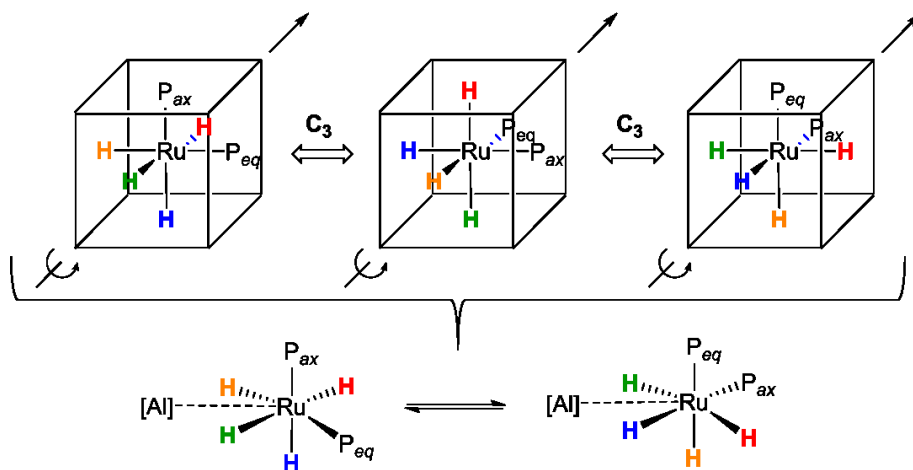


Figure 4.3 Proposed dissociative mechanism for the exchange of ligands around ruthenium in ^{Mes}Al•Ru complex

Isolation of these ^{Ar}Al•Ru (Ar = Mes, 2,6-Xylyl) heterobimetallic hydride complexes was unsuccessful as dimerization, at 25 °C within 1 day, occurred to form ^{Ar}Al₂•Ru₂ with the concomitant loss of PCy₃ and dihydrogen (Scheme 4.6). The dimeric ^{Ar}Al₂•Ru₂ complexes can be synthesised directly from the starting materials and heating the reaction at 40 °C for 1 day. ^{Mes}Al₂•Ru₂ was characterised by a diagnostic broad singlet at $\delta_{\text{H}} = -14.20$ ppm (fwhm = 47 Hz) at 25 °C in the ¹H NMR spectrum which integrated to 6H relative to the backbone of the β -diketiminato ligand ($\delta_{\text{H}} = 5.28$ ppm, 2H). A phosphorous decoupled ¹H NMR spectrum was not acquired for this reaction as this could have sharpened the broad singlet for the hydride resonance of ^{Mes}Al₂•Ru₂ to give more confidence in the integration value of the resonance. Low temperature ¹H NMR spectroscopy failed to decoalesce the hydride resonance however T₁ measurements were taken across a 193 – 293 K temperature range to give a T₁(min) time of 221 ms which was indicative of classical hydride behaviour.²⁸

Following the dimerization reaction by ³¹P{¹H} NMR spectroscopy, free PCy₃ ligand was observed ($\delta_{\text{P}} = 9.8$ ppm) along with reduction in intensity of the peak for ^{Mes}Al•Ru ($\delta_{\text{P}} = 69.9$ ppm) and growth of a new sharp singlet at $\delta_{\text{P}} = 74.0$ ppm assigned to the ^{Mes}Al₂•Ru₂ complex. Again, no decoalescence of this phosphorous signal was observed for this dimeric species. The variable temperature NMR spectroscopy data would point to either a symmetrical molecule with no magnetically inequivalent PCy₃ ligands or hydrides or that the temperature was not low enough to resolve the fluxional exchange process of the ligands around the metal centres. The IR spectrum of ^{Mes}Al₂•Ru₂ showed a weak broad absorbance between 1610 – 1654 cm⁻¹ which corresponded with the range known

for Ru–H–Al motifs (CHAPTER 3). Only $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectroscopy data were obtained for $^{2,6\text{-Xylyl}}\text{Al}_2\cdot\text{Ru}_2$ dimeric complex showing similar characteristics to $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$. Subjecting $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$ to an atmosphere of H_2 (1 atm) and excess PCy_3 failed to reform the monomeric $^{\text{Mes}}\text{Al}\cdot\text{Ru}$ complex which suggested the dimeric form of this complex was a thermodynamic sink.

$^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$ crystallised upon storage in concentrated hydrocarbon solutions under an N_2 atmosphere at $-35\text{ }^\circ\text{C}$ (Figure 4.4). The X-ray data showed that only two PCy_3 ligands remained ligated in $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$, in agreement with the NMR spectroscopic data, however the hydrides could not be located from the Fourier transform map. Measured Ru–Al bond lengths were similar to previous reported aluminium ruthenium heterobimetallic complexes (*vide supra*). The Al_2Ru_2 core was best described as a distorted parallelogram with small deviation away from planarity of the Al_2Ru_2 core ($< 10^\circ$). Similar dimeric $\text{Al}_2\cdot\text{Rh}_2$ ²⁹ and $\text{Al}_2\cdot\text{Pd}_2$ ³⁰ compounds have previously been isolated by our group with the X-ray crystallographic data obtained and the hydrides located above and below the plane of core for $\text{Al}_2\cdot\text{Rh}_2$ case and the hydrides located on the same plane as the core for $\text{Al}_2\cdot\text{Pd}_2$ case. In both the rhodium and palladium dimeric species the structures were described as Rh(III)/Al(I) and Pd(II)/Al(I) systems.

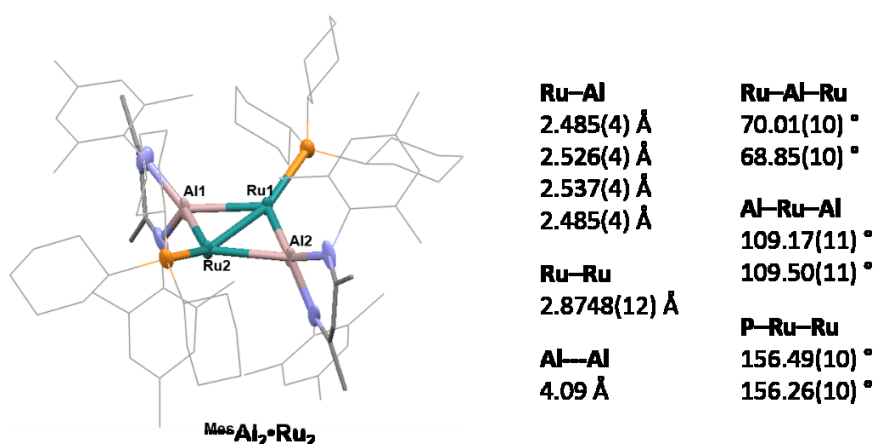


Figure 4.4 Crystal structure of $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$ with selected bond lengths (Å) and bond angles (°). Hydrogens omitted for clarity

Instead, computational analysis was performed from the X-ray crystallographic data of $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$ to reproduce the position of the heavy atoms in comparison to the X-ray crystallographic data but also to assign the number and location of hydrides in this complex. In addition, computational analysis was also performed on the monomeric $^{\text{Mes}}\text{Al}\cdot\text{Ru}$ complex with the starting coordinates obtained from modified X-ray crystallographic data of the ruthenium aluminium oxide of this complex which was formed from contamination with oxygen during synthesis. (Figure A 64).

All computational studies in this chapter (excluding the solid state NMR simulations) were conducted using Gaussian 09. The $\omega\text{B97x-D}$ functional was employed.³¹ Ru and Al centres were

described with Stuttgart RECPs and associated basis sets,^{32–34} the 6-31++G(d,3pd) basis set was used for all hydrides, 6-31G* basis set was used to describe C and H atoms and 6-311+G* basis set was used to describe N and P atoms.^{35–37}

An optimised minimum was located for the monomeric ^{Mes}Al•Ru complex with the ruthenium found in a distorted octahedral environment and the phosphine ligands *cis* to each other, one in the equatorial and one in the axial position – in agreement with the NMR spectroscopy data (Figure 4.5).

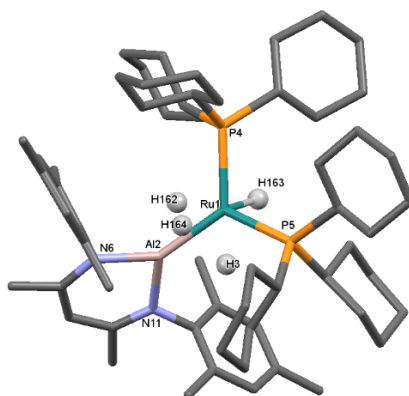


Figure 4.5 Optimised structure of ^{Mes}Al•Ru from DFT calculations

Similar to the heterobimetallic hydride complexes synthesised in chapter 3, the aluminium fragment deviated away from the equatorial plane of the ruthenium fragment ($P_{ax}-Ru-Al = 124.0^\circ$). The bond lengths calculated suggested there were two bridging hydride Al–H–Ru (Figure 4.5, H162, H164) motifs and two terminal Ru–H (Figure 4.5, H163, H3) hydrides in ^{Mes}Al•Ru however the calculated WBI (Figure 4.6) showed some residual but sizeable interaction between the terminal Ru–H_{ax} with the aluminium centre which suggested potentially three μ^2 -(H) interactions within this complex. The Ru–Al bond length was calculated to be 2.27 Å which was within the sum of single bond radii³⁸ and the WBI was calculated to be 0.19 which again was small but significant.

Only a bond critical path between ruthenium and aluminium was located by QTAIM calculations and no *bcps* were located between any of the hydrides and the aluminium centre. The overall picture the DFT and QTAIM analysis suggested a heterobimetallic complex whereby the two metal centres were coordinated through two main bridging hydride interactions, but smaller interactions existed between the two metal centres as well. In addition, the NPA charge showed a highly negative [Ru(H)₄][−] fragment stabilised by the highly positive [Al(Mes)]⁺ fragment.

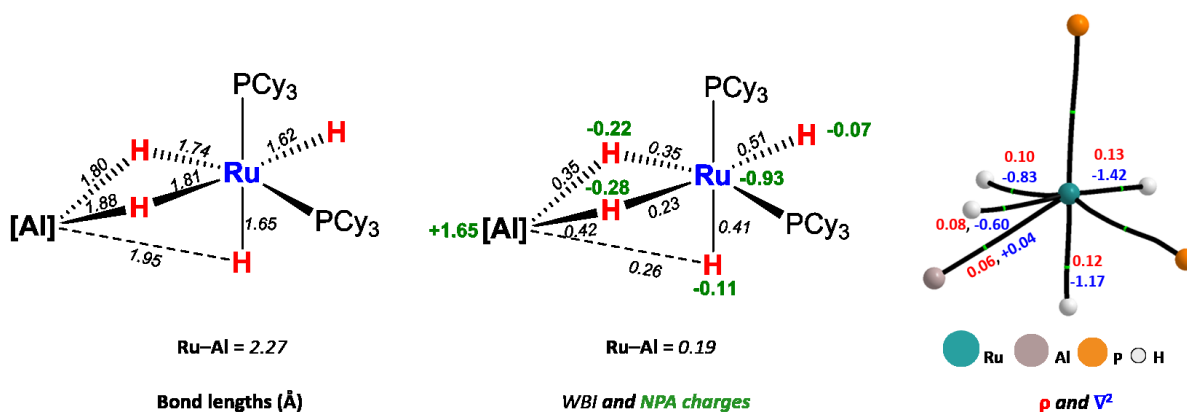


Figure 4.6 Calculated bond lengths of $\text{MesAl}\cdot\text{Ru}$ (left) and analysis by NBO (middle) and QTAIM (right) calculations

Using the covalent bond classification in combination with the experimental and computational analysis indicated that the aluminium centre in $\text{MesAl}\cdot\text{Ru}$ complex is best described as an $\text{Al}(\text{LX}_3)$ system and ruthenium as a $\text{Ru}(\text{L}_4\text{X}_2)$ system where the ‘true’ two bridging hydrides are acting as 3centre,2electron interactions but both $\sigma(\text{Al-H})$ bond are donating into the empty Ru d-orbitals of the correct symmetry. This is in contrast to the heterobimetallic complexes discussed in chapter 3 whereby one of the $\sigma(\text{M-H})$ orbital of the bridging hydride is donating into the empty Ru d-orbital complemented by donation of the $\sigma(\text{Ru-H})$ orbital of the other bridging hydride into the main group empty p- or s-orbital (Figure 4.7).^{24,39}

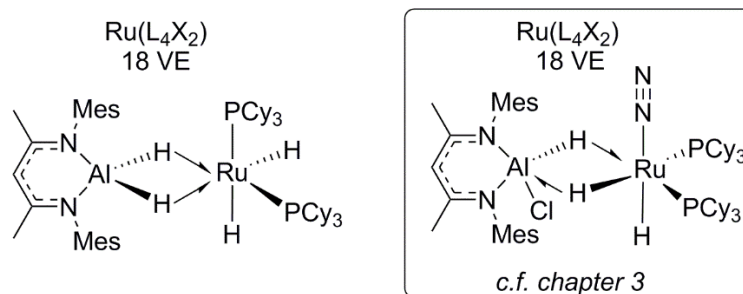


Figure 4.7 Comparison of the CBC and half-arrow notation of the ruthenium aluminium heterobimetallic complexes

The starting coordinates for the heavy atoms in the dimeric $\text{MesAl}_2\cdot\text{Ru}_2$ was obtained from the X-ray crystal data however, the hydrides were not located from the Fourier transform map. Instead, the only indication of the number of hydrides present in the dimer was from the ^1H NMR spectrum of $\text{MesAl}_2\cdot\text{Ru}_2$. Nevertheless, using the integration values of the ^1H NMR spectrum may not be accurate due to line shape broadening affects associated with fluxional process of the hydrides and coupling to quadrupolar ^{27}Al nuclei. The resonance of the hydride integrated closest to 6 hydrides for both the

$\text{MesAl}_2\text{Ru}_2$ and $^{2,6\text{-Xyly}}\text{Al}_2\text{Ru}_2$ dimer however complexes containing 4, 6 and 8 hydrides were optimised by DFT calculations and the SCF energies were compared to the starting materials, the kinetic product $\text{MesAl}\cdot\text{Ru}$ and to each other (Figure 4.8). Due to the large computational resource required for these large dimers, the optimised minima of the dimers were not confirmed by frequency calculation. The optimised geometries around the heavier atoms (Al_2Ru_2 core) were also compared to the X-ray crystallographic data (Figure 4.4).

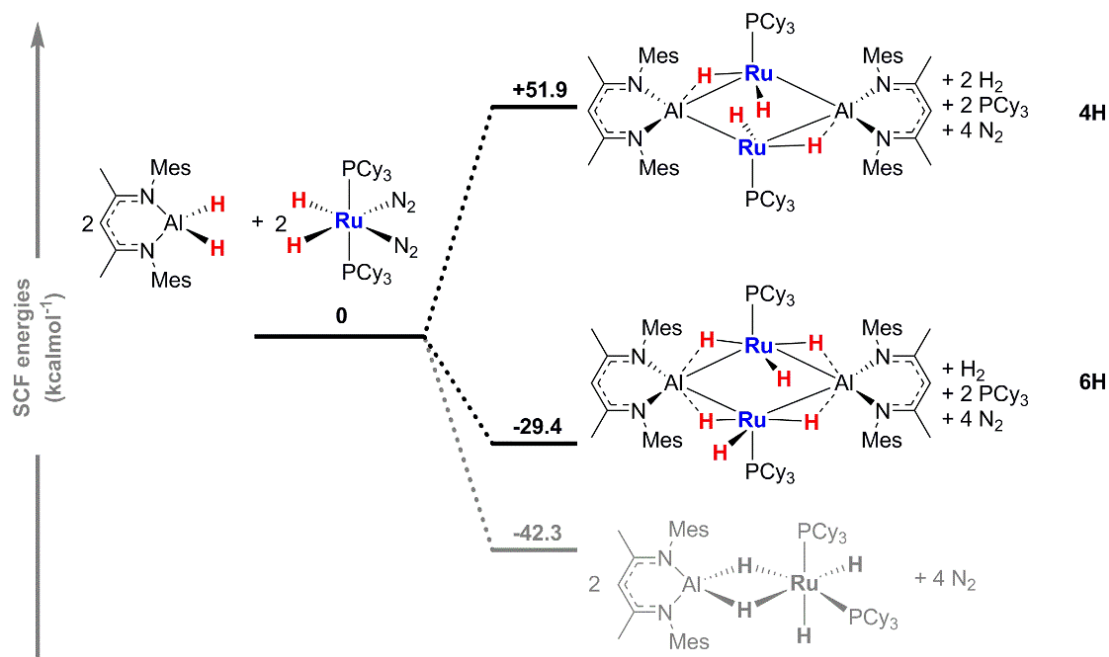


Figure 4.8 SCF energy values from gas phase DFT calculations of MesBDIAI(H)_2 , 1 , $\text{MesAl}\cdot\text{Ru}$ and $\text{MesAl}_2\cdot\text{Ru}_2$ with different number of hydrides

The optimised structure of $\text{MesAl}_2\cdot\text{Ru}_2$ containing 4H resulted in unfavourable calculated thermodynamics with the product being more unfavourable in energy than the starting materials, 1 and MesBDIAI(H)_2 , by $\Delta G^\circ = 51.9 \text{ kcal mol}^{-1}$. The optimised structure contained two terminal Ru–H hydrides in an *anti*-arrangement with respect to the plane of the ring and two bridging hydrides found within the same plane of the Al_2Ru_2 ring (Figure 4.9). Alternative starting coordinates whereby all 4 hydrides were planar to the Al_2Ru_2 core and on all 4 sides of the ring optimised to the same structure. In addition, the *anti*-arrangement of the hydrides was also found to be more favourable than the *syn*-arrangement of the hydrides by $\Delta\Delta G^\circ = 1.0 \text{ kcal mol}^{-1}$. However, the calculated geometries of the *anti*-4H of $\text{MesAl}_2\cdot\text{Ru}_2$ were in good agreement with the X-ray crystallographic bond lengths and angles (Table 4.2).

On the other hand, the calculated energy of the optimised structure of $\text{MesAl}_2\cdot\text{Ru}_2$ containing 6H was more favourable than the starting materials however less favourable than the kinetic product $\text{MesAl}\cdot\text{Ru}$ ($\Delta\Delta G^\circ = 13.8 \text{ kcal mol}^{-1}$). The optimised structure contained 4 bridging hydrides on each side

of the Al_2Ru_2 ring which were slightly above and below the plane of the ring in an alternating fashion with the remaining 2 terminal Ru–H hydrides calculated to be *syn* to each other. The calculated geometries for $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$ containing 6H were less comparable to the X-ray data obtained for the dimer (Table 4.2). In addition, $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$ containing 6H would result in a paramagnetic compound whereby the extreme bonding modes of the aluminium and ruthenium centre were described as Al(I)/Ru(III) system or Al(III)/Ru(I) system making the 6H configuration of $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$ unlikely.

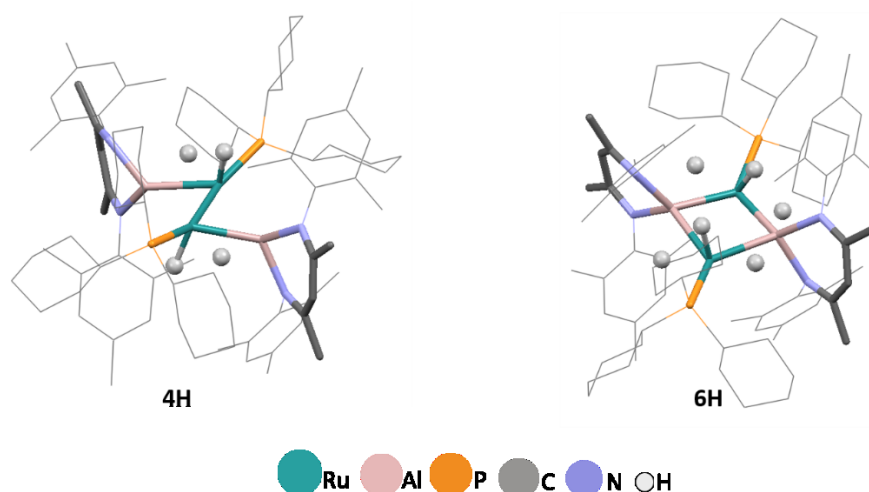


Figure 4.9 Optimised structures of $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$ containing 4H and 6H respectively by DFT.

The calculated energy for the optimised structure $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$ with 8H was incomplete however the SCF energies of the last 29 points of the optimisation calculation were similar in energy (difference of $0.01 \text{ kcal mol}^{-1}$) and therefore the true optimised structure was anticipated to sit around these local points. Furthermore, the geometry of the Al_2Ru_2 core and hydrides did not change significantly during these last 29 points and only the methyl groups on the mesitylene group rearranged slightly. The energy of the last local point towards the theoretical optimised minima was calculated to be $\Delta G^\circ = -11.7 \text{ kcal mol}^{-1}$ which was lower than the starting materials but not the kinetic product. The geometry of the Al_2Ru_2 core did not match closely with the bond length and bond angles acquired from the X-ray structure of $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$ (Table 4.2). Lengthening of the Al–Ru bonds lengths was observed in the 8H structure, most likely to accommodate the large number of hydrides around the core which resulted in the structure dissociation towards two moieties (Figure 4.10). In addition, the formation of the analogous $\text{Al}_2\cdot\text{Rh}_2$ ²⁹ and $\text{Al}_2\cdot\text{Pd}_2$ ³⁰ required partial dehydrogenation of the aluminium hydride reagent and therefore would suggest 8H configuration of $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$ seemed unlikely.

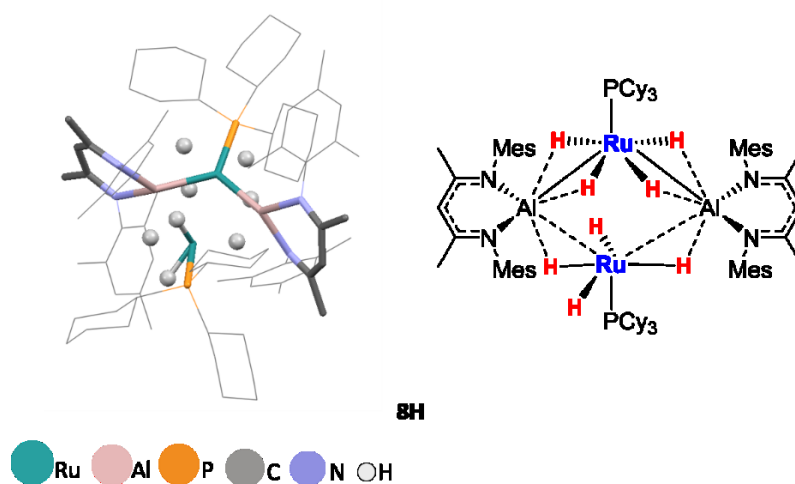


Figure 4.10. (Left) Calculated structure of $\text{MesAl}_2\text{Ru}_2$ containing 8H by DFT, not optimised. (Right) Line drawing of $\text{MesAl}_2\text{Ru}_2$ containing 8H

The combination of experimental and computational analysis of $\text{MesAl}_2\text{Ru}_2$ indicated the dimer contained 4 hydrides around the Al_2Ru_2 core. The geometries from the optimised structure of 4H matched closest with the geometries obtained from the X-ray structure of $\text{MesAl}_2\text{Ru}_2$. The diamagnetic nature of this complex ruled out a system containing 6 hydrides and furthermore, a system containing 8 hydrides resulted in the partial dissociation of the dimer. The unfavourable energy calculated for the 4H structure prevented absolute confidence in the assignment of $\text{MesAl}_2\text{Ru}_2$ however this could be attributed to the computational method used for this large structure not being a good model. Nevertheless, based on the current data, $\text{MesAl}_2\text{Ru}_2$ was assigned as a dimeric complex containing 4 hydrides.

		X-ray	DFT		
			4H	6H	8H ^[a]
Bond Lengths / Å	Ru–Al	2.485(4)	2.41	2.40	2.34
		2.485(4)	2.43	2.40	2.32
		2.526(4)	2.66	2.50	2.65
		2.537(4)	2.75	2.50	2.77
	Ru–P	2.295(3)	2.30	2.35	2.32
		2.295(3)	2.33	2.35	2.34
	Ru–Ru	2.8748(12)	2.61	2.61	3.10
	Bond Angles / °	Ru–Al–Ru	68.85(10)	60.3	81.4
70.01(10)			61.5	81.4	74.4
Al–Ru–Al		109.17(11)	119.5	97.5	93.4
		109.50(11)	115.4	97.5	115.4
P–Ru–Ru		156.49(10)	159.2	174.5	177.4
		156.26(10)	161.6	174.5	159.0

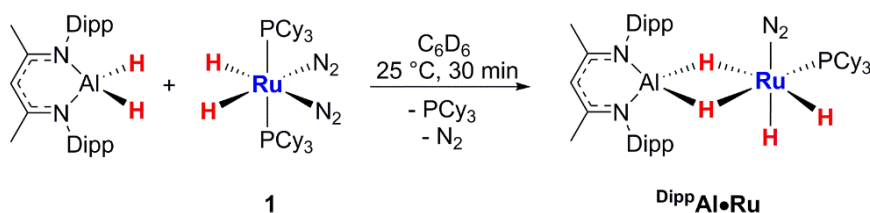
^[a]Structure not optimised

^[a]Structure not optimised

Table 4.2. Comparison of measured and calculated bond lengths and angles of ^{Mes}Al₂•Ru₂

4.2.1.2 Ar = Dipp

The reaction of 1 equivalent of [Ru(H)₂(N₂)₂(PCy₃)₂] (**1**) with 1 equivalent of ^{Dipp}BDIAL(H)₂ proceeded cleanly at 25 °C to generate the ^{Dipp}Al•Ru heterobimetallic hydride complex (Scheme 4.7). This complex demonstrated 3 resonances for the hydride environments at 25 °C in the ¹H NMR spectrum, δ_H = −9.05 (br s, 2H), −9.73 (d, *J*_{HP} = 41.6 Hz, 1H), −16.11 (d, *J*_{HP} = 15.8 Hz) ppm. At 233 K, the resonance at δ_H = −9.05 ppm was resolved into two peaks at δ_H = −7.83 and −10.49 ppm to overall give 4 resonances for the 4 magnetically inequivalent hydrides in ^{Dipp}Al•Ru. T₁ measurements were taken across the 333 – 193 K range at 400 MHz and the 4 hydride signals exhibited a T₁(min) between 200 – 250 ms which indicated more classical hydride behaviour for all 4 hydrides.²⁸ Following the reaction by ³¹P{¹H} NMR spectroscopy the signal for free PCy₃ was observed as well as one new resonance at δ_P = 73.6 ppm and this new signal exhibited no decoalescence during low temperature NMR spectroscopy experiments. The presence of free PCy₃ in solution suggested ^{Dipp}Al•Ru contained only one PCy₃ ligand and therefore to satisfy the closed shell 18 valence electron configuration around ruthenium another L-type ligand must still be bound – dinitrogen. The presence of a dinitrogen ligand in ^{Dipp}Al•Ru was confirmed by IR spectroscopy with a strong absorbance observed at ν_{N–N} = 2135 cm^{−1} and the corresponding terminal and bridging hydrides stretches observed at ν_{Ru–H} = 1908 and 1872 cm^{−1}.



Scheme 4.7 Preparation of **DippAl•Ru** heterobimetallic hydride complex

The structure of **DippAl•Ru** was ultimately confirmed by X-ray crystallography (Figure 4.11). The ruthenium sat in an octahedral environment however differing to the structure postulated for **ArAl•Ru** (Ar = Mes, 2,6-Xylyl) a dinitrogen ligand was indeed still coordinated to the ruthenium centre with loss of one of the PCy₃ ligands – in agreement with the NMR and IR spectroscopic data. The measured Ru–Al bond length was within the sum of the single bond radii³⁸ and towards the shorter side of known Ru–Al bonds. The measured bridging Ru–H–Al and terminal Ru–H bond lengths were in the expected range as well (*vide supra*).

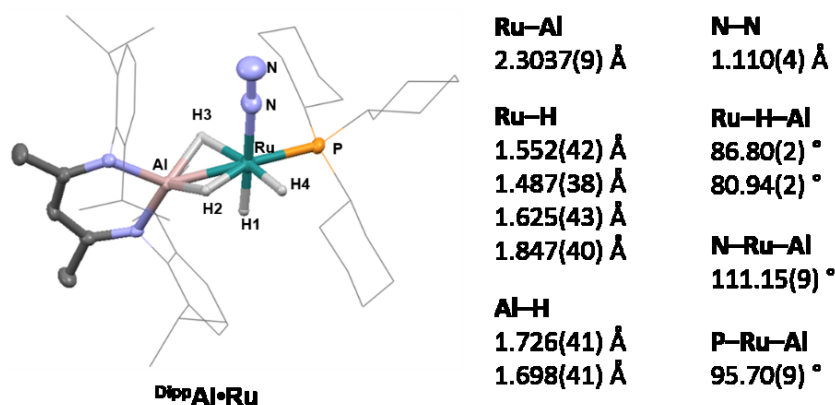


Figure 4.11 Crystal structure of **DippAl•Ru** with selected bond lengths (Å) and bond angles (°). Hydrogens omitted for clarity

Computational analysis was performed on **DippAl•Ru** with the starting coordinates obtained from the X-ray crystallography data. The DFT calculation reproduced the position of the heavy atoms and the calculated bond lengths and bond angles of the hydrides were satisfactory in comparison to the X-ray crystallographic data. DFT confirmed the slightly distorted octahedral configuration of the ruthenium and, again, the slippage of the aluminium fragment away from the axial position (N–Ru–Al; X-ray = 111.5(9) °, DFT = 112.0 °) however the slippage was not as extreme as **MesAl•Ru**. Although the Ru–Al bond length was short, the calculated WBI was small in comparison to the other WBI interactions found within the complex (Figure 4.12). This small covalent interaction was further substantiated by the small ionic contribution calculated from QTAIM methods in the form of the

parameters ρ and ∇^2 . The small ρ and ∇^2 values also indicated that a majority of the electron density resided on the actual atoms and not on the bond between the two atoms in questions. This concentration of electron density on the atoms agreed with the description from the calculated NPA charges of the complex showing a negative $[\text{Ru}(\text{H})_4]^-$ fragment stabilised by the positive $[\text{Al}]^+$ fragment. Applying the same pragmatic identification, the aluminium centre was best described as Al(III) in $\text{DippAl}\cdot\text{Ru}$ with the covalent bond classification²⁴ with respect to aluminium as $\text{Al}(\text{LX}_3)$ and with respect to ruthenium as $\text{Ru}(\text{L}_4\text{X}_2)$.

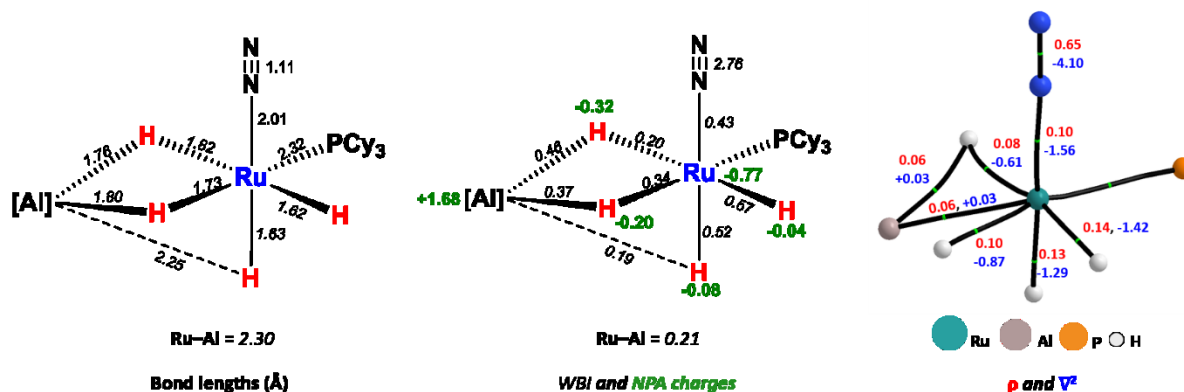
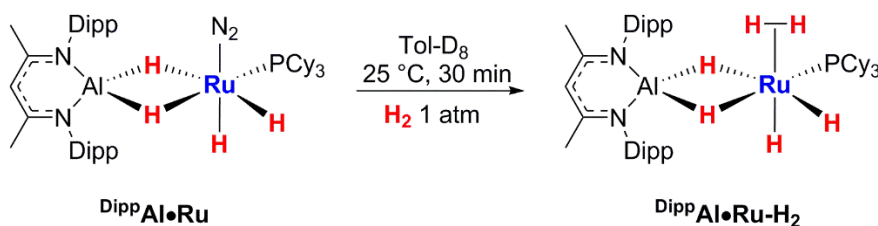


Figure 4.12 Calculated bond lengths of $\text{DippAl}\cdot\text{Ru}$ (left) and analysis by NBO (middle) and QTAIM (right) calculations

Confirmation of the N_2 ligand present in $\text{DippAl}\cdot\text{Ru}$ was further corroborated by placement of $\text{DippAl}\cdot\text{Ru}$ under an atmosphere of H_2 (1 atm) which resulted in formation of $\text{DippAl}\cdot\text{Ru}\cdot\text{H}_2$ (Scheme 4.8). $\text{DippAl}\cdot\text{Ru}\cdot\text{H}_2$ displayed a single broad diagnostic resonance at $\delta_{\text{H}} = -9.67$ ppm (fwhm = 16 Hz) in ^1H NMR spectrum for all 6 hydrides which failed to decoalesce at low temperatures however a $T_1(\text{min})$ of 53 ms was measured indicative of non-classical hydride behaviour.²⁸ The facile fluxional process occurring between all 6 hydrides most likely resulted in a much longer $T_1(\text{min})$ than the true value for the H_2 ligand in $\text{DippAl}\cdot\text{Ru}\cdot\text{H}_2$ as observed for the $\text{M}\cdot\text{Ru}\cdot\text{H}_2$ ($\text{M} = \text{Al}, \text{Zn}, \text{Mg}$) complexes in Chapter 3. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum one resonance was observed at $\delta_{\text{P}} = 81.6$ ppm which again did not decoalesce at lower temperatures.

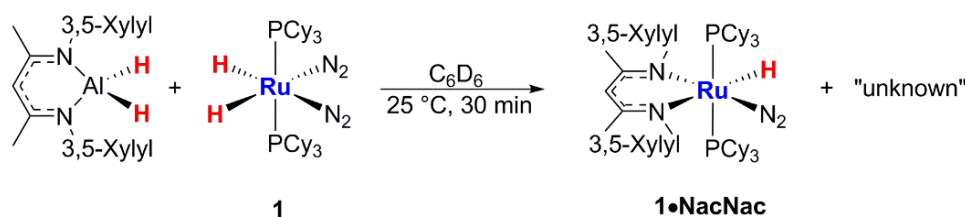


Scheme 4.8 Reactivity of $\text{DippAl}\cdot\text{Ru}$ with H_2

4.2.1.3 Ar = 3,5-Xylyl

The size of the aryl group on the β -diketiminate ligand has a huge effect on the reactivity observed between the reactions of **1** with these aluminium dihydride reagents. The Dipp ligand is incredibly bulky and prevented the dimerization of $^{\text{Dipp}}\text{Al}\cdot\text{Ru}$ differing to the reactivity observed with $^{\text{Ar}}\text{Al}\cdot\text{Ru}$ (Ar = Mes, 2,6-Xylyl) heterobimetallic hydride complexes. Beyond this divergent reactivity, the actual structure of the monomeric $\text{Al}\cdot\text{Ru}$ species also differed around the ruthenium in terms of what ligands were coordinated onto the metal centre. The $^{3,5\text{-Xylyl}}\text{BDIAl(H)}_2$ provides even less steric protection around the aluminium centre compared to the Mes, 2,6-Xylyl and Dipp analogues of the aluminium dihydride.

The reaction of 1 equivalent of $[\text{Ru(H)}_2(\text{N}_2)_2(\text{PCy}_3)_2]$ (**1**) with 1 equivalent of $^{3,5\text{-Xylyl}}\text{BDIAl(H)}_2$ at 25 °C resulted in a mixture of products after 30 minutes. The ^1H NMR spectrum showed multiple signals for the methine proton on the β -diketiminate backbone. The Ru–H region of the ^1H NMR spectrum showed a major broad peak overlapping with other peaks. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, showed presence of free PCy_3 ligand and formation of 2 major resonances found at $\delta_{\text{P}} = 74.0$ and 79.5 ppm. Single crystals suitable for X-ray crystallography were grown from this reaction mixture to reveal the structure of **1**•**NacNac** as a component in the reaction mixture (Scheme 4.9).



Scheme 4.9 Identification of **1**•**NacNac** as a by-product in reaction of **1** with $^{3,5\text{-Xylyl}}\text{BDIAl(H)}_2$

1•**NacNac** was the product from the redistribution of ligands around **1** and the aluminium dihydride. The geometry around ruthenium was distorted octahedral with the β -diketiminate ligand acting as a $\kappa^2\text{-LX}$ ligand (Figure 4.13).²⁴ The N–Ru–N bond angle was strained ($88.28(10)^\circ$) compared to the N–Al–N bond angle from the parent aluminium dihydride compound (DFT: 94.0°) and the dinitrogen bond length was slightly stretched compared to the ruthenium *bis*(dinitrogen) complex **1** (CHAPTER 1). No further spectroscopic data was acquired for **1**•**NacNac** as isolation of this compound away from the mixture was difficult.

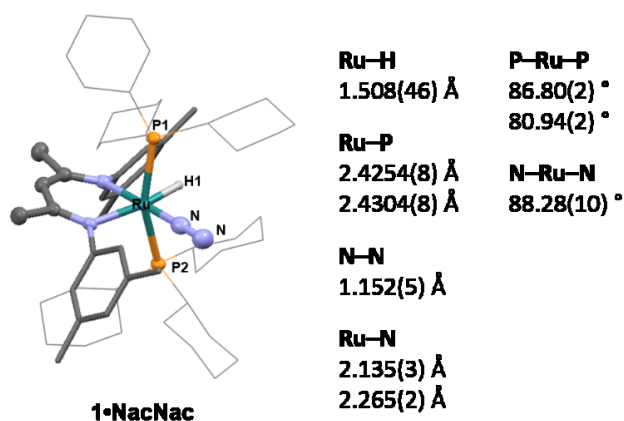


Figure 4.13 Crystal structure of **1•NacNac** with selected bond lengths (Å) and bond angles (°)

The remainder of the unidentified species in the reaction of **1** with ^{3,5-Xylyl}BDIAL(H)₂ was postulated to be a mixture of ruthenium aluminium complexes with multiple metal–metal bonds based on unpublished work in the group from similar reaction but using [Pd(PCy₃)₂] as the transition metal fragment. An analogous reaction between **1** and ^{Ph}BDIAL(H)₂ was also performed with a similar outcome with a number of unidentified products forming in the reaction as analysed by multinuclear NMR spectroscopy.

4.2.2 ²⁷Al MAS NMR spectroscopy

The ²⁷Al MAS NMR spectroscopy data herein have been acquired and analysed by Dr. Nathan Barrow and Dr. Andrew Tatton (Johnson Matthey). Dr. Tom Hooper is thanked for donation of Al₂•Pd₂³⁰ complex and Dr. Clare Bakewell is thanked for donation of ^{Dipp}BDIAL(I)⁴, Al•Norbornene⁴⁰ and Al•Zn⁴¹ complex.

²⁷Al NMR spectroscopy has been used as a tool to assign coordination number of the aluminium centres as well as identifying the number of aluminium environments in a sample, however nothing has been reported on the use of this spectroscopic technique to identify oxidation state of the aluminium centre. One of the obstacles is building a library of unambiguous Al(I) complexes to measure the chemical shift but as to date there is only one neutral monomeric Al(I) complex in the solid state, at standard conditions, published.⁴ A second obstacle of solution state ²⁷Al NMR spectroscopy is the presence of aluminium in the NMR spectrometer probe which will have a large broad signal itself that often masks the signal of the desired sample. Turning to solid state ²⁷Al NMR spectroscopy helps to mitigate the background aluminium signal and, depending on rotor size available, only ~ 10 mg of sample is required for a good signal to noise ratio.

Analysis of the 12 aluminium containing complexes (Figure 4.14) helped to answer additional questions beyond the relationship of the isotropic chemical shift and oxidation state of aluminium: (i)

Are the chemical shifts obtained from solid state and solution state ^{27}Al NMR spectroscopy in agreement? (ii) Can a ^{27}Al NMR spectroscopy chemical shift be obtained for $^{Dipp}\text{BDIAI(I)}$? (iii) Does the aryl group on the β -diketiminato ligand have a bigger effect on chemical shift than the oxidation state of aluminium? And (iv) Does formation of a metal–aluminium bond have a bigger effect on chemical shift than the oxidation state of aluminium?

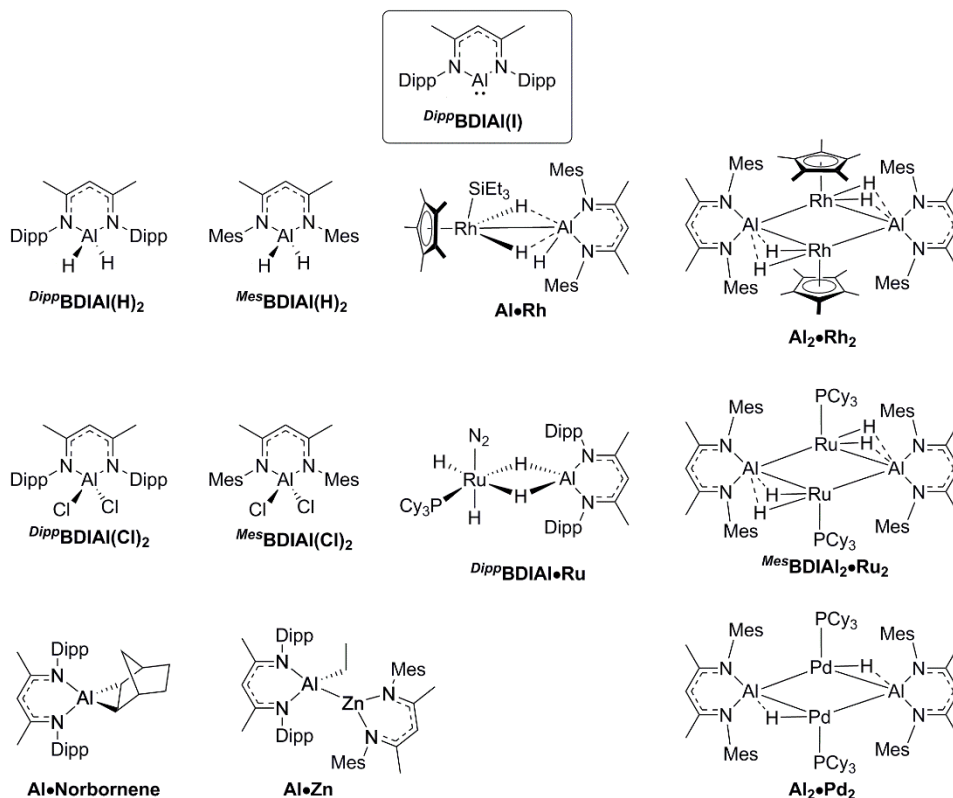


Figure 4.14 Aluminium containing complexes studied with solid state ^{27}Al NMR spectroscopy

Chemical shift values obtained from solution state ^{27}Al NMR spectroscopy reported in literature for $^{Dipp}\text{BDIAI(H)}_2$ ($\delta_{\text{Al}} = 130$ ppm)²⁵, $^{Dipp}\text{BDIAI(Cl)}_2$ ($\delta_{\text{Al}} = 100$ ppm)²⁵ and $\text{Al}\cdot\text{Rh}$ ($\delta_{\text{Al}} = 145$ ppm)²⁹ were compared with isotropic chemical shifts obtained from solid state ^{27}Al NMR spectroscopy acquired in here and the values were in good agreement allowing for confidence in reproducibility of data obtained from two different methods (Figure 4.16). In the original publication by Roesky *et al.*,⁴ the observation of a resonance for $^{Dipp}\text{BDIAI(I)}$ by solution state ^{27}Al NMR spectroscopy failed and this was confirmed by our own solution state ^{27}Al NMR spectroscopic measurement, however repeating the same analysis by solid state ^{27}Al MAS NMR spectroscopic technique yielded a broad isotropic chemical shift of $\delta_{\text{Al}} = 120$ ppm (Figure 4.15 – black line). The same isotropic chemical shift was obtained from 3 independently synthesised samples of $^{Dipp}\text{BDIAI(I)}$. In all 3 samples of the Al(I) complex there were 2 major alumina impurities, one that matched a very disordered γ -alumina phase (6 coordinate alumina, $\delta_{\text{Al}} = 72$ ppm) and another impurity characterised as 4 coordinate alumina which was present in all the

samples in varying amounts. Upon exposure of $^{Dipp}BDIAL(I)$ to air a visible change in colour from orange to colourless was observed and the sample was analysed again by ^{27}Al MAS NMR spectroscopy. The ^{27}Al MAS NMR spectra obtained confirmed the degradation of the Al(I) complex into 6 coordinate alumina paralleled by the loss of the Al(I) resonance. DFT calculations were also performed on $^{Dipp}BDIAL(I)$ to obtain magnetic resonance parameters for the aluminium sites. With these calculated parameters the powder pattern under MAS was computed in pNMRsim software (Figure 4.15 – red line). The downfield signal of this $^{Dipp}BDIAL(I)$ compound was unexpected as literature precedence would have indicated a more upfield resonance (Table 4.1) however it is worth noting that one of the lowest chemical shifts measured for an Al(III) compound was reported by Schnöckel *et al.* in 1993 for $[AlCp^*_2]^+$. This cationic aluminium compound displayed a chemical shift of $\delta_{Al} = -115$ ppm, fwhm = 50 Hz and was also characterised by X-ray crystallography.⁴² This data would suggest that absolute values of the isotropic chemical shift of aluminium may not be a good indicator of oxidation state of aluminium and furthermore Schnöckel *et al.* commented that the type ligand ligated on aluminium has a large effect on the chemical shift observed as well as the coordination number around aluminium (coordination number of 10 in the case of $[AlCp^*_2]^+$).¹⁷

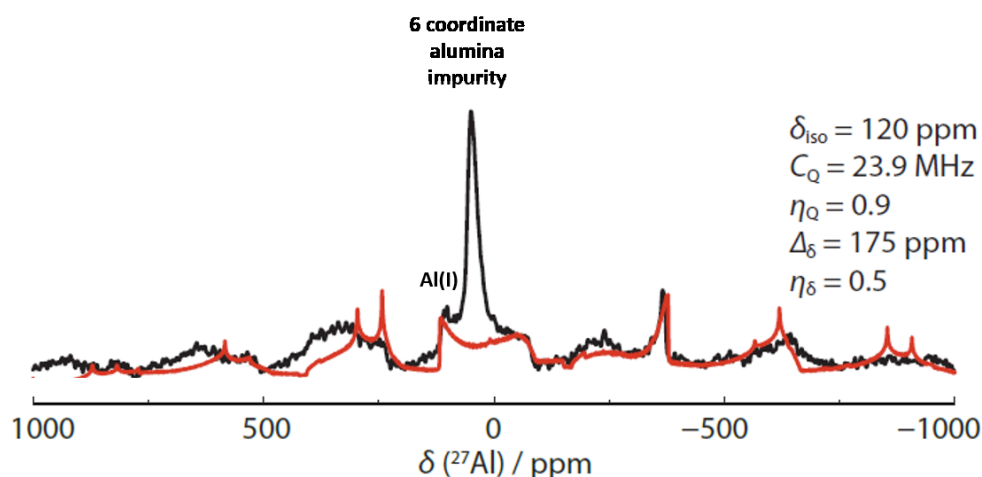


Figure 4.15 Solid state ^{27}Al MAS NMR spectrum of $^{Dipp}BDIAL(I)$ complex (black line) overlaid with pNMRsim calculations from DFT parameters (red line)

Analysis of the δ_{iso} of $^{Dipp}BDIAL(I)$ and $^{Dipp}BDIAL(H)_2$ provided a direct comparison of the difference in the oxidation state of aluminium whilst ensuring the aluminium was ligated by the same β -diketiminato ligand. The isotropic chemical shift of $^{Dipp}BDIAL(H)_2$ was measured as $\delta_{Al} = 130$ ppm (Figure 4.16). This represented a small $\Delta\delta_{iso}$ of 10 ppm from the isotropic chemical shift of $^{Dipp}BDIAL(I)$ ($\delta_{Al} = 120$ ppm). Instead, comparison of isotropic chemical shift of $^{Dipp}BDIAL(H)_2$ and $^{Mes}BDIAL(H)_2$ ($\delta_{Al} = 100$ ppm) provided a greater $\Delta\delta_{iso}$ of 30 ppm. These results further substantiated that the oxidation state of the aluminium centre may not affect the aluminium chemical shift of the complex as much as other factors.

Plotting the aluminium δ_{iso} of the remaining aluminium complexes on a scale restated that the oxidation state has minimal effect on the aluminium δ_{iso} (Figure 4.16). For example, β -diketiminato aluminium(III) complexes were found both further downfield and upfield relative to the resonance for *Dipp*BDIAL(I). The most downfield δ_{iso} measured was for the $\text{Al}_2\cdot\text{Pd}_2$ complex ($\delta_{\text{Al}} = 230$ ppm) whereby the aluminium centres were postulated to be in the +1 oxidation state. Instead, the information ascertained from the chemical shift of $\text{Al}_2\cdot\text{Pd}_2$ could be interpreted that the aluminium sites in this complex was in a 4 coordinate environment and therefore this would suggest weak interactions between the hydride and the aluminium consistent with the assignment of an Al(I) centre in this dimeric compound.

The quadrupolar coupling constant (C_Q) was also measured from the solid state ^{27}Al MAS NMR spectra of the 12 compounds (Figure 4.17). The C_Q is an indicator of the electronic asymmetry around the aluminium site. Low C_Q value indicates a more electronically spherical aluminium site and high C_Q values indicates a more planar arrangement of bonds. The C_Q value is therefore a measurement based on the direct effect the surrounding ligands have on the aluminium site and therefore, in theory, should provide an indirect correlation to the oxidation state of the aluminium centre. Plotting the C_Q values of the 12 aluminium complexes on a scale displayed a better trend between the C_Q values with the oxidation state of the aluminium site than the isotropic chemical shift and oxidation state of the aluminium site however the trend was not faultless.

*Dipp*BDIAL(I) had the highest C_Q value of 23.9 Hz, indicative of the high asymmetry of the aluminium site. This asymmetry made sense for *Dipp*BDIAL(I) whereby aluminium was described as Al(LX) system under the covalent bond classification²⁴ with the lone pair occupying one of the *sp*-hybridised orbital. For the β -diketiminato stabilised aluminium(III) complexes the covalent bond classification was Al(LX₃) and these complexes exhibited lower C_Q values on the scale (Figure 4.17). Furthermore, different aryl group on the β -diketiminato ligand (*Dipp* versus *Mes*) had low impact on the difference in C_Q values of similar aluminium complexes. Nevertheless, the C_Q metric was a better indication of coordination number and type of ligand (X, L or Z-type) around the aluminium site and not the oxidation state of aluminium. For example, the dimeric $\text{Al}_2\cdot\text{Rh}_2$ complex (postulated to be an Al(I) site) had a lower C_Q value of 5.8 Hz than its monomeric form $\text{Al}\cdot\text{Rh}$ (postulated to be an Al(III) site) which had a C_Q value of 9.2 Hz.

^{27}Al MAS NMR spectroscopy was a useful tool in assigning the isotropic chemical shifts of these aluminium compounds, especially the elusive chemical shift of *Dipp*BDIAL(I), however it was not useful to assign the oxidation state of the aluminium centre. Nevertheless, the combined data from other spectroscopic techniques and computational analysis can aid in interpreting the parameters obtained from ^{27}Al MAS NMR spectroscopy to understand the intricate bonding description of these more complicated aluminium heterobimetallic complexes.

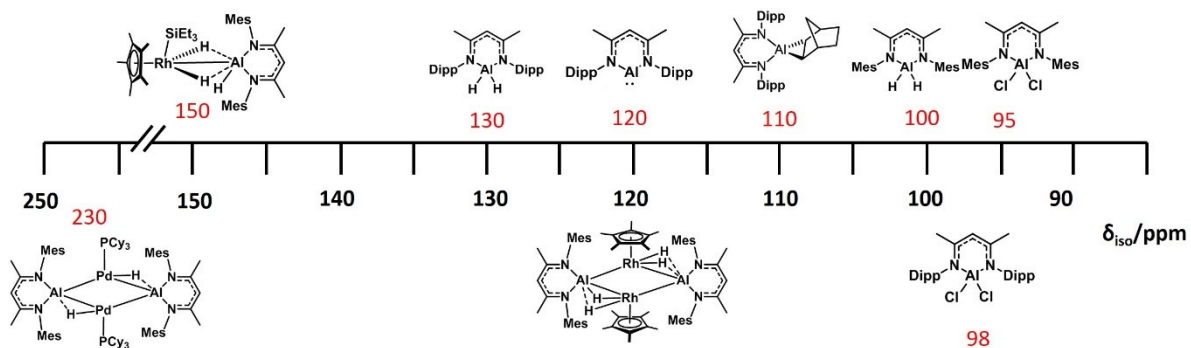


Figure 4.16 Solid state ^{27}Al NMR spectroscopy δ_{iso} chemical shifts of aluminium containing molecules

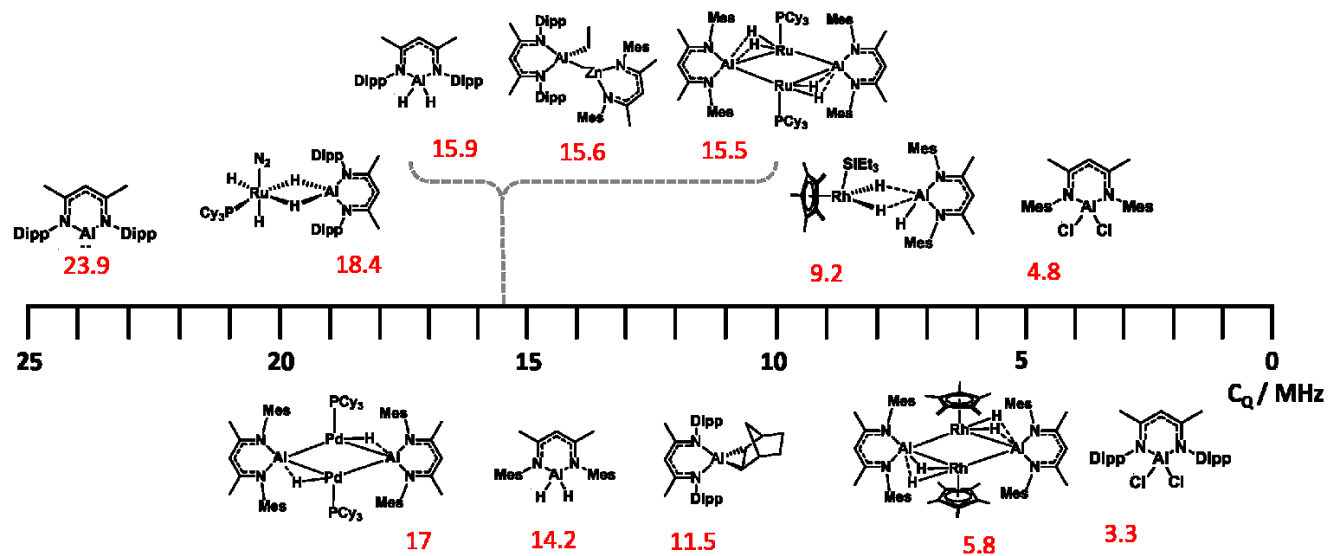


Figure 4.17 Solid state ^{27}Al NMR spectroscopy C_q values of aluminium containing molecules

4.3 CONCLUSION

The synthesis and characterisation of a number of new Al•Ru complexes from the reaction of **1** with β -diketiminate stabilised aluminium dihydride reagents was reported. Different reactivity was demonstrated which was dependent on the size of the aryl groups connected to the nitrogen of the β -diketiminate ligand and therefore the proximity of the aryl groups to the aluminium centre. Formation of a kinetic and thermodynamic heterobimetallic product was observed when the aryl group was Mes or 2,6-Xylyl however when the aryl group was larger (Dipp) only one product was observed. The formation of just $^{Dipp}Al\bullet Ru$ was attributed to the Dipp groups surrounding the coordination sphere of aluminium and preventing dimerization of the complex. When the aryl group was smaller *i.e.* Ph or 3,5-Xylyl the products formed were not stable and underwent additional reactivity to form ligand redistribution ruthenium complex (**1•NacNac**) and unidentified products postulated as aggregates from the catenation of Ru–Ru or Al–Al bonds.

Solid state ^{27}Al MAS NMR spectroscopy was performed on a number of aluminium compounds to determine if there was a correlation between the oxidation state of aluminium and the isotropic chemical shift it exhibited. As with previous studies by Schnöckel *et al.*^{14,17} it would seem other factors beyond oxidation state of aluminium play a much more important role in affecting the aluminium chemical shift of the compound, namely coordination number and the type of ligand on the aluminium site. Nevertheless, a resonance was observed for $^{Dipp}BDIAI(I)$ in the ^{27}Al MAS NMR spectrum ($\delta_{Al} = 120$ ppm) showing the utility of solid state NMR compared to solution state for ^{27}Al NMR spectroscopy in certain situations.

4.4 FUTURE WORK

DFT calculations have proven to be an invaluable tool to complement experimental data. With this in mind, the inability to locate an optimised minimum for $^{Mes}Al_2\bullet Ru_2$ complex has limited the ability to probe the bonding within this dimer or provide a satisfactory answer as to how many hydrides were in this complex. The starting coordinates of $^{Mes}Al_2\bullet Ru_2$ have been modelled on its own X-ray crystallographic data as well as modified coordinates based on the X-ray crystallographic data of the $Al_2\bullet Pd_2$ and $Al_2\bullet Rh_2$ systems to no success. It may be the method employed was not suitable for these large dimers and therefore more in-depth research is required into the computational methods to locate an optimised minimum for $^{Mes}Al_2\bullet Ru_2$.

A potential alternative route to figuring out the number of hydrides within $^{Mes}Al_2\bullet Ru_2$ complex would be to react this dimer with a known amount of a hydrogen acceptor, *i.e.* 3,3-dimethylbut-1-ene, and working out the equivalents of the alkane formed to work out the the number of hydrogen atoms transferred from the dimer to the alkene.

In addition to experimental data, our group have used NPA charges as a means to probe the oxidation state of aluminium by analysing if there is a significant change in the NPA charge of aluminium in a reaction whereby the aluminium was postulated to go from +1 (less electropositive) $\rightarrow$ +3 (more electropositive) or *vice versa* from starting material to product.^{30,40} Therefore, the NPA charge was used more as a comparative metric than an absolute value metric. Comparison of the NPA charges for the parent aluminium hydrides (^{Mes}BDIAL(H)₂ = 1.45 and ^{Dipp}BDIAL(H)₂ = 1.47) with the respective ^{Mes}Al•Ru (1.65) and ^{Dipp}Al•Ru (1.68) heterobimetallic hydride complexes showed very little change in the NPA charge which indicated the aluminium does not undergo any reduction during this reaction and would be in agreement with the conclusion from analysing the experimental and computation data (*vide supra*). Therefore, performing NBO calculations on ^{Mes}Al₂•Ru₂, whereby the aluminium was postulated to be an Al(I), would provide more evidence in using NPA charges as a means to scrutinise the oxidation state of the aluminium if the values indicated a significant change from the starting parent aluminium hydride to the dimer – although this would be after the prerequisite of locating an optimised minima for ^{Mes}Al₂•Ru₂.

4.5 REFERENCES

- 1 S. Aldridge, in *The Group 13 Metals Aluminium, Gallium, Indium and Thallium: Chemical Patterns and Peculiarities*, Wiley, 2011, pp. 76–98.
- 2 H. Schnöckel, *Zeitschrift für Naturforsch. B*, 1976, **31**, 1291–1292.
- 3 H. W. Roesky and S. S. Kumar, *Chem. Commun.*, 2005, 4027–4038.
- 4 C. Cui, H. W. Roesky, H. G. Schmidt, M. Noltemeyer, H. Hao and F. Cimpoesu, *Angew. Chemie Int. Ed.*, 2000, **39**, 4274–4276.
- 5 T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fettinger, G. J. Long and P. P. Power, *Science (80-.)*, 2005, **310**, 844–847.
- 6 S. Green, C. Jones and A. Stasch, *Science (80-.)*, 2007, **318**, 1754–1758.
- 7 I. Resa, E. Carmona, E. Gutierrez-Puebla and A. Monge, *Science (80-.)*, 2004, **305**, 1136–1138.
- 8 P. J. Durrant and B. Durrant, in *Introduction To Advanced Inorganic Chemistry*, Longman, 1962, p. 532.
- 9 C. Dohmeier, D. Loos and H. Schnöckel, *Angew. Chemie Int. Ed.*, 1996, **35**, 129–149.
- 10 C. Dohmeier, C. Robl, M. Tacke and H. Schnöckel, *Angew. Chemie Int. Ed. i*, 1991, **30**, 564–565.
- 11 A. Ecker and H. Schnöckel, *Zeitschrift für Anorg. und Allg. Chemie*, 1996, **622**, 149–152.
- 12 C. Schnitter, H. W. Roesky, C. Röpken, R. Herbst-Irmer, H.-G. Schmidt and M. Noltemeyer, *Angew. Chemie Int. Ed.*, 1998, **37**, 1952–1955.
- 13 A. Purath, C. Dohmeier, A. Ecker, H. Schnöckel, K. Amelunxen, T. Passler and N. Wiberg, *Organometallics*, 1998, **17**, 1894–1896.
- 14 H. Sitzmann, M. F. Lappert, C. Dohmeier, C. Üffing and H. Schnöckel, *J. Organomet. Chem.*, 1998, **561**, 203–208.
- 15 A. Purath and H. Schnöckel, *J. Organomet. Chem.*, 1999, **579**, 373–375.
- 16 M. Schiefer, N. D. Reddy, H. W. Roesky and D. Vidovic, *Organometallics*, 2003, **22**, 3637–3638.
- 17 J. Gauss, U. Schneider, R. Ahlrichs, C. Dohmeier and H. Schnöckel, *J. Am. Chem. Soc.*, 1993, **115**, 2402–2408.
- 18 S. Schulz, H. W. Roesky, H. J. Koch, G. M. Sheldrick, D. Stalke and A. Kuhn, *Angew. Chemie Int. Ed. English*, 1993, **32**, 1729–1731.
- 19 A. Haaland, K. G. Martinsen, S. A. Shlykov, H. V. Volden, C. Dohmeier and H. Schnöckel, *Organometallics*, 1995, **14**, 3116–3119.
- 20 M. Tacke and H. Schnöckel, *Inorg. Chem.*, 1989, **28**, 2895–2896.
- 21 S. Nagendran and H. W. Roesky, *Organometallics*, 2008, **27**, 457–492.
- 22 T. Chu, I. Korobkov and G. I. Nikonov, *J. Am. Chem. Soc.*, 2014, **136**, 9195–9202.
- 23 M. R. Crimmin, M. J. Butler and A. J. P. White, *Chem. Commun.*, 2015, **51**, 15994–15996.
- 24 M. L. H. Green, *J. Organomet. Chem.*, 1995, **500**, 127–148.
- 25 A. B. Altman, C. D. Pemmaraju, C. Camp, J. Arnold, S. G. Minasian, D. Prendergast, D. K. Shuh and T. Tylliszczak, *J. Am. Chem. Soc.*, 2015, **137**, 10304–10316.
- 26 X. Li, X. Cheng, H. Song and C. Cui, *Organometallics*, 2007, **26**, 1039–1043.
- 27 J. Hicks, P. Vasko, J. M. Goicoechea and S. Aldridge, *Nature*, 2018, **557**, 92–95.
- 28 D. G. Hamilton and R. H. Crabtree, *J. Am. Chem. Soc.*, 1988, **110**, 4126–4133.
- 29 O. Ekkert, A. J. P. White, H. Toms and M. R. Crimmin, *Chem. Sci.*, 2015, **6**, 5617–5622.
- 30 T. Hooper, M. Garçon, A. J. P. White and M. R. Crimmin, *Chem. Sci.*, 2018, **9**, 5435–5440.
- 31 J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615–6620.
- 32 D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123–141.
- 33 A. Bergner, M. Dolg, W. Küchle, H. Stoll and H. Preuß, *Mol. Phys.*, 1993, **80**, 1431–1441.
- 34 J. M. L. Martin and A. Sundermann, *J. Chem. Phys.*, 2001, **114**, 3408–3420.
- 35 W. J. Hehre, K. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261.
- 36 T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294–301.
- 37 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213–222.
- 38 L. Pauling, *J. Am. Chem. Soc.*, 1947, **69**, 542–553.

- 39 J. C. Green, M. L. H. Green and G. Parkin, *Chem. Commun.*, 2012, **48**, 11481–11503.
- 40 C. Bakewell, A. J. P. White and M. R. Crimmin, *Angew. Chemie Int. Ed.*, 2018, **57**, 6638–6642.
- 41 C. Bakewell, B. J. Ward, A. J. P. White and M. R. Crimmin, *Chem. Sci.*, 2018, **9**, 2348–2356.
- 42 C. Dohmeier, H. Schnöckel, U. Schneider, R. Ahlrichs and C. Robl, *Angew. Chemie Int. Ed.*, 1993, **32**, 1655–1657.

5 CHAPTER FIVE – SUPPORTING INFORMATION

5.1 GENERAL

All manipulations were carried out under standard Schlenk-line and glovebox techniques under an inert atmosphere of argon or dinitrogen. An MBraun Labmaster glovebox was employed operating at <0.1ppm O₂ and <0.1ppm H₂O. Solvents were dried over activated alumina from an SPS (solvent purification system) based upon the Grubbs design and degassed before use. Glassware was dried for 12 hours at 120°C prior to use. d₆-Benzene and d₈-toluene were freeze-pump-thaw degassed and stored over 3 Å molecular sieves prior to use.

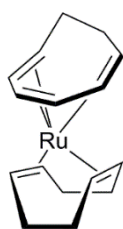
Solution state NMR spectra were obtained on BRUKER 400 or 500 MHz machines by the author, Mr. Pete Haycock or Mr. Dick Shepard. All peaks were referenced against residual solvent peak or an internal standard peak with values quoted in ppm. Solution state NMR spectroscopy data were processed in Topspin or MestReNova. Solid state NMR spectra were acquired at a static magnetic field strength of 9.4 T (400 MHz) on a BRUKER Advance III console by Dr. Nathan Barrow. Solid state NMR spectroscopy data were processed in Topsis 3.1 software. A wide-bore Bruker 2.5 mm BB/1H/19F DVT MAS probe was used and the probe was tuned to 104.27 MHz for ²⁷Al and referenced to YAG at 0.0 ppm. Powdered samples for solid state NMR spectroscopy were packed under argon into zirconia MAS rotors with Vespel caps. Infrared spectra were recorded on a Perkin Elmer FT-IR Paragon 1000 spectrometer with the solid sample impregnated into a KBr disk. Samples for elemental analysis were prepared in a dinitrogen glovebox and elemental analyses were performed by Stephen Boyer at SACS, London Metropolitan University. Crystallographic data was collected using Agilent Xcalibur PX Ultra A or Agilent Xcalibur 3E diffractometers by Dr. Andrew White, and the structures were refined using the Olex2, SHELXTL, SHELX-97, and SHELX-2013 program systems.

5.2 CHAPTER ONE: EXPERIMENTAL

5.2.1 Materials

1,5-Cyclooctadiene was freeze-pump-thaw degassed and stored over 3 Å molecular sieves prior to use. Ethanol was dried over magnesium, distilled and stored over 3 Å molecule sieve prior to use. Chemicals were purchased from Sigma Aldrich, Alfa Aesar and Fluorochem and used without further purification unless stated.

5.2.2 Synthesis

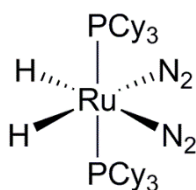


Synthesis of $[Ru(\eta^4\text{-}1,5\text{-COD})(\eta^6\text{-}1,3,5\text{-COT})]$ follows procedure from literature.¹

$RuCl_3 \cdot nH_2O$ (2.0g, 1 mmol) was weighed into an ampoule and dissolved in EtOH (30 mL). 1,5-Cyclooctadiene (40 mL, 1 mmol) and Zn powder (4.0 g, 1 mmol) were added into the ampoule and the reaction mixture was sealed and left to stir at 80 °C. The reaction mixture was allowed to cool to 25 °C then filtered and concentrated *in vacuo* giving a straw brown oily residue. The residue was extracted with *n*-hexane (30 mL) and filtered through Al_2O_3 resulting in a deep yellow solution. The volume of the yellow solution was reduced and left in freezer at -35 °C to give yellow sharp needles as the product (0.98 g, 41 % yield).

^1H NMR (C_6D_6 , 400 MHz, 298 K) δ /ppm: 0.82 (m, 2H), 1.68 (m, 2H), 2.24 (br, 8H), 2.91 (br, 4H), 3.77 (m, 2H), 4.71 (t, $^3J_{HH} = 7.6$ Hz, 2H), 5.19 (dd, $J_{HH} = 5.1$ Hz and 1.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6 , 125 MHz, 298 K) δ /ppm: 31.7 (CH_2), 33.9 (CH_2), 76.5 (CH), 99.2 (CH), 101.4 (CH).

[Literature data:¹ ^1H NMR (C_6D_6 , 60 MHz, 298 K) δ /ppm: 0.90 (m, 2H), 1.64 (m, 2H), 2.22 (m, 8H), 2.92 (m, 4H), 3.79 (m, 2H), 4.78 (m, 2H), 5.22 (dd, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6 , 22.63 MHz, 298 K) δ /ppm: 31.6 (CH_2), 33.0 (CH_2), 70.1(CH), 76.7 (CH), 99.3 (CH), 101.4 (CH)].



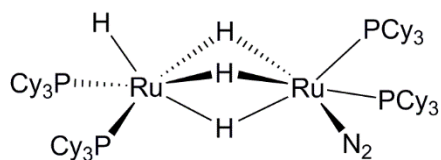
Synthesis of $[Ru(H)_2(N_2)_2(PCy_3)_2]$ (1) follows procedure from literature.² In a

dinitrogen glovebox, $[Ru(\eta^4\text{-}1,5\text{-COD})(\eta^6\text{-}1,3,5\text{-COT})]$ (0.60 g, 1.9 mmol) and PCy_3 (1.0 g, 3.7 mmol) were weighed into an ampoule and dissolved in *n*-hexane (40 mL). The ampoule was removed from the glovebox and hydrogen gas was bubbled through the solution for 3 h resulting in formation of a colourless precipitate $[RuH_2(\eta^2\text{-}H_2)(PCy_3)_2]$. The precipitate was isolated and washed with *n*-hexane (3×10 mL) then recrystallised and dried under an atmosphere of dinitrogen allowing for the conversion of $[Ru(H)_2(\eta^2\text{-}H_2)(PCy_3)_2]$ into the $[Ru(H)_2(N_2)_2(PCy_3)_2]$ complex. The product was collected as pale yellow crystals (0.57 g, 41 % yield).

^1H NMR (C_6D_6 , 400 MHz, 298 K) δ /ppm: -12.96 (br, 2H, RuH), 1.15 – 2.25 (m, 66H, Cy); $^{31}P\{^1H\}$ NMR (C_6D_6 , 162 MHz, 298 K) δ /ppm: 59.3; $^{13}C\{^1H\}$ NMR (C_6D_6 , 100 MHz, 298 K) δ /ppm: 27.2 (m, Cy), 28.2 (m, Cy), 30.4 (m, Cy), 37.2 (t, $^1J_{CP} = 8.9$ Hz, Cy). FT-IR (ν/cm^{-1}) 1918, 1986 ($Ru-H$),

2131, 2163 (N≡N). **Elemental Analysis** calc. for C₃₆H₆₈N₄P₂Ru C, 60.06; H 9.52; N, 7.78 found C, 59.94; H, 9.61; N, 7.67. *T*₁ (Tol-D₈, 193 K, 400 MHz) = 1.08 s (Ru–H).

[Literature data:² ¹H NMR (C₆D₆, 200.13 MHz, 298 K) δ/ppm: –12.83 (t, ²*J*_{HP} = 22 Hz, 2H, RuH); FT-IR (ν/cm^{–1}) 2126, 2163 (N≡N)].

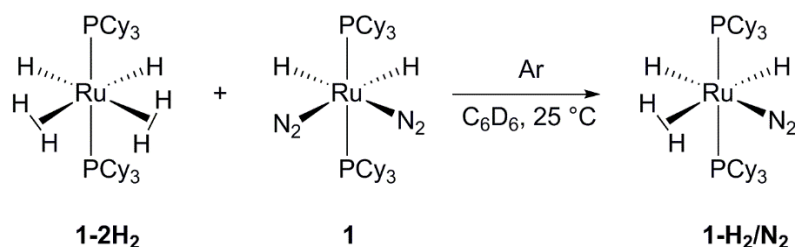


In a dinitrogen glovebox, [*Ru*(η⁴-1,5-COD)(η⁶-1,3,5-COT)] (0.93 g, 3.0 mmol) and PCy₃ (1.65 g, 5.9 mmol) were weighed into an ampoule and dissolved in *n*-hexane (40 mL). The ampoule was removed from the glovebox and hydrogen gas (1.01 bar) was bubbled through the solution for 3 h resulting in formation of a colourless precipitate, [RuH₂(η²-H₂)(PCy₃)₂]. The precipitate was collected and the filtrate transferred into another ampoule. Hydrogen gas (1.01 bar) was bubbled through the filtrate once more for 3 h and the ampoule was sealed up and left for 3 weeks to yield purple crystals. The purple crystals were taken into the dinitrogen glovebox, isolated and recrystallized in minimum hexane giving the dimer, [Ru₂(H)₄(N₂)(PCy₃)₄], as product (0.58 g, 29 % yield).

¹H NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: –12.49 (br, 4H, RuH), 1.14 – 2.68 (m, 132H, Cy); ³¹P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 75.7 (br). FT-IR (ν/cm^{–1}) 1446 (Ru–H), 2084 (N≡N). **Elemental Analysis** calc. for C₇₂H₁₃₆N₂P₄Ru₂ C, 63.78; H 10.11; N, 2.07 found C, 63.89; H, 9.97; N, 1.95).

[Literature data:³ ¹H NMR (Tol-D₈, 250 MHz, 303 K) δ/ppm: –12.4 (s, 4H, RuH); FT-IR (ν/cm^{–1}) 1935 (Ru–H), 2145 (N≡N). **Elemental Analysis** calc. for C₇₂H₁₃₆N₂P₄Ru₂ C, 63.78; H 10.11; N, 2.07; P, 9.1 found C, 62.5; H, 9.9; N, 2.2; P, 8.2.]

5.2.3 Intermediate 1-H₂/N₂



In an argon glovebox, [Ru(H)₂(N₂)₂(PCy₃)₂] (**1**) (8 mg, 0.11 mmol) and [Ru(H)₂(η²-H₂)₂(PCy₃)₂] (**1-2H₂**) (7 mg, 0.10 mmol) were dissolved into C₆D₆ (600 μL) by micropipette and then transferred into a J. Young NMR tube. The reaction was left at 25 °C and monitored by NMR spectroscopy.

In situ NMR data for **1**: ^1H NMR (C_6D_6 , 400 MHz, 298 K) δ/ppm : -12.96 (br, 2H, RuH), 1.15 – 2.25 (m, 66H, Cy); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz, 298 K) δ/ppm : 59.3. T_1 (Tol- D_8 , 193 K, 400 MHz) = 1.08 s (Ru–H).

In situ NMR data for **1-2H₂**: ^1H NMR (C_6D_6 , 400 MHz, 298 K) δ/ppm : -7.84 (br, 6H, RuH); 1.08 – 2.32 (m, 66H, Cy); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz, 298 K) δ/ppm : 76.28. T_1 (Tol- D_8 , 193 K, 400 MHz) = 52.3 ms (Ru–H). [Literature data:⁴ ^1H NMR (Tol- D_8 , 90 MHz, 298 K) δ/ppm : -7.84 (br, 6H, RuH); $^{31}\text{P}\{^1\text{H}\}$ NMR (Tol- D_8 , 60 MHz, 298 K) δ/ppm : 79.2].

In situ NMR data for **1-H₂/N₂**: ^1H NMR (C_6D_6 , 400 MHz, 298 K) δ/ppm : -8.48 (br, 4H, RuH); 1.13 – 2.22 (m, 66H, Cy); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz, 298 K) δ/ppm : 68.78. T_1 (Tol- D_8 , 193 K, 400 MHz) = 217 ms (Ru–H).

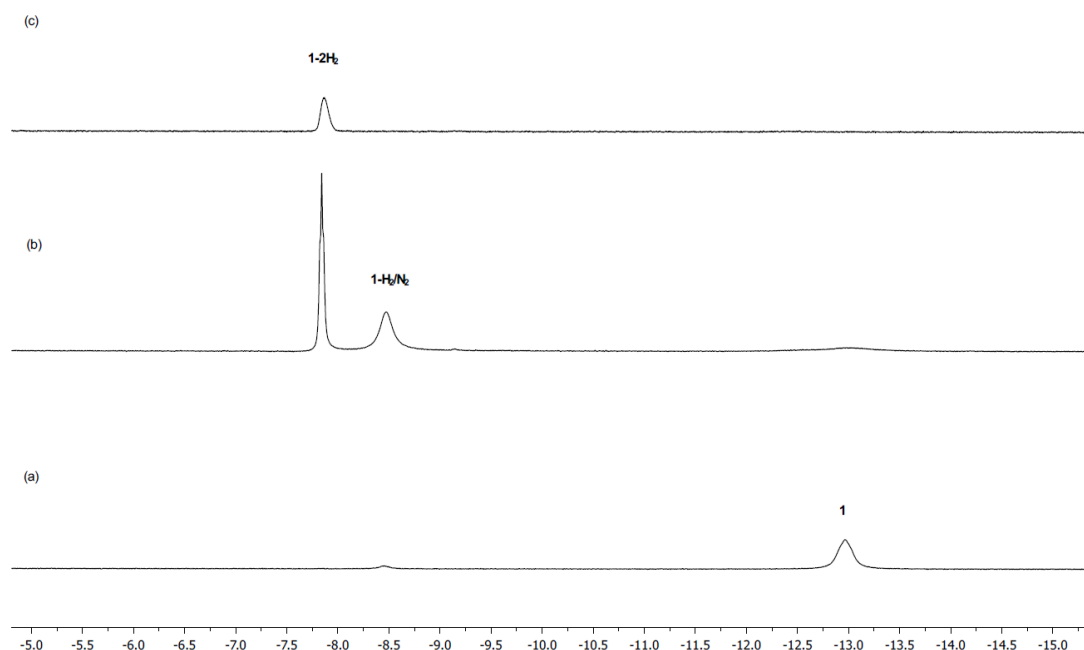


Figure S 5.1. ^1H NMR (C_6D_6 , 400 MHz, 298 K) stack plot of reaction **1** with **1-2H₂**. Only Ru–H region shown for clarity where (a) is a spectrum of **1**, (b) is a mixture of **1** + **1-2H₂** in solution at 25 °C for 30 min and (c) is a spectrum of **1-2H₂**

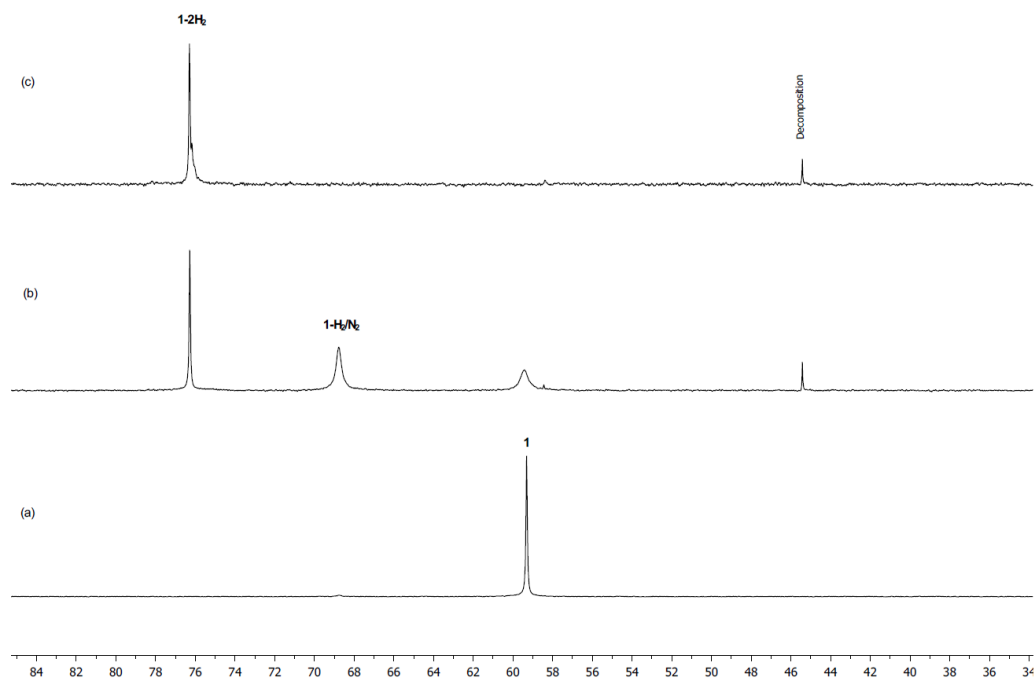


Figure S 5.2. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz, 298 K) stack plot of reaction **1** with **1-2H₂** where (a) is a spectrum of **1**, (b) is a mixture of **1** + **1-2H₂** in solution at 25 °C for 30 min and (c) is a spectrum of **1-2H₂**

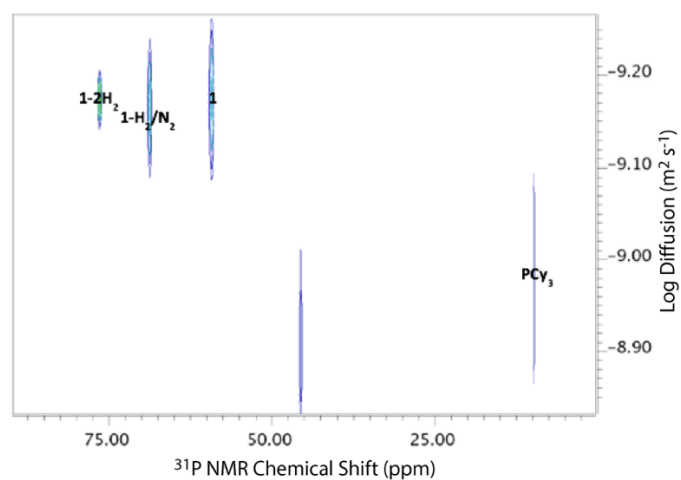


Figure S 5.3. $^{31}\text{P}\{^1\text{H}\}$ DOSY NMR of the mixture of **1-2H₂**, **1** and **1-H₂/N₂**.

Complex	δ / ppm	$D \times 10^{-10}$ ($\text{m}^2 \text{s}^{-1}$)
1	59.3	6.6
1-2H₂	76.2	6.6
1-H₂/N₂	68.7	6.7

5.3 CHAPTER TWO: EXPERIMENTAL

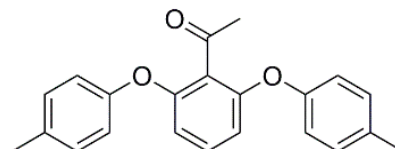
5.3.1 Materials

Solvents were freeze-pump-thaw degassed and stored over 3 Å molecular sieves prior to use. Chemicals were purchased from Sigma Aldrich, Alfa Aesar and Fluorochem and used without further purification unless stated.

5.3.2 Synthesis

Synthesis of 2,6-Bis-p-tolyloxy(phenyl)acetophenone (3b).

2,6-dichloroacetophenone (2.0 g, 11 mmol, 1 equiv), 4-methylphenol (2.8 g, 26 mmol, 2.5 equiv), K₂CO₃ (3.5 g, 25 mmol, 2.5 equiv), (CuOTf)₂•PhH (70 mg, 0.28 mmol, 5.0 mol% Cu) and ethyl acetate

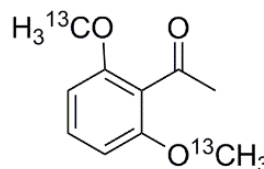


(0.5 mL, 5 mmol, 0.5 equiv) were dissolved in toluene (100 mL). A reflux was set up and the reaction mixture was left to heat at 110 °C under N₂ for 72 h resulting in a brown solution. The solution was cooled to rt then quenched with 9M NaOH (10 mL) and the organic layer was then washed sequentially with water (2 × 20 mL) then brine (2 × 20 mL). The organic layer was dried over MgSO₄, filtered then concentrated *in vacuo* leaving a brown oily residue. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 1/5) giving an off-white yellow solid (R_f = 0.28). The solid was washed with cold hexane and air dried resulting in a colourless powdered solid (1.49 g, 48 %).

¹H NMR (400 MHz, C₆D₆, 298 K) δ/ppm: 2.03 (s, 6H, ArCH₃), 2.46 (s, 3H, COCH₃), 6.46 (d, *J*_{HH} = 8.3 Hz, 2H, ArH_m), 6.72 (t, *J*_{HH} = 8.3 Hz, 1H, ArH_p), 6.85 (d, *J*_{HH} = 8.3 Hz, 4H, ArH), 6.87 (d, *J*_{HH} = 8.6 Hz, 4H, ArH); **¹³C{¹H} NMR (125 MHz, C₆D₆, 298 K) δ/ppm:** 20.6 (ArCH₃), 32.2 (C(O)CH₃), 112.7 (C_m), 119.8 (OCC_o), 130.4 (CH₃CC_m), 130.6 (C_p), 133.5 (CH₃C), 155.0 (OC_i), 155.9 (C_o), 198.6 (C=O) **Elemental Analysis** calc. for C₂₂H₂₀O₃, 79.50; H 6.07 found C, 79.38; H, 6.10.

Synthesis of double ¹³C-labelled 2,6-dimethoxyacetophenone (¹³C₂-3a):

2,6-dihydroxyacetophenone (0.54 g, 3.5 mmol, 1 equiv), K₂CO₃ (0.72 g, 5.2 mmol, 1.5 equiv) and ¹³CH₃I (1.0 g, 7.0 mmol, 2 equiv) were stirred in DMF (40 mL) at 100 °C under N₂ for 48 h. Reaction was quenched with 5 mol %

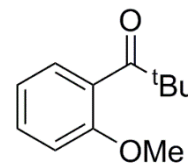


NaOH and water and then extracted with Et₂O (2 × 20 mL). The organic layers were combined and washed sequentially with H₂O (2 × 20 mL) then with brine (2 × 20 mL). The organic layer was dried over MgSO₄, filtered then concentrated *in vacuo* resulting in an off yellow solid (0.20 g, 34 %).

¹H-NMR (400 MHz, C₆D₆, 298 K) δ/ppm: 2.43 (s, 3H, C(O)CH₃), 3.19 (d, *J*_{CH} = 144.2 Hz, 6H, OCH₃), 6.18 (d, *J*_{HH} = 8.4 Hz, 2H, ArH_m), 6.97 (t, *J*_{HH} = 8.4 Hz, 1H, ArH_p); **¹³C{¹H} NMR (125 MHz, C₆D₆,**

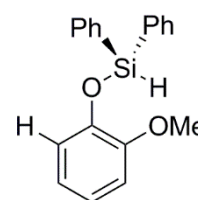
298 K) δ /ppm: 32.32 (C(O)CH₃), 55.40 (OCH₃), 104.31 (*C_m*), 130.14 (*C_p*), 157.11 (*C_o*), 199.95 (C=O).
ESI-MS (Hi-res. for C₈¹³C₂H₁₂O₃): calc. 183.0932 [M+H]⁺, found 183.0934 [M+H]⁺.

Synthesis of 1-(2-methoxyphenyl)-2,2-dimethyl-1-propanone (2d). Anisole (2 mL, 18.4 mmol, 1 equiv) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (2.6 mL, 17.3 mmol, 1 equiv) were dissolved in Et₂O (30 mL). The solution was cooled to -78 °C and *n*-BuLi (11.5 mL, 1.6 M in *n*-hexane, 18.4 mmol, 1 equiv) was added rapidly over 2 minutes. The solution was warmed to 25 °C and then stirred for 5 h with the solution becoming a yellow milky solution. The solution was cooled to -78 °C and trimethylacetyl chloride (2.3 mL, 18.7 mmol, 1 equiv) was added over 15 mins ensuring the temperature didn't exceed -60 °C. The solution was warmed to 25 °C and stirred for a further 12 h becoming a white milky solution. The reaction was quenched with brine and saturated NH₄Cl solution resulting in an aqueous and organic layer. The layers were separated and the organic layer was washed with brine and saturated NH₄Cl solution till the organic layer became clear. Organic layer was dried over MgSO₄, filtered then concentrated *in vacuo* leaving an oily yellow residue. Vacuum distillation of the oily residue yielded a colourless oil as the product (1.64 g, 50 %).



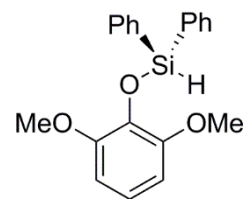
¹H NMR (400 MHz, C₆D₆, 298 K) δ /ppm: 1.20 (s, 9H, CH₃), 3.16 (s, 3H, OCH₃), 6.44 (d, *J_{HH}* = 8.3 Hz, 1H, ArH), 6.73 (td, *J_{HH}* = 7.4 Hz and 0.9 Hz, 1H, ArH), 6.93 (dd, *J_{HH}* = 7.4 Hz and 1.7 Hz, 1H, ArH), 7.03 (ddd, *J_{HH}* = 8.3 Hz, 7.5 Hz and 1.7 Hz, 1H, ArH). **¹³C{¹H} NMR (125 MHz, C₆D₆, 298 K) δ /ppm:** 27.00 (C(CH₃)₃), 44.77 (C(CH₃)₃), 54.94 (OCH₃), 111.23 (*C_m*), 120.46 (*C_i*), 126.82 (*C_m*), 129.78 (*C_o*), 132.13 (*C_p*), 155.77 (COMe), 211.58 (CO).

Synthesis of (2-methoxyphenoxy)diphenylsilane (9a). In dinitrogen glovebox chlorodiphenylsilane (0.5 mL, 2.5 mmol) and guaiacol (0.28 mL, 2.5 mmol) were dissolved in toluene (20 mL). NEt₃ (0.35 mL, 2.5 mmol) was added to the mixture, left to stir for 1 h at 25 °C. The reaction was then filtered through micro-glass fibre and the solvent removed *in vacuo* leaving a cloudy oily residue. Purification by vacuum distillation (130-140 °C, 1 × 10⁻¹ mmHg) to give a colourless oil (0.1 g, 40 %).



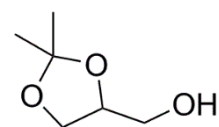
¹H NMR (400 MHz, C₆D₆, 298 K) δ /ppm: 3.17 (s, 3H, CH₃), 6.03 (s, 1H, SiH, ¹*J_{SiH}* = 225 Hz), 6.49 (dd, *J_{HH}* = 7.8 and 1.7 Hz, 1H, ArH), 6.71 (td, *J_{HH}* = 7.6 and 1.8 Hz, 1H, ArH), 6.76 (td, *J_{HH}* = 7.7 and 1.8 Hz, 1H, ArH), 7.08 (dd, *J_{HH}* = 7.7 and 1.8 Hz, 1H, ArH), 7.15 (m, 6H, Ph), 7.75 (m, 4H, Ph). **¹³C{¹H} NMR (125 MHz, C₆D₆, 289 K) δ /ppm:** 55.0 (CH₃) 112.7 (*C_o*), 120.7 (*C_m*), 121.5 (*C_m*), 122.5 (*C_p*), 128.2 (*C_p*), 130.4 (*C_m*), 134.9 (*C_o*), 145.4 (CO), 150.8 (COCH₃). **²⁹Si (99 MHz, C₆D₆, 298 K) δ /ppm:** -13.3 (¹*J_{SiH}* = 225 Hz).

Synthesis of (2,6-dimethoxyphenoxy)diphenylsilane (9b). In dinitrogen glovebox chlorodiphenylsilane (1 mL, 5 mmol) and 2,6-dimethoxyphenol (0.78g, 5 mmol) were dissolved in toluene (20 mL). NEt_3 (0.71 mL, 5 mmol) was added to the mixture, left to stir for 1 h at 25 °C. The reaction was then filtered, washed with cold *n*-hexane and then reduced *in vacuo* under dinitrogen leaving a crystalline colourless solid as product (0.55g, 64 %).



^1H NMR (400 MHz, C_6D_6 , 298 K) δ /ppm: 3.28 (s, 6H, CH_3), 6.12 (s, 1H, SiH, $^1J_{\text{SiH}} = 227$ Hz), 6.32 (d, $J_{\text{HH}} = 8.3$ Hz, 2H, ArH_m), 6.71 (t, $J_{\text{HH}} = 8.3$ Hz, 1H, ArH_p), 7.17 (m, 6H, Ph), 7.88 (m, 4H, Ph). **$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6 , 289 K) δ /ppm:** 55.6 (CH_3), 105.9 (C_m), 121.4 (C_p), 130.3 (C_o), 135.0 (C_m), 135.7 (C_p), 151.9 (COCH_3). **^{29}Si (99 MHz, C_6D_6 , 298 K) δ /ppm:** -12.8 ($^1J_{\text{SiH}} = 227$ Hz).

Synthesis of (2,2-Dimethyl-1,3-dioxolan-4-yl)methanol (solketal) prepared according to modified literature procedure.⁵ Glycerol (3 mL, 41 mmol), 2,2-dimethoxy propane (5.4 mL, 44 mmol), dry acetone (30 mL) and *p*-toluene sulfonic acid (15 mg, 0.079 mmol) were stirred in a Schlenk for 24 h. The solvent and any unreacted starting materials were removed under vacuum leaving a yellow oily residue. Purification by vacuum distillation giving (2,2-Dimethyl-1,3-dioxolan-4-yl)methanol as a colourless oily residue (3.26 g, 60%).



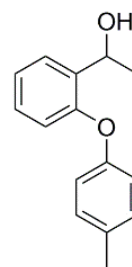
^1H NMR (400 MHz, CDCl_3 , 298 K) δ /ppm: 1.26 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 3.00 (m, 1H, OH), 3.49 (dt, $J_{\text{HH}} = 11.5$ Hz and 5.6 Hz, 1H, OCH_2), 3.56 (dt, $J_{\text{HH}} = 10.3$ Hz and 5.1 Hz, 1H, OCH_2), 3.66 (dd, $J_{\text{HH}} = 8.1$ Hz and 6.6 Hz, 1H, CH_2), 3.93 (dd, $J_{\text{HH}} = 8.2$ Hz and 6.6 Hz, 1H, CH_2), 4.11 (m, 1H, CH). **$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 298 K) δ /ppm:** 25.45 (CH_3), 26.88 (CH_3), 63.07 (COH), 66.09 ($\text{C}(\text{H}_2)\text{O}$), 76.70 ($\text{C}(\text{H})\text{O}$), 109.21 ($\text{C}(\text{CH}_3)_2$). [Lit.⁵ **^1H NMR (400 MHz, CDCl_3 , 298 K) δ /ppm:** 1.37 (s, 3H), 1.44 (s, 3H), 3.57-3.62 (dd, 1H), 3.69-3.72 (dd, 1H), 3.76-3.80 (dd, 1H), 4.02-4.06 (dd, 1H), 4.22-4.24 (m, 1H). **$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ /ppm:** 24.6 (CH_3), 26.6 (CH_3), 63.1 (COH), 65.7 ($\text{C}(\text{H}_2)\text{O}$), 76.1 ($\text{C}(\text{H})\text{O}$), 109.3 ($\text{C}(\text{CH}_3)_2$).

5.3.3 General Procedure for Reduction of Arylketone to Arylethanol

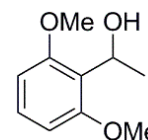
Arylketone (4.4mmol, 1 equiv) was weighed into a schlenk and dissolved in THF (15 mL). LiAlH_4 (2.2 mmol, 0.5 equiv) was weighed out into a separate schlenk and dissolved in THF (20 mL). LiAlH_4 solution was cooled to -78 °C and the arylketone solution was added dropwise over the course of 20 min. Once addition was completed the reaction was allowed to warm to rt and left to stir overnight. The reaction was quenched with THF/ H_2O / NaOH (80/10/10) and the organic layer was then washed

sequentially with H₂O (2 × 10 mL) then brine (2 × 10 mL). The organic layer was dried over MgSO₄ then concentrated *in vacuo* to give product. Product used in reactions without further purification.

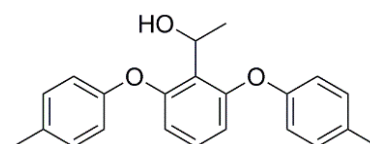
Synthesis of 2,6-*p*-tolylloxy(phenyl)arylethan-1-ol (2b-H₂): Cloudy viscous liquid (0.64 g, 64 %). ¹H NMR (400 MHz, C₆D₆, 298 K) δ/ppm: 1.48 (d, *J*_{HH} = 6.4 Hz, 3H, C(OH)CH₃), 2.07 (s, 3H, ArCH₃), 2.40 (br, 1H, OH), 5.26 (m, 1H, CH), 6.76 (dd, *J*_{HH} = 7.5 Hz and 1.8 Hz, 1H, ArH_m), 6.82 (d, *J*_{HH} = 8.7 Hz, 2H, ArH_o), 6.87 (d, *J*_{HH} = 8.4 Hz, 2H, ArH_m), 6.95 (m, 2H, ArH), 7.62 (dd, *J*_{HH} = 6.5 Hz and 2.6 Hz, 1H, ArH_o). ¹³C{¹H} NMR (125 MHz, C₆D₆, 298 K) δ/ppm: 20.6 (ArCH₃), 24.6 (C(OH)CH₃), 65.3 (CH), 118.7 (C_m), 118.7 (OCCO), 123.9 (C_m), 127.0 (C_o), 128.3 (C_p), 130.6 (CH₃CC_m), 132.6 (CCH₃), 137.8 (C(OH)C_i), 154.3 (C_o), 155.7 (OC_i). **Elemental Analysis:** calc. for C₁₅H₁₆O₂ C, 78.92; H 7.06; found C, 79.00; H, 7.14.



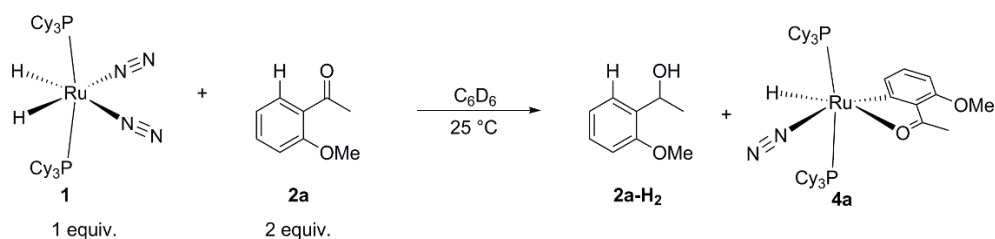
Synthesis of 1-(2,6-dimethoxyphenyl)ethanol-1-ol (3a-H₂): Yellow-white solid (0.565 g, 56 %). ¹H NMR (400 MHz, C₆D₆, 298 K) δ/ppm: 1.74 (d, *J*_{HH} = 6.7 Hz, 3H, CH₃), 3.16 (s, 6H, OCH₃), 4.02 (d, *J*_{HH} = 11.8 Hz, 1H, OH), 5.84 (dq, *J*_{HH} = 13.3 Hz and 6.7 Hz, 1H, CH), 6.24 (d, *J*_{HH} = 8.4 Hz, 2H, ArH_m), 6.97 (t, *J*_{HH} = 8.3 Hz, 1H, ArH_p). ¹³C{¹H} NMR (125 MHz, C₆D₆, 298 K) δ/ppm: 24.4 (C(OH)CH₃), 55.2 (OCH₃), 64.3 (CH), 104.6 (C_m), 159.0 (C_p). [Literature data:⁶ ¹H-NMR (400 MHz, CDCl₃, 298 K) δ/ppm: 1.50 (d, *J* = 6.2 Hz, 3H), 3.85 (s, 6H), 3.88 (br. s, 1H), 5.33 (m, 1H), 6.58 (d, *J* = 8.2 Hz, 2H), 7.16 (t, *J* = 8.2 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃, 298 K) δ/ppm: 23.6 (CH₃), 55.7 (CH₃), 64.0 (CH), 104.3 (CH), 121.0 (CH), 128.1 (C), 157.4 (C)].



Synthesis of 2,6-Bis-*p*-tolylloxy(phenyl)arylethan-1-ol (3b-H₂): Yellow-white solid (0.41 g, 80 %). ¹H NMR (400 MHz, C₆D₆, 298 K) δ/ppm: 1.75 (d, *J*_{HH} = 6.7 Hz, 3H, C(OH)CH₃), 2.05 (s, 6H, ArCH₃), 3.53 (d, *J*_{HH} = 11.5 Hz, 1H, OH), 5.83 (dt, *J*_{HH} = 11.3 Hz and 6.7 Hz, 1H, CH), 6.49 (d, *J*_{HH} = 8.2 Hz, 2H, ArH_m), 6.72 (dd, *J*_{HH} = 8.5 Hz and 8.0 Hz, 1H, ArH_p), 6.85 (s, 8H, ArH). ¹³C{¹H} NMR (125 MHz, C₆D₆, 298 K) δ/ppm: 20.6 (ArCH₃), 24.5 (C(OH)CH₃), 64.6 (CH), 113.6 (C_m), 119.5 (OCCO), 128.3 (C_p), 130.7 (CH₃CC_m), 133.3 (CCH₃), 155.1 (OC_i), 156.5 (C_o). **ESI-MS (Hi-res for C₂₂H₂₂O₃):** calc. 333.1467 [M-H]⁺, found 333.1491 [M-H]⁺.



5.3.4 Ru-Mediated C–H Bond Activation



C–H Activation of 2-methoxyacetophenone (2a): In a dinitrogen glovebox, $[Ru(H)_2(N_2)_2(PCy_3)_2]$ (**1**) (200 μ L, 0.07 M, C_6D_6 , 1 equiv), 2-methoxyacetophenone (**2a**) (120 μ L, 0.23 M, C_6D_6 , 2 equiv) and ferrocene (80 μ L, 0.17 M, C_6D_6 , 1 equiv) were added by micropipette into a J. Young NMR tube and the solvent volume was made up to 600 μ L with C_6D_6 . The J. Young NMR tube was sealed and the reaction left at $25\text{ }^{\circ}C$ for 24 h with a colour change from straw yellow to deep purple/red observed. The reaction was monitored by ^1H -NMR and $^{31}P\{^1H\}$ -NMR spectroscopy and yields calculated against internal standards; ferrocene for ^1H -NMR and PPh_3 in a borosilicate capillary tube for $^{31}P\{^1H\}$ -NMR. Formation of **2a-H₂** was confirmed by comparison against a genuine sample of the substrate bought commercially. **4a** was observed at >99 % yield and **2a-H₂** was observed at 87 % yield. Isolation of **4a** was achieved from scale-up synthesis of the above reaction in toluene and recrystallization in hexamethyldisiloxane to give an orange powder as the product (53 mg, 57 %).

Data for **4a**: ^1H NMR (C_6D_6 , 400 MHz, 298 K) δ/ppm : -14.90 (t, $J_{HP} = 24.5$ Hz, 1H, RuH), $1.03 - 2.24$ (m, 66H, Cy), 2.95 (s, 3H, CH_3), 3.36 (s, 3H, OCH₃), 6.08 (d, $J_{HH} = 7.9$ Hz, 1H, ArH_m), 7.02 (t, $J_{HH} = 7.7$ Hz, 1H, ArH_p), 7.76 (d, $J_{HH} = 7.5$ Hz, 1H, ArH_m); $^{13}C\{^1H\}$ NMR (C_6D_6 , 125 MHz, 298 K) δ/ppm : 27.5 (m, Cy), 28.4 (m, Cy), 30.1 (m, Cy), 31.8 (CH_3), 35.9 (t, $^1J_{CP} = 8.2$ Hz, Cy), 54.2 (OCH₃), 100.7 (C_m), 130.1 (C_p), 136.6 (C_m), 162.3 (COCH₃), 204.3 (C=O), 212.3 (Ru–C); $^{31}P\{^1H\}$ NMR (C_6D_6 , 162 MHz, 298 K) δ/ppm : 39.11 . FT-IR (ν/cm^{-1}): 1964 (Ru–H), 2078 (N $\equiv$ N). Due to the sensitivity of this complex repeated attempts to acquire CHN analysis failed to provide satisfactory results.

In situ NMR data for **2a-H₂**: ^1H NMR (C_6D_6 , 400 MHz, 298 K) δ/ppm : 1.49 (d, $J_{HH} = 6.5$ Hz, 3H, CH_3), 3.20 (s, 3H, OCH₃), 5.17 (q, $J_{HH} = 5.9$ Hz, 1H, CH), 6.48 (d, $J_{HH} = 8.3$ Hz, 1H, ArH_m), 6.90 (t, $J_{HH} = 7.2$ Hz, 1H, ArH_m), 7.06 (td, $J_{HH} = 9.4$ Hz and $1.9z$ Hz, 1H, ArH_p), 7.44 (d, $J_{HH} = 7.2$ Hz, 1H, ArH_o). $^{13}C\{^1H\}$ NMR (C_6D_6 , 125 MHz, 298 K) δ/ppm : 23.9 (CH_3), 54.7 (OCH₃), 66.0 (C(H)OH), 110.5 (C_m), 121.1 (C_m), 126.4 (C_o), 128.4 (C_p), 134.9 (C_i), 156.6 ($C_o(OMe)$).

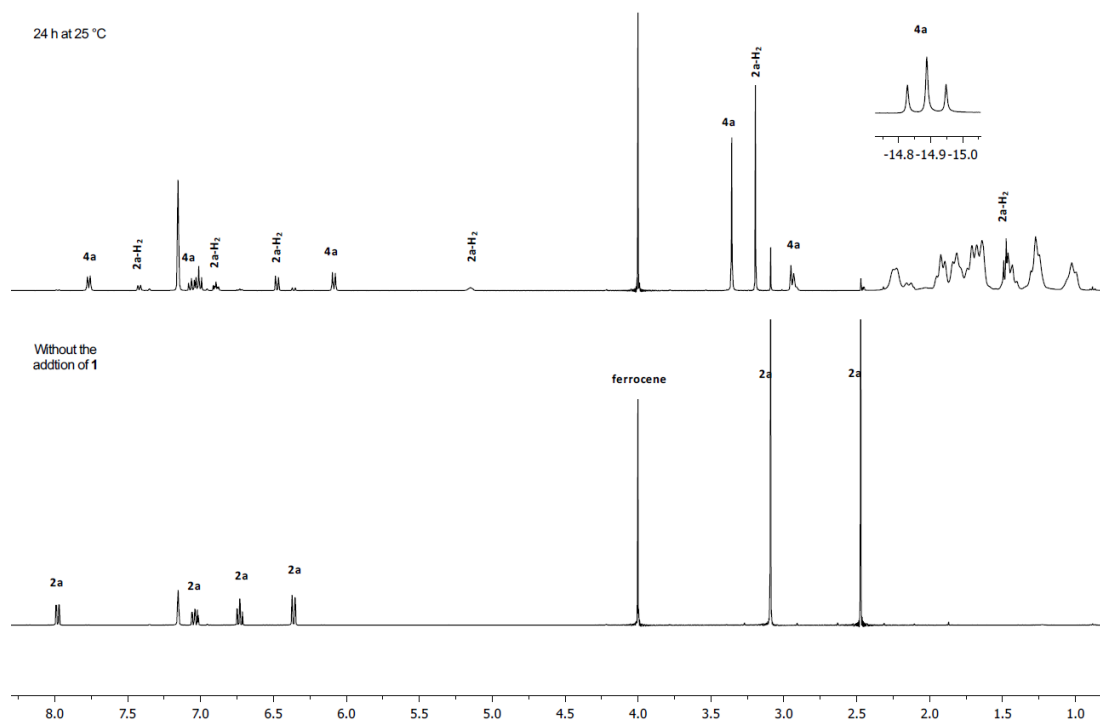


Figure S 5.4. ^1H NMR (C_6D_6 , 400 MHz, 298 K) stack plot for C–H activation of 2-methoxyacetophenone

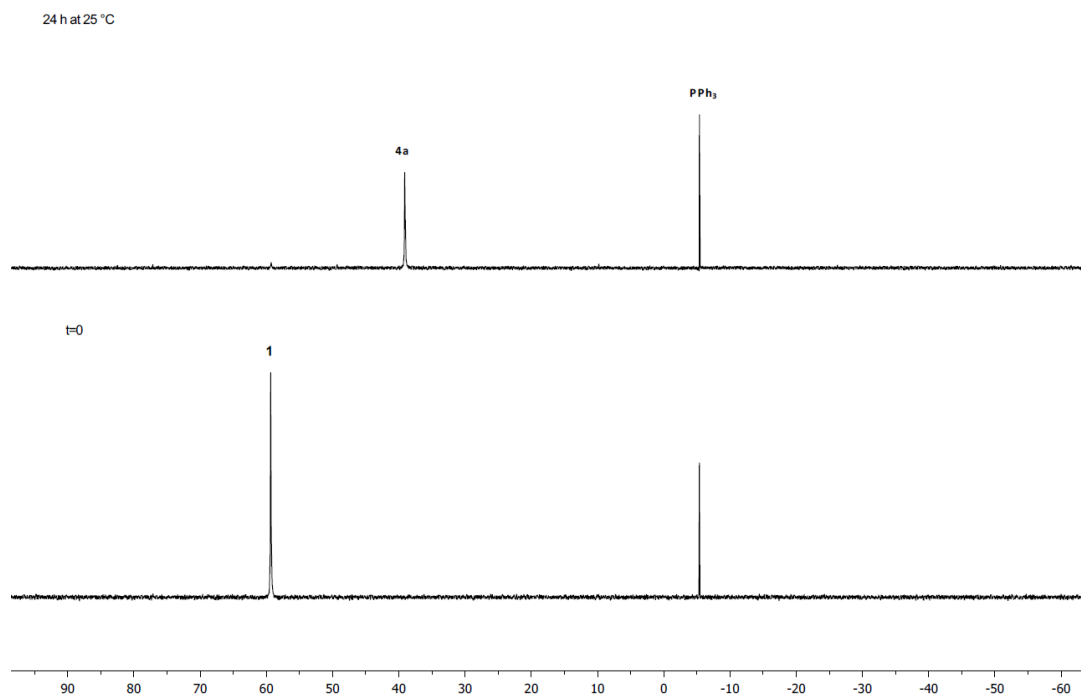
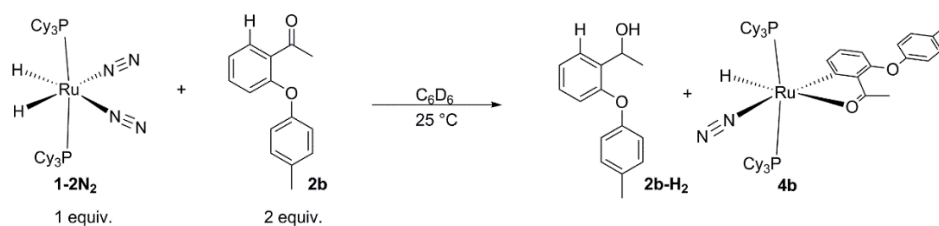


Figure S 5.5. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz, 298 K) stack plot for C–H activation of 2-methoxyacetophenone



C–H Activation of 1-(2-(p-tolyloxy)phenyl)ethanone (2b): In a dinitrogen glovebox, [Ru(H)₂(N₂)₂(PCy₃)₂] (**1**) (200 μL, 0.07 M, C₆D₆, 1 equiv), 1-(2-(p-tolyloxy)phenyl)ethanone (**2b**) (120 μL, 0.23 M, C₆D₆, 2 equiv) and ferrocene (80 μL, 0.17 M, C₆D₆, 1 equiv) were added by micropipette into a J. Young NMR tube and the solvent volume was made up to 600 μL with C₆D₆. The J. Young NMR tube was sealed and the reaction mixture was left at 25 °C for 24 h with a colour change from straw yellow to deep orange observed. The reaction was monitored by ¹H-NMR and ³¹P{¹H}-NMR spectroscopy and yields calculated against internal standards; ferrocene for ¹H-NMR and PPh₃ in a borosilicate capillary tube for ³¹P{¹H}-NMR. Formation of **2b-H₂** was confirmed by comparison against a genuine synthesised sample of the substrate. **4b** was observed at 89 % yields and **2b-H₂** was observed at 91 % yield. Isolation of **4b** was achieved from scale-up synthesis of the above reaction in toluene and recrystallization in *n*-hexane to give deep purple crystalline solid as the product (26 mg, 68 %).

Data for **4b**: ¹H NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: −14.82 (t, *J* = 24.1 Hz, 1H, RuH), 1.10 – 1.47 (m, 24H, Cy), 1.67 – 2.00 (m, 36H, Cy), 2.07 (s, 3H, CH₃), 2.25 (m, 6H, Cy), 2.98 (s, 3H, C(O)CH₃), 6.33 (d, *J* = 7.7 Hz, 1H, ArH_m), 6.92 (m, 1H, ArH_p), 6.93 (d, *J* = 8.6 Hz, 2H, OArH_m), 7.00 (d, *J* = 8.6 Hz, 2H, OArH_o), 7.81 (d, *J* = 7.5 Hz, 1H, ArH_m); ¹³C{¹H} NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 20.53 (ArCH₃), 26.7 (m, Cy), 27.7 (m, Cy), 29.9 (m, Cy), 31.3 (C(O)CH₃), 35.8 (t, ¹*J*_{CP} = 8.2 Hz, Cy), 108.9 (*C_m*), 119.0 (OCCO), 130.2 (*C_p*), 131.0 (CH₃CC_m), 138.9 (*C_m*), 204.3 (C=O), 212.2 (Ru–C); ³¹P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 39.87. FT-IR (ν/cm^{−1}): 1983 (Ru–H), 2106 (N≡N). **Elemental Analysis** calc. for C₅₁H₈₀N₂O₂P₂Ru C, 66.86; H 8.80; N, 3.06 found C, 67.11; H, 8.81; N, 2.96.

In situ NMR data for **2b-H₂**: ¹H NMR (400 MHz, 298 K, C₆D₆) δ/ppm: 1.46 (d, *J*_{HH} = 6.4 Hz, 3H, C(OH)CH₃), 2.06 (s, 3H, ArCH₃), 5.20 (m, 1H, CH), 6.77 (dd, *J*_{HH} = 7.4 Hz and 1.9 Hz, 1H, ArH_m), 6.82 (d, *J*_{HH} = 8.7 Hz, 2H, ArH_o), 6.86 (d, *J*_{HH} = 8.7 Hz, 2H, ArH_m), 6.94 (m, 2H, ArH), 7.58 (dd, *J*_{HH} = 6.8 Hz and 2.5 Hz, 1H, ArH_o). ¹³C {¹H} NMR (125 MHz, 298 K, C₆D₆) δ/ppm: 20.6 (ArCH₃), 26.5 (C(OH)CH₃), 118.7 (*C_m*), 118.7 (OCCO), 123.8 (*C_m*), 128.4 (*C_o*), 128.4 (*C_p*), 130.6 (CH₃CC_m), 132.6 (CCH₃), 154.4 (*C_o*), 155.7 (OC_i).

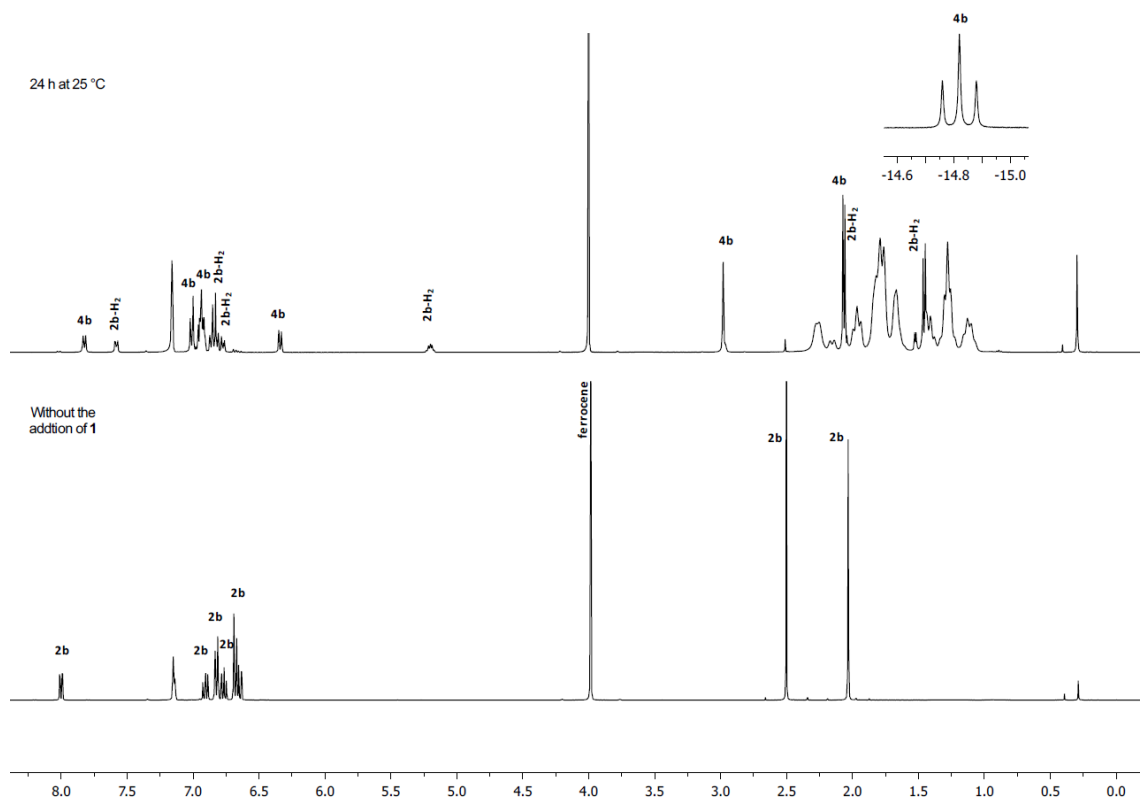


Figure S 5.6. ^1H NMR (C_6D_6 , 400 MHz, 298 K) stack plot of C–H activation of 1-(2-(p-tolyloxy)phenyl)ethanone

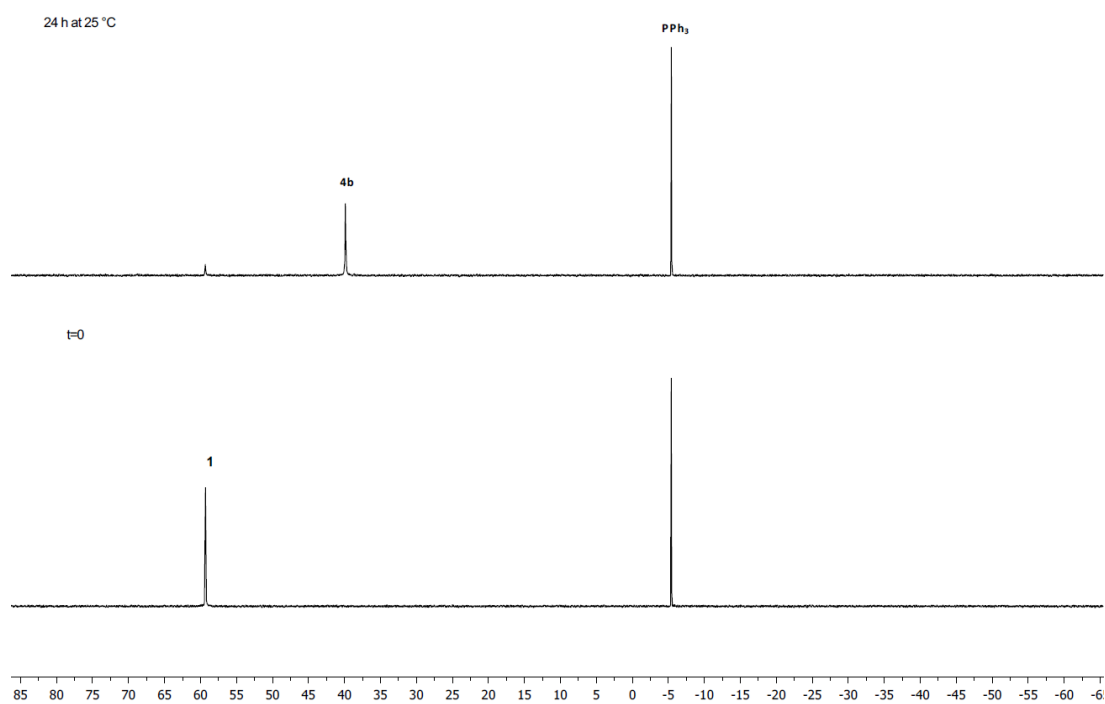
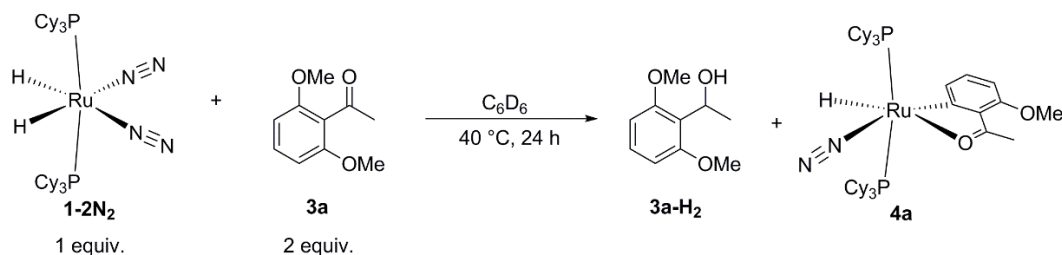


Figure S 5.7. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz, 298 K) stack plot of C–H activation of 1-(2-(p-tolyloxy)phenyl)ethanone

5.3.5 Ru-Mediated C–O Bond Activation



C–O Activation of 2,6-Dimethoxyacetophenone (3a): In a dinitrogen glovebox, $[\text{Ru}(\text{H})_2(\text{N}_2)_2(\text{PCy}_3)_2]$ (**1**) (200 μL , 0.07 M, C_6D_6 , 1 equiv), 2,6-dimethoxyacetophenone (**3a**) (120 μL , 0.23 M, C_6D_6 , 2 equiv) and ferrocene (80 μL , 0.17 M, C_6D_6 , 1 equiv) were added by micropipette into a J. Young NMR tube and the solvent volume was made up to 600 μL with C_6D_6 . The J. Young NMR tube was sealed and the reaction mixture heated at $40\text{ }^\circ\text{C}$ for 24 h with a colour change from straw yellow to deep red observed. The reaction was monitored by ^1H -NMR and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy and yields calculated against internal standards; ferrocene for ^1H -NMR and PPh_3 for $^{31}\text{P}\{^1\text{H}\}$ -NMR in a borosilicate capillary tube. Formation of **3a-H₂** was confirmed by comparison against a genuine synthesised sample of the substrate. **4a** was observed at 52 % yield and **3a-H₂** was observed at 98 % yield.

In situ NMR data for **4a** same as above.

In situ NMR data for **3a-H₂**: ^1H NMR (C_6D_6 , 400 MHz, 298 K) δ/ppm : 1.73 (d, $J = 6.6\text{ Hz}$, 3H, CH_3), 3.17 (s, 6H, OCH_3), 5.82 (dt, $J = 13.3$ and 6.7 Hz , 1H, CH), 6.25 (d, $J = 8.3\text{ Hz}$, 2H, ArH_m), 6.97 (t, $J = 8.4\text{ Hz}$, 1H, ArH_p). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz, 298 K) δ/ppm : 24.2 (CH_3), 55.2 (OCH_3), 64.1 (COH), 104.6 (C_m), 158.0 (C_p).

A peak in $^{31}\text{P}\{^1\text{H}\}$ -NMR at 64.43 ppm was identified as the major by-product $[\text{RuH}_2(\text{CO})(\text{N}_2)(\text{PCy}_3)_2]$ (**5-N₂**) in this reaction. The yield of **5-N₂** was 28 %.

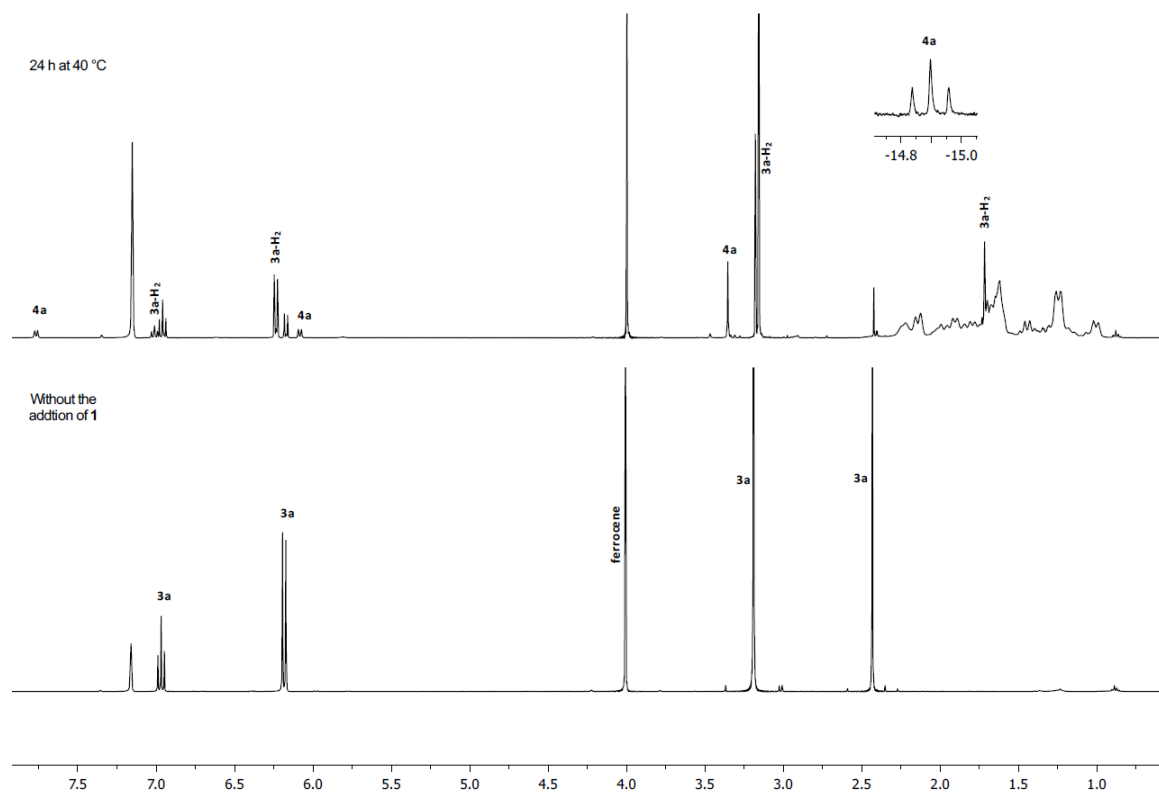


Figure S 5.8. ^1H NMR (C_6D_6 , 400 MHz, 298 K) stack plot of C–O activation of 2,6-dimethoxyacetophenone.

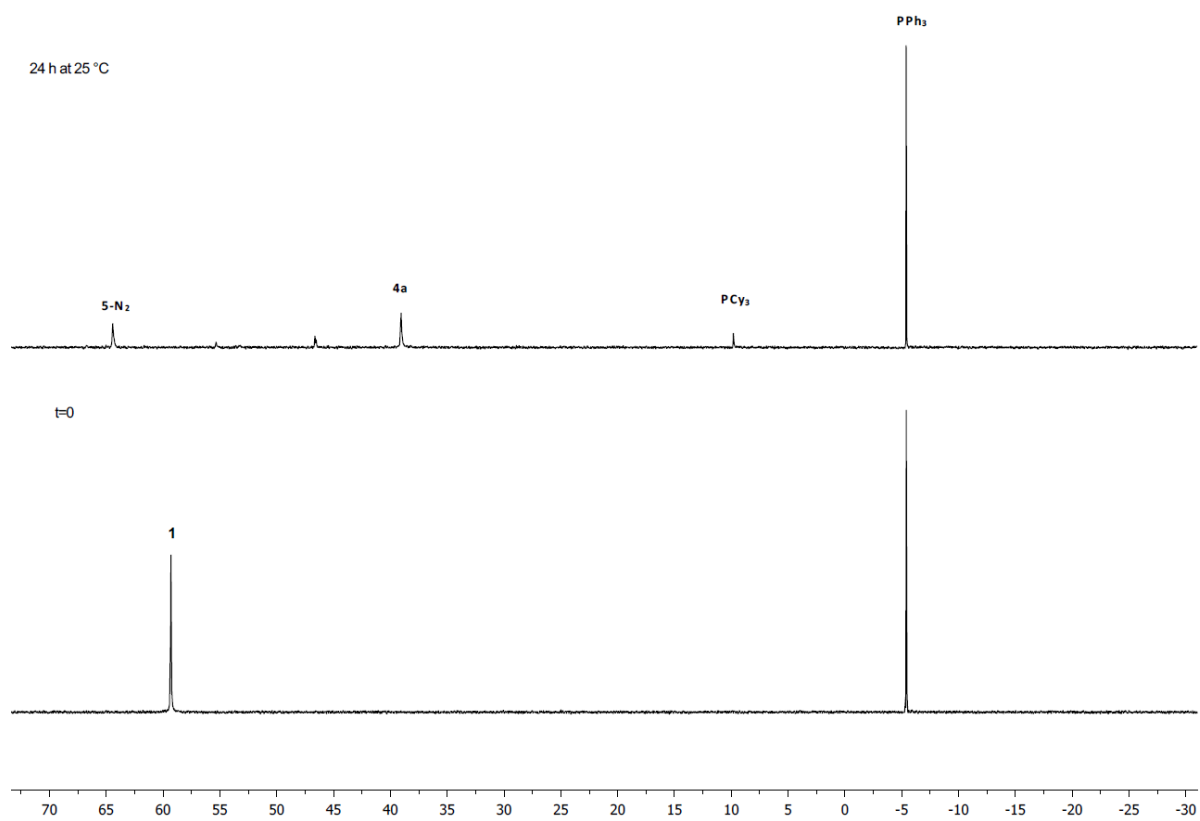
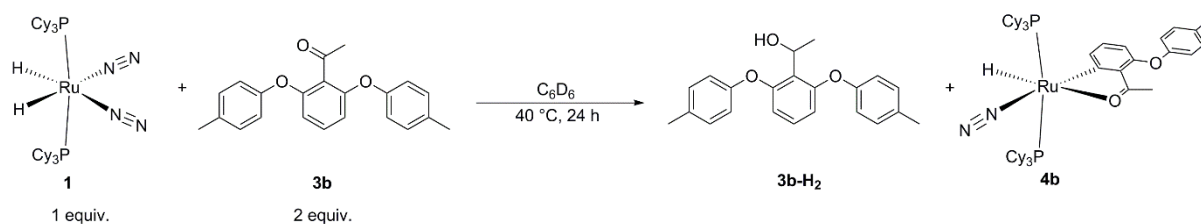


Figure S 5.9. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz, 298 K) stack plot of C–O activation of 2,6-dimethoxyacetophenone.



C–O Activation of 2,6-bis-*p*-tolylloxyacetophenone (3b**):** In a dinitrogen glovebox, [Ru(H)₂(N₂)₂(PCy₃)₂] (**1**) (200 μL, 0.07 M, C₆D₆, 1 equiv), 2,6-bis-*p*-tolylloxy(phenyl)acetophenone (**3b**) (120 μL, 0.23 M, C₆D₆, 2 equiv) and ferrocene (80 μL, 0.17 M, C₆D₆, 1 equiv) were added by micropipette into a J. Young NMR tube and the solvent volume was made up to 600 μL with C₆D₆. The J. Young NMR tube was sealed and the reaction mixture left to react at 40 °C for 24 h with a colour change from straw yellow to deep orange observed. The reaction was monitored by ¹H-NMR and ³¹P{¹H}-NMR spectroscopy and yields calculated against internal standards; ferrocene for ¹H-NMR and PPh₃ in a borosilicate capillary tube for ³¹P{¹H}-NMR. Formation of **3b-H₂** was confirmed by comparison against a genuine synthesised sample of the substrate. **4b** was observed at 54 % yield and **3b-H₂** was observed at 96 % yield.

In situ NMR data for **4b** same as above.

In situ NMR data for **3b-H₂**: ¹H NMR (400 MHz, C₆D₆, 298 K) δ/ppm: 1.75 (d, *J*_{HH} = 6.3 Hz, 3H, C(OH)CH₃), 2.05 (s, 6H, ArCH₃), 5.84 (dq, *J*_{HH} = 13.4 Hz and 6.8 Hz, 1H, CH), 6.50 (d, *J*_{HH} = 8.2 Hz, 2H, ArH_m), 6.73 (d, *J*_{HH} = 8.3 Hz, 1H, ArH_p), 6.85 (s, 8H, ArH); ¹³C{¹H} NMR (125 MHz, C₆D₆, 298 K) δ/ppm: 20.6 (ArCH₃), 24.4 (C(OH)CH₃), 113.6 (C_m), 119.5 (OCC_O), 128.2 (C_p), 130.6 (CH₃CC_m), 133.3 (CCH₃), 155.1 (OC_i), 156.7 (C_o).

A peak in ¹H-NMR at -25.87 ppm (t, *J*_{HP} = 19.8 Hz, 1H, RuH) and a peak in ³¹P{¹H}-NMR at 42.94 ppm was identified as the major by-product in this reaction **6a** [RuH(N₂)(*p*-OC₆H₄(CH₃))(PCy₃)₂]. The yield of **6a** was 20 %. In addition, **7a** and **8a** were observed as minor by-products in <5 % yield.

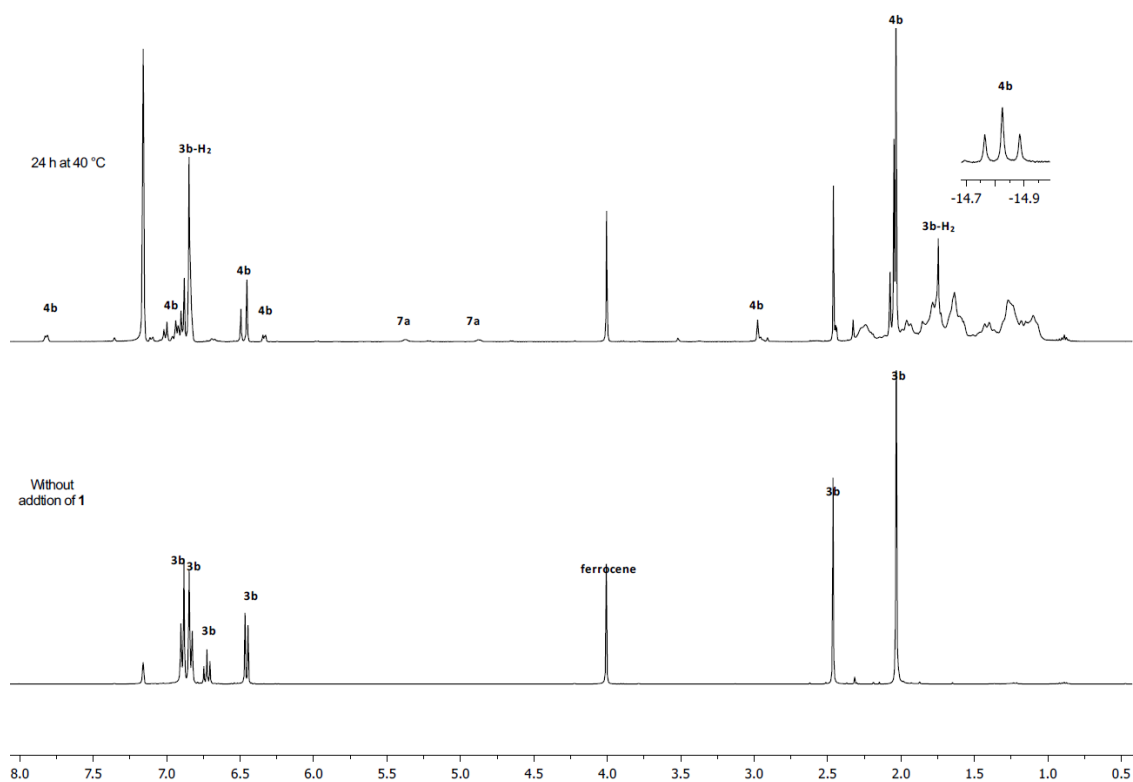


Figure S 5.10. ^1H NMR (C_6D_6 , 400 MHz, 298 K) stack plot of C–O activation of 2,6-bis-p-tolyloxy(phenyl)acetophenone.

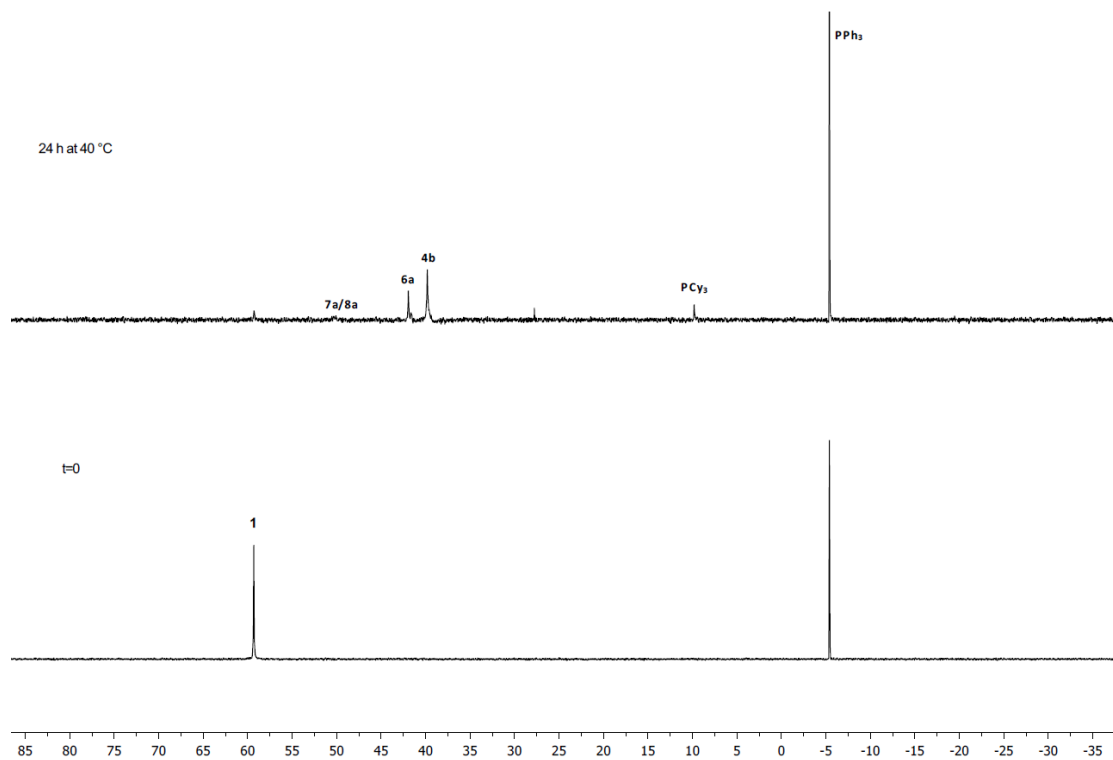
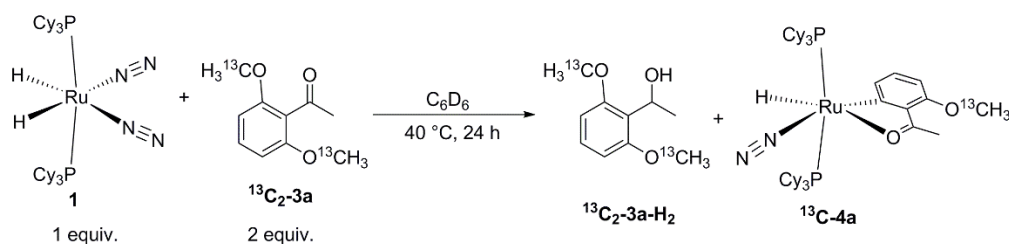


Figure S 5.11. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz, 298 K) stack plot of C–O activation of 2,6-bis-p-tolyloxy(phenyl)acetophenone.



*C–O Activation of double ¹³C-labelled 2,6-dimethoxyacetophenone (¹³C₂-**3a**):* In a dinitrogen glovebox, [Ru(H)₂(N₂)₂(PCy₃)₂] (**1**) (200 μL, 0.07 M, C₆D₆, 1 equiv), ¹³C₂-**3a** (120 μL, 0.23 M, C₆D₆, 2 equiv) and ferrocene (80 μL, 0.17 M, C₆D₆, 1 equiv) were added by micropipette into a J. Young NMR tube and the solvent volume was made up to 600 μL with C₆D₆. The J. Young NMR tube was sealed and the reaction mixture heated at 40 °C for 24 h with a colour change from straw yellow to deep orange observed. The reaction was monitored by ¹H-NMR and ³¹P{¹H}-NMR spectroscopy. Structure determination of ¹³C₂-**3a**-H₂ and ¹³C-**4a** were compared to NMR data obtained for **3a**-H₂ and **4a** as the chemical shifts of the signals are anticipated to be near identical except for the ¹³C-labelled carbon atoms on methoxy group.

In situ NMR data for ¹³C-**4a**: ¹H NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: −14.89 (t, *J*_{HP} = 24.2 Hz, 1H, RuH), 0.95 – 2.31 (m, 66H, Cy), 3.36 (d, *J*_{CH} = 143.6 Hz, 3H, O¹³CH₃), 6.09 (d, *J*_{HH} = 7.8 Hz, 1H, ArH_m), 7.02 (t, *J*_{HH} = 7.7 Hz, 1H, ArH_p), 7.77 (d, *J*_{HH} = 7.5 Hz, 1H, ArH_m); ¹³C{¹H} NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 26.7 (m, Cy), 27.9 (m, Cy), 29.9 (m, Cy), 31.6 (CH₃), 35.8 (t, ¹*J*_{CP} = 8.3 Hz, Cy), 54.2 (O¹³CH₃), 100.7 (*C*_m), 130.2 (*C*_p), 136.6 (*C*_m), 162.4 (COCH₃), 207.3 (C=O), 212.4 (Ru–C); ³¹P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 39.06.

In situ NMR data for ¹³C₂-**3a**-H₂: ¹H NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: 1.72 (s, 3H, CH₃), 3.17 (d, *J*_{CH} = 144.1 Hz, 6H, O¹³CH₃), 5.82 (m, 1H, CH), 6.25 (d, *J*_{HH} = 8.3 Hz, 2H, ArH_m), 6.97 (t, *J*_{HH} = 8.4 Hz, 1H, ArH_p). ¹³C{¹H} NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 24.2 (CH₃), 55.2 (O¹³CH₃), 64.0 (COH), 104.6 (*C*_m), 158.0 (*C*_p).

Peaks in ³¹P{¹H}-NMR at 64.5 ppm and in ¹³C{¹H}-NMR at 207.3 ppm (¹³C=O) allowed identification of [RuH₂(¹³CO)(N₂)(PCy₃)₂] (¹³C-**5-N₂**) as the major by-product in this reaction.

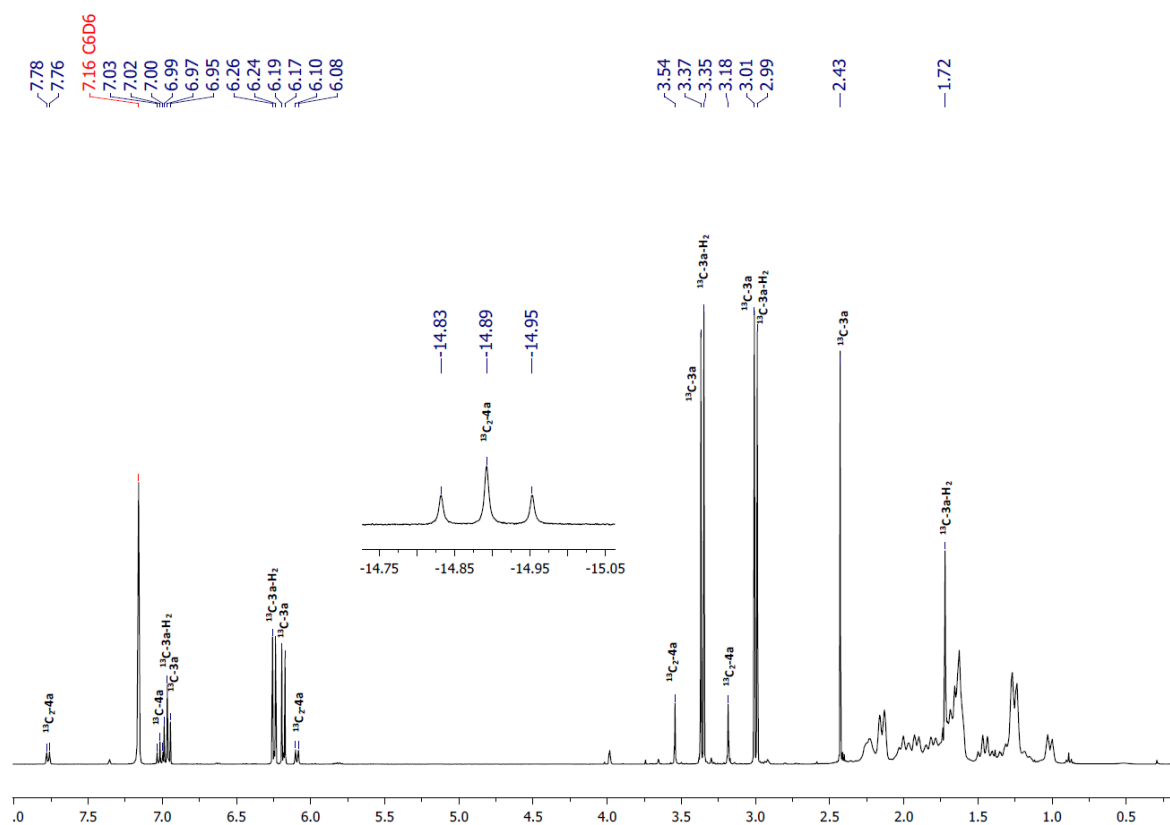


Figure S 5.12. ^1H NMR (C_6D_6 , 400 MHz, 298 K) of C–O activation of ^{13}C -labelled 2,6-dimethoxyacetophenone

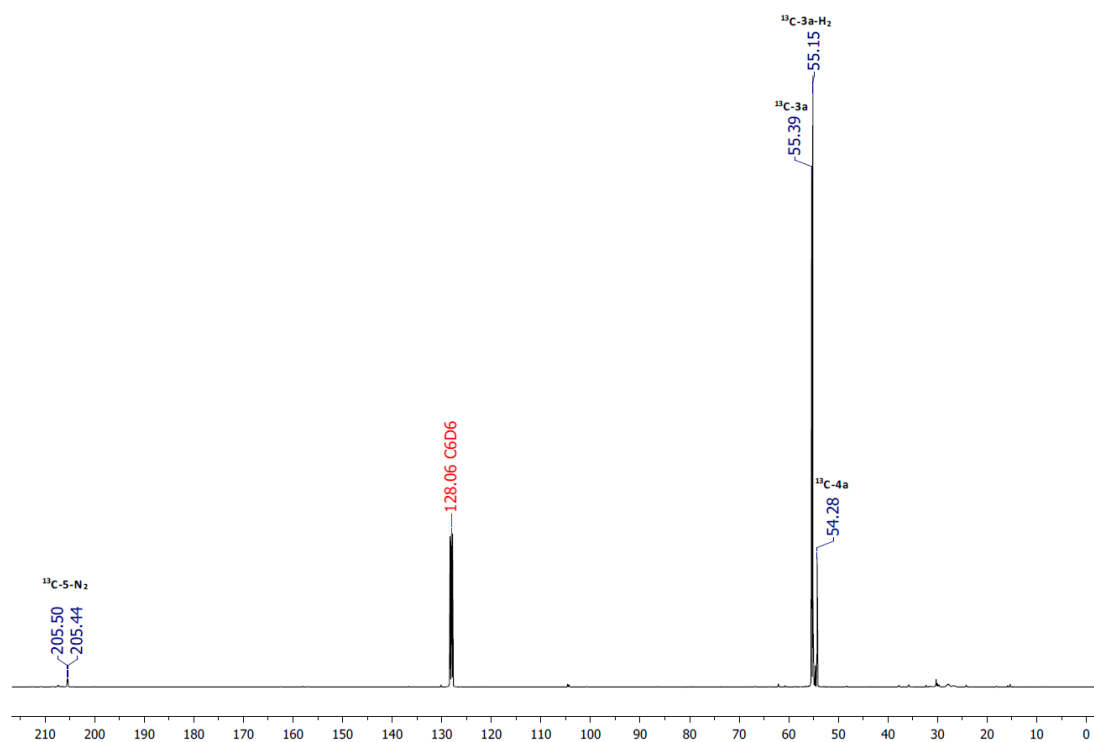


Figure S 5.13. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz, 298 K) of C–O activation of double ^{13}C -labelled 2,6-dimethoxyacetophenone.

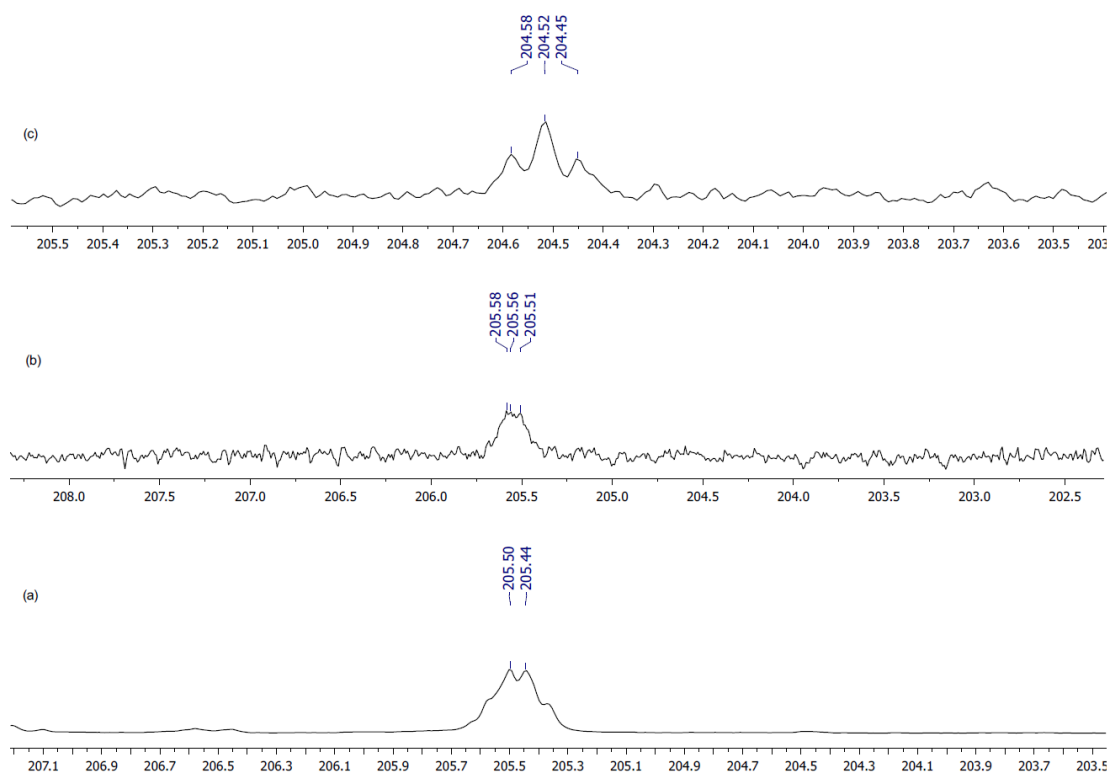


Figure S 5.14. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz, 298 K) stack plot showing only Ru-CO peak for comparison where (a) is the C-O cleavage reaction with $^{13}\text{C}_2\text{-3a}$, (b) is **5-N₂** and (c) is **5-H₂**

5.3.6 Identification of By-Products from C–O Bond Activation

A number of literature known carbonyl complexes and arene complexes of the $\{\text{Ru}(\text{PCy}_3)_2\}$ fragment are known. Selected examples, including spectroscopic data, are included below for reference.^{2,7–10}

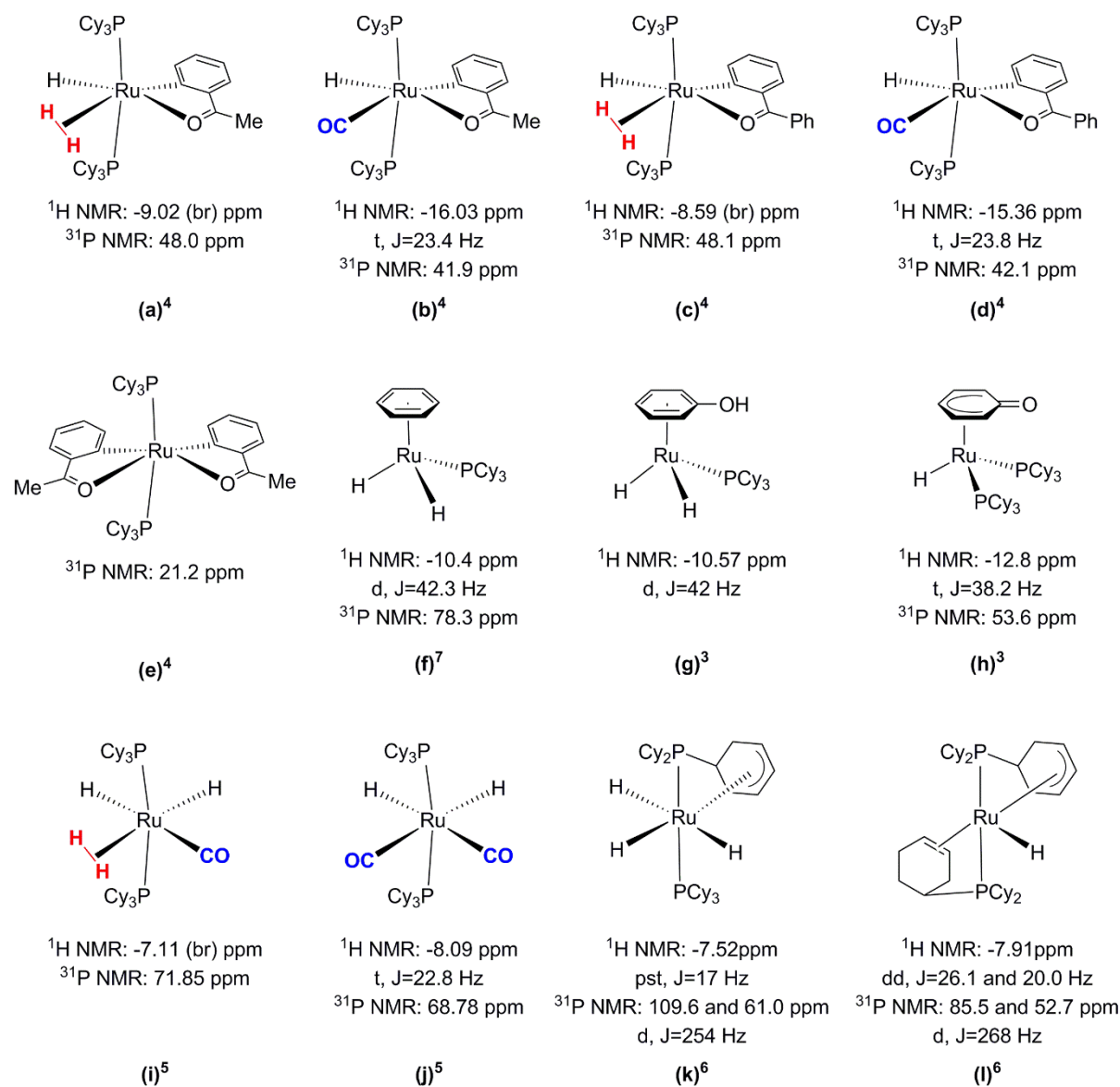
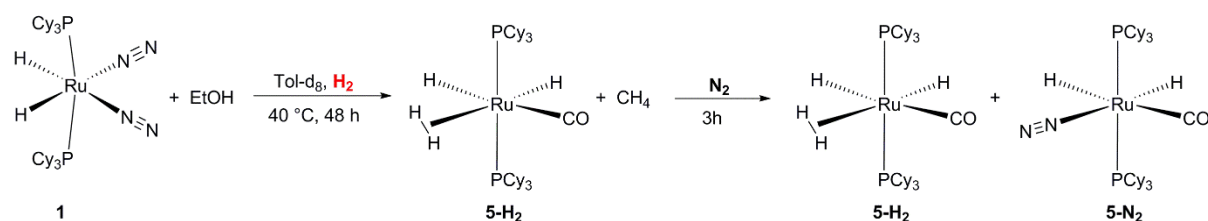


Figure S 5.15. Previously identified $\{\text{Ru}(\text{PCy}_3)_2\}$ complexes relevant to by-product identification.

1.1.1.1 C–O Bond Activation of 2,6-Dimethoxyacetophenone with **1**



*Reaction of **1** with ethanol:* In a dinitrogen glovebox, [Ru(H)₂(N₂)₂(PCy₃)₂] (**1**) (200 μL, 0.07 M, 1 equiv) and ethanol (1 μL, 0.02 mmol, 1 equiv) were added by micropipette into a J. Young NMR tube and made up to 600 μL with Tol-D₈. The J. Young NMR tube was sealed and removed from the glovebox. The reaction mixture was subjected to a freeze-pump-thaw procedure and then exposed to a dihydrogen atmosphere (1 bar). The J. Young NMR tube was sealed and then heated at 40 °C for 48 h. A colour change from straw yellow to deep yellow was observed. The reaction was monitored by ¹H-NMR and ³¹P{¹H}-NMR spectroscopy showing clean formation of **5-H₂** and methane. The J. Young tube was taken back into the glovebox and left open to the dinitrogen atmosphere for 3 h. ¹H-NMR and ³¹P{¹H}-NMR spectroscopy showed a mixture of both **5-H₂** and **5-N₂** as the products.

In situ NMR data for **5-H₂**: ¹H-NMR (Tol-D₈, 400 MHz, 233 K) δ/ppm: -7.08 (br s, 4H, RuH), 1.12 – 2.26 (m, 66H, Cy); ³¹P{¹H}-NMR (Tol-D₈, 162 MHz, 233K) δ/ppm: 71.57; isolated ¹³C{¹H}-NMR data for **5-H₂**: ¹³C{¹H}-NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 27.2 (m, Cy), 28.2 (t, *J*_{CP} = 4.9 Hz, Cy), 30.6 (m, Cy), 38.6 (¹*J*_{CP} = 10.5 Hz, Cy), 204.5 (t, ²*J*_{CP} = 8.3 Hz, C=O).

[Literature data for **5-H₂**:⁹ ¹H-NMR (C₆D₆, 400 MHz, 301 K) δ/ppm: -7.0 (br s, 4H, RuH), 2.28 – 1.29 (m, 66H, Cy); ³¹P{¹H}-NMR (C₆D₆, 162 MHz, 301K) δ/ppm: 72.1; ¹³C{¹H}-NMR (C₆D₆, 100 MHz, 301 K) δ/ppm: 27.0 (s, Cy), 28.0 (t, *J*_{CP} = 5.1 Hz), 30.3 (s, Cy), 38.3 (t, *J*_{CP} = 10.7 Hz), 204.2 (t, *J*_{CP} = 3.7 Hz, C=O)].

In situ NMR data for **5-N₂**: ¹H-NMR (Tol-D₈, 400 MHz, 233 K) δ/ppm: -13.51 (td, *J*_{HP} = 21.4 Hz and *J*_{HH} = 6.6 Hz, 1H, RuH), -6.68 (td, *J*_{HP} = 23.4 Hz and *J*_{HH} = 6.3 Hz, RuH) 1.03 – 2.38 (m, 66H, Cy); ³¹P{¹H}-NMR (Tol-D₈, 162 MHz, 233K) δ/ppm: 63.86; isolated ¹³C{¹H} NMR data for **5-N₂**: ¹³C{¹H}-NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 27.1 (m, Cy), 28.2 (t, *J*_{CP} = 4.8 Hz, Cy), 30.4 (m, Cy), 37.9 (t, ¹*J*_{CP} = 8.2 Hz, Cy), 205.6 (m, C=O).

Comparison of the multinuclear NMR data allowed identification of **5-N₂** as the major by-product of C–O cleavage of 2,6-dimethoxyacetophenone.

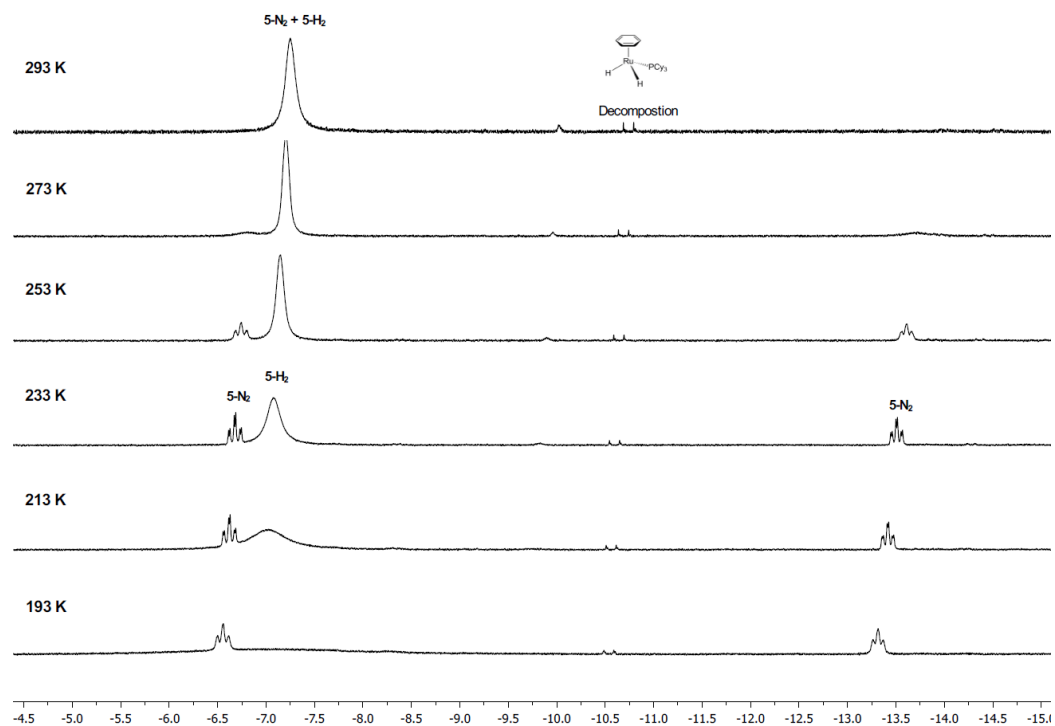


Figure S 5.16. VT ^1H -NMR on a mixed sample of **5-N₂** and **5-H₂** generated from the reaction of **1** and EtOH dissolved in Tol-D₈. Only Ru-H region shown for clarity.

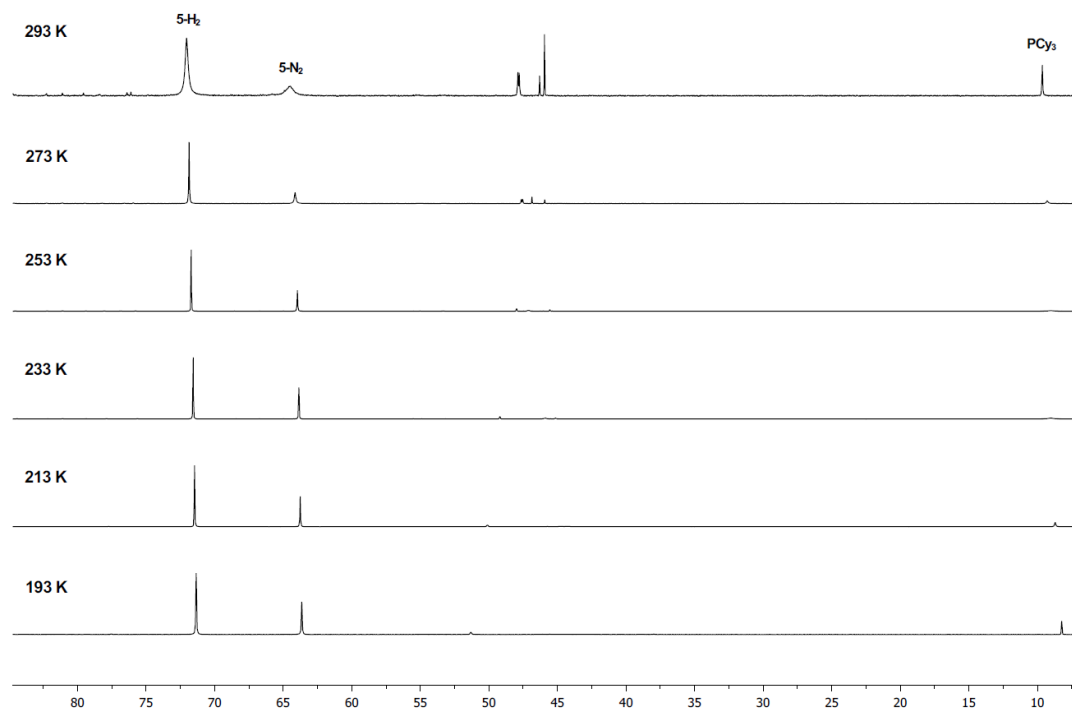


Figure S 5.17. VT $^{31}\text{P}\{^1\text{H}\}$ -NMR on a mixed sample of **5-N₂** and **5-H₂** generated from the reaction of **1** and EtOH dissolved in Tol-D₈.

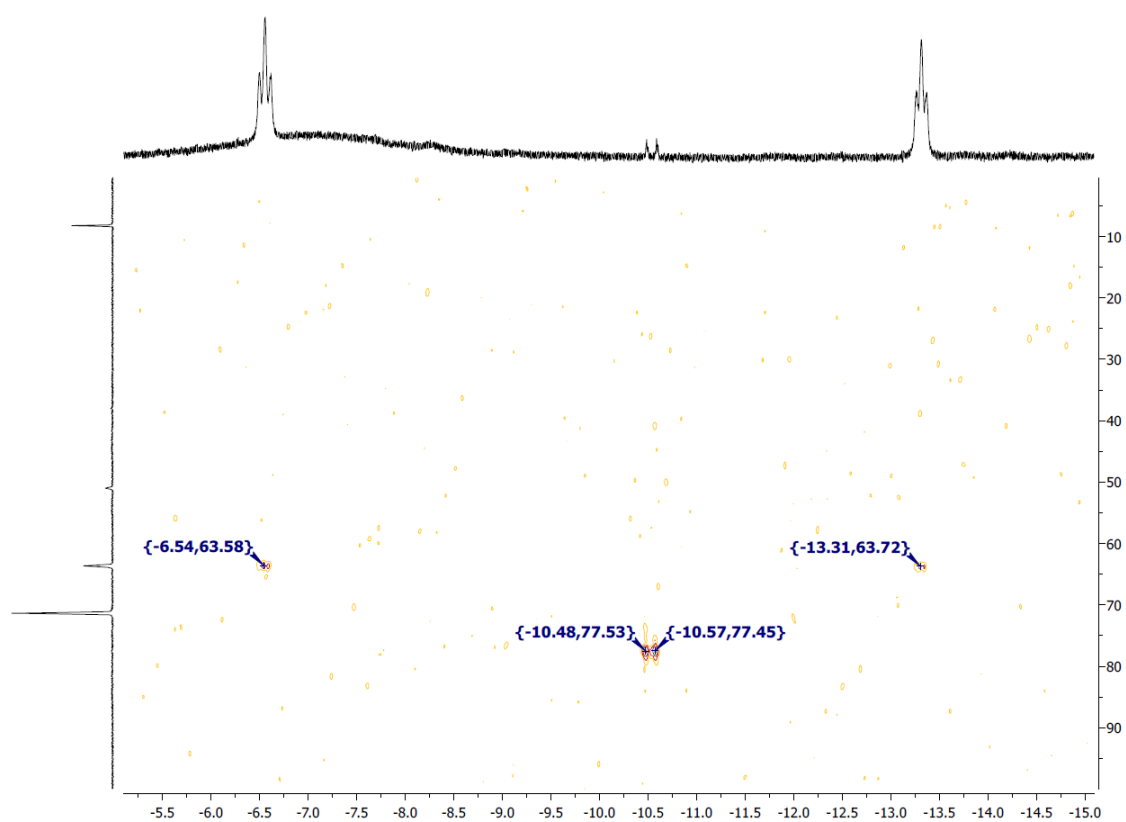
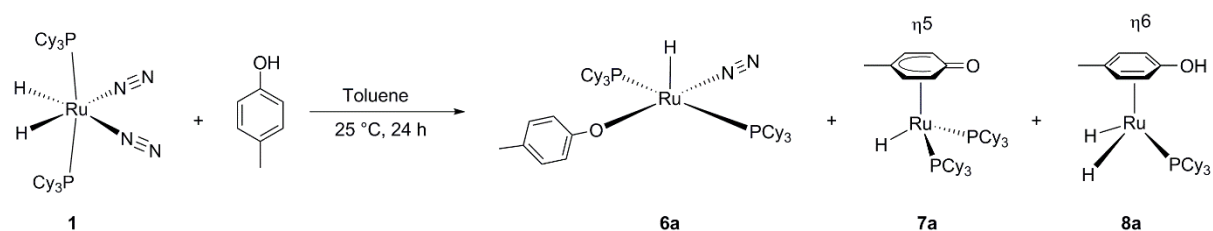


Figure S 5.18. $^1\text{H}-^{31}\text{P}\{^1\text{H}\}$ HMBC on a mixed sample of **5-N₂** and **5-H₂** generated from the reaction of **1** and EtOH at 193 K dissolved in Tol-D₈

1.1.1.2 C–O Bond Activation of 2,6-bis-*p*-tolyoxy(phenyl)acetophenone with **1**

In order to identify the major by-product during C–O bond activation of 2,6-bis-*p*-tolyoxy(phenyl)acetophenone with **1**, reactions were carried out with both 4-methylphenol and 4-*tert*-butylphenol. The latter was used as a surrogate for the former in order to facilitate product separation and purification by crystallization. A combination of NMR spectroscopy and single x-ray crystallography was used to determine the structures of the products from both the reaction of **1** with 4-methylphenol and 4-*tert*-butyl phenol.



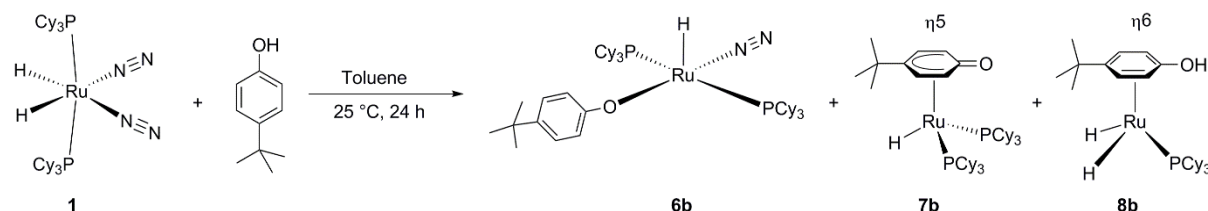
Reaction of **1 with 4-methylphenol:** In a dinitrogen glovebox, [Ru(H)₂(N₂)₂(PCy₃)₂] (**1**) (54 mg, 0.08 mmol, 1 equiv) and 4-methylphenol (9 mg, 0.08 mmol, 1 equiv) were weighed into a 20 mL scintillation vial and dissolved in toluene (2 mL). The mixture was left to stir in the glovebox at 25 °C for 24 h. A colour change from straw yellow to deep orange/brown was observed. The solvent was removed *in vacuo* to leave a brown oily residue which was extracted with n-hexane (2 mL) resulting in a yellow precipitate forming in the brown solution. The yellow precipitate was isolated and washed with cold pentane (1 mL) and left to dry to give a yellow powder as a mixed product of **7a/8a** (22 mg). The mother liquor from this reaction was reduced *in vacuo* to give a brown powder as **6a** contaminated with the decomposition product [Ru(H)₂(η⁶-C₆D₆)PCy₃].¹¹ Multiple attempts to isolate **6a** cleanly were unsuccessful.

In situ NMR data for **6a**: ¹H-NMR (C₆D₆, 500 MHz, 298 K) δ/ppm: -25.86 (t, *J*_{HP} = 19.2 Hz, 1H, RuH); ³¹P{¹H}-NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 41.94.

NMR data for **7a**: ¹H NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: -11.51 (br s, 1H, RuH), 1.06 – 2.09 (m, 66H, Cy), 1.93 (s, 3H, CH₃), 5.01 (d, *J*_{HH} = 5.6 Hz, 2H, ArH_m), 5.16 (d, *J*_{HH} = 5.6 Hz, 2H, ArH_o); ¹³C{¹H} NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 27.1 (s, Cy), 28.3 (br s, Cy), 31.0 (m, Cy), 35.2 (CH₃), 77.3 (C_m), 95.8 (C_o), 137.0 (C_p), 163.0 (C=O); ³¹P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 50.44 (br).

NMR data for **8a**: ¹H NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: -11.51 (br s, 2H, RuH), 1.06 – 2.09 (m, 33H, Cy), 2.16 (s, 3H, CH₃), 7.05 (d, *J*_{HH} = 8.1 Hz, 2H, ArH_m), 7.38 (d, *J*_{HH} = 7.9 Hz, 2H, ArH_o), 11.66 (s, 1H, OH); ¹³C{¹H} NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 20.4 (CH₃), 27.1 (s, Cy), 28.3 (br s, Cy), 31.0 (m, Cy), 116.0 (C_o), 127.0 (C_p), 128.3 (C_i), 130 (C_o); ³¹P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 50.44 (br).

Comparison of the multinuclear NMR data (including those for reaction of 4-*tert*-butyl phenol below) allowed identification of **6a** as the major by-product of C–O cleavage of 2,6-bis-*p*-tolylxy(phenyl)acetophenone.



Reaction of 1 with 4-*tert*-butyl phenol: In a dinitrogen glovebox, [Ru(H)₂(N₂)₂(PCy₃)₂] (**1**) (33 mg, 0.05 mmol, 1 equiv) and 4-*tert*-butyl phenol (8 mg, 0.05 mmol, 1 equiv) were weighed into a scintillation vial and dissolved in toluene (2 mL). The mixture was left to stir in the glovebox at 25 °C for 24 h. A colour change from straw yellow to deep orange/red was observed. The solvent was removed *in vacuo* to leave a dark red oily residue which was extracted with hexane (2 mL) resulting in a yellow precipitate forming in an orange solution. The yellow precipitate was isolated and washed with cold pentane (1 mL) and left to dry to give a yellow powder as a mixed product of **7b/8b** (<10 mg). The mother liquor from this reaction was left in glovebox freezer at -35 °C overnight to give red crystals **6b** (15 mg, 49 %).

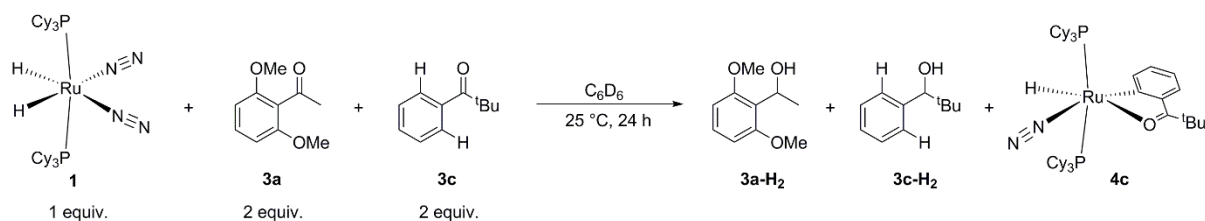
NMR data for **6b**: ¹H NMR (Tol-D₈, 500 MHz, 298 K) δ/ppm: -25.80 (t, *J*_{HP} = 18.7 Hz, 1H, RuH), 1.03 – 2.30 (m, 66H, Cy), 1.39 (s, 9H, C(CH₃)₃), 6.67 (d, *J*_{HH} = 8.6 Hz, 2H, ArH_m), 7.27 (d, *J*_{HH} = 8.7 Hz, 2H, ArH_o); ¹³C{¹H} NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 27.13 (s, Cy), 28.2 (m, Cy), 30.3 (s, Cy), 30.8 (s, Cy), 32.3 (C(CH₃)₃), 33.6 (t, ¹*J*_{CP} = 8.4 Hz, Cy), 33.9 (C(CH₃)₃), 118.5 (C_o), 125.9 (C_m), 135.2 (C_p), 167.0 (C–O); ³¹P{¹H} NMR (Tol-D₈, 162 MHz, 298 K) δ/ppm: 41.9. FT-IR (ν/cm⁻¹): 1893 (Ru–H), 2044 (N≡N).

NMR data for **7b**: ¹H NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: -11.09 (br s, 1H, RuH), 0.97 (s, 9H, C(CH₃)₃), 1.06 – 2.35 (m, 66H, Cy), 5.30 (d, *J*_{HH} = 7.0 Hz, 2H, ArH_o), 5.44 (d, *J*_{HH} = 6.8 Hz, 2H, ArH_m); ¹³C{¹H} NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 31.7 (C(CH₃)₃), 33.8 (C(CH₃)₃), 84.1 (C_o), 96.3 (C_m), 111.0 (C_p), 164.5 (C=O); ³¹P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 75.1.

NMR data for **8b**: ¹H NMR (400 MHz, C₆D₆, 298 K) δ/ppm: -11.07 (d, *J*_{HP} = 17.0 Hz, 2H, RuH), 1.06 – 2.35 (m, 33H, Cy), 1.26 (s, 9H, (C(CH₃)₃), 7.23 (m, 4H, ArH), 10.11 (s, 1H, OH); ¹³C{¹H} NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 31.9 (C(CH₃)₃), 34.0 (C(CH₃)₃), 115.8 (C_m), 126.4 (C_o), 141.1 (C_p), 156.7 (C–OH); ³¹P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 75.1.

¹ The remaining ¹³C resonances of the PCy₃ ligands could not be assigned due to the overlapping signals in the mixture of **8a/8b** which could not be resolved by HSQC, HMBC or DEPT NMR experiments.

5.3.7 Competition and Inhibition Reactions

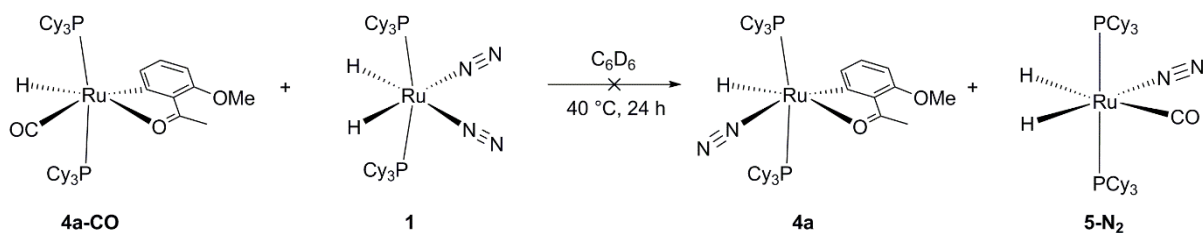


Intermolecular C–H bond versus C–O bond activation: In a dinitrogen glovebox, [Ru(H)₂(N₂)₂(PCy₃)₂] (**1**) (200 μ L, 0.07 M, C₆D₆, 1 equiv), 2,6-dimethoxyacetophenone (**3a**) (120 μ L, 0.23 M, C₆D₆, 2 equiv), 2,2-dimethylpropiophenone (4.7 μ L, 0.028 mmol, C₆D₆, 2 equiv) and ferrocene (80 μ L, 0.17 M, 1 equiv) were added by micropipette into a J. Young NMR tube and the solvent volume was made up to 600 μ L with C₆D₆. The J. Young NMR tube was sealed and the reaction left at 25 $^\circ$ C for 24 h with a colour change from straw yellow to deep red observed. The reaction was monitored by ¹H-NMR and ³¹P{¹H}-NMR spectroscopy and yields calculated against the internal standard-ferrocene. **4c** was observed at >99 % yield, **3c-H₂** was observed in 59 % yield and **3a-H₂** was observed in 27 % yield.

In situ NMR data for **4c**: ¹H NMR (C₆D₆, 400 MHz, 298 K) δ /ppm: –14.76 (t, $J_{\text{HP}} = 25.7$ Hz, 1H, RuH), 0.86 – 1.03 (m, 6H, Cy), 1.20 – 1.35 (m, 12H, Cy), 1.40 – 2.00 (m, 42H, Cy), 1.52 (s, 9H, C(CH₃)₃), 2.10 – 2.25 (m, 6H, Cy), 6.77 (t, $J_{\text{HH}} = 7.4$ Hz, 1H, ArH_m), 7.00 (m, 1H, ArH_p), 7.96 (dd, $J_{\text{HH}} = 8.1$ Hz and 1.3 Hz, 1H, ArH_o), 8.21 (d, $J_{\text{HH}} = 7.6$ Hz, 1H, ArH_m); ¹³C{¹H} NMR (C₆D₆, 125 MHz, 298 K) δ /ppm: 27.4 (m, Cy), 29.3 (C(CH₃)₃), 29.7 (s, Cy), 30.1 (s, Cy), 36.1 (t, $^1J_{\text{CP}} = 8.4$ Hz), 43.6 (C(CH₃)₃), 117.8 (C_m), 128.7 (C_p), 130.5 (C_o), 144.9 (C_m), 209.6 (Ru–C), 211.4 (C=O); ³¹P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ /ppm: 36.9. FT-IR (ν/cm^{–1}): 2046 (Ru–H), 2089 (N≡N). **Elemental Analysis** calc. for C₄₇H₈₀N₂O₂P₂Ru C, 66.24; H 9.46; N, 3.29 found C, 66.33; H, 9.27; N, 3.15.

In situ NMR data for **3c-H₂**: ¹H NMR (C₆D₆, 400 MHz, 298 K) δ /ppm: 0.91 (s, 9H, C(CH₃)₃), 4.05 (d, $J_{\text{HH}} = 2.9$ Hz, 1H, CH), 7.09–7.21 (m, 5H, ArH); ¹³C{¹H} NMR (C₆D₆, 125 MHz, 298 K) δ /ppm: 26.1 (C(CH₃)₃), 35.6 (C(CH₃)₃), 82.13 (CH), 128.0 (C_{Ar}).

In situ NMR data for **3a-H₂** same as above.

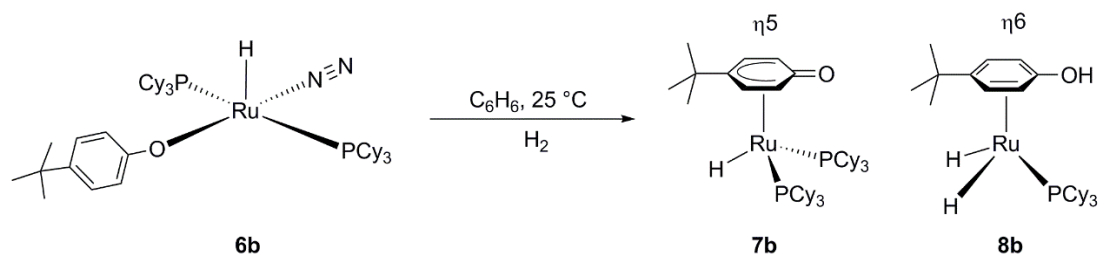


Complexation of CO versus N₂ to ruthenium: In a dinitrogen glovebox, [RuH(N₂)(*o*-C₆H₄C(O)OMe)(PCy₃)₂] (**4a**) (5 mg, 0.006 mmol) was weighed and dissolved in C₆D₆ (500 μL) and transferred into a J. Young NMR tube. A ferrocene internal standard capillary insert was added to the J. Young NMR tube. The J. Young NMR tube was sealed and removed from the glovebox. The reaction mixture was subjected to a freeze-pump-thaw procedure and then exposed to a CO atmosphere (1.05 bar) resulting in an immediate colour change from orange to straw yellow. ¹H and ³¹P{¹H}-NMR confirmed full conversion of **4a** into [RuH(CO)(*o*-C₆H₄C(O)OMe)(PCy₃)₂] (**4a-CO**). The solvent and excess CO was removed *in vacuo* leaving a yellow solid. [RuH₂(N₂)₂(PCy₃)₂] (**1**) (100 μL, 0.07 M) was added by micropipette into the J. Young NMR tube and the solution volume was made up to 500 μL with C₆D₆ then the reaction mixture was heated at 40 °C for 24 h. The reaction was monitored by ¹H-NMR and ³¹P{¹H}-NMR spectroscopy and yields calculated against the internal standard. **4a** was observed at <10 % yield.

In situ NMR data for **4a-CO**: ¹H NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: −15.19 (t, *J*_{HP} = 23.4 Hz, 1H, RuH), 0.91 – 2.37 (m, 66H, Cy), 2.88 (s, 3H, CH₃), 3.36 (s, 3H, OCH₃), 6.21 (d, *J*_{HH} = 7.8 Hz, 1H, ArH_m), 7.12 (t, *J*_{HH} = 7.4 Hz, 1H, ArH_p), 8.00 (d, *J*_{HH} = 7.1 Hz, 1H, ArH_m); ³¹P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 41.9.

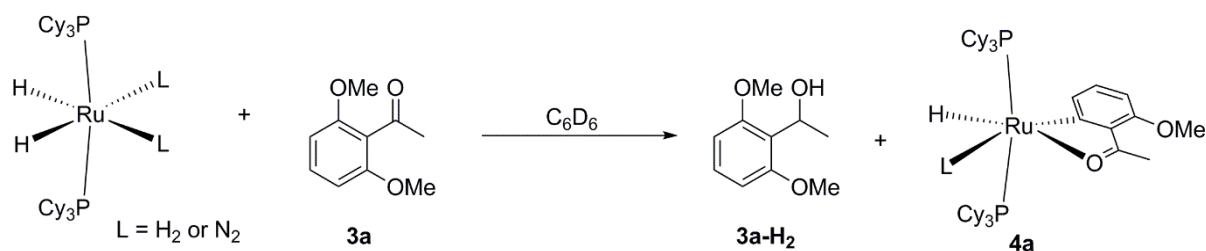
In situ NMR data for **4a** same as above.

In situ NMR data for **5-N₂** same as above.



Conversion of 6b into 7b and 8b: In a dinitrogen glovebox, $[\text{RuH}(\kappa^1\text{-OC}_6\text{H}_5\text{C}(\text{CH}_3)_3)(\text{N}_2)(\text{PCy}_3)_2]$ (**6b**) (15 mg, 0.02 mmol) was dissolved in benzene (1.8 mL) and transferred into a J. Young NMR tube along with ferrocene (50 μL , 0.17 M). The J. Young NMR tube was sealed and removed from the glovebox. The reaction mixture was subjected to a freeze-pump-thaw procedure and then exposed to a dihydrogen atmosphere (1.01 bar). The reaction was monitored by ^1H -NMR and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy and yields calculated against ferrocene showing the conversion of **6b** into **7b** and **8b**.

In situ NMR data for **6b**, **7b** and **8b** same as above.

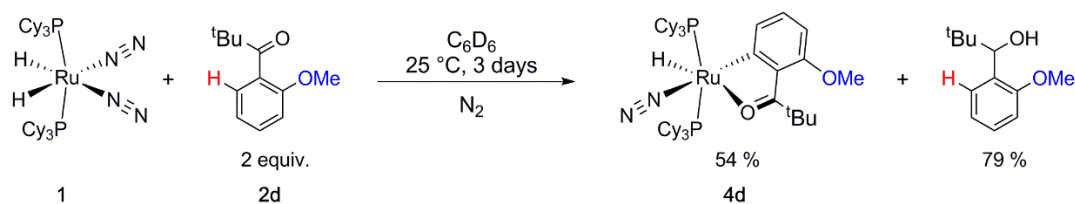


[Ru] complex	Ru : 3a	Temp / °C	Time / h	Atmosphere	Yield 4a / %	$T_{1/2}$ / h ^a
$[\text{Ru}(\text{H})_2(\text{N}_2)_2(\text{PCy}_3)_2]$	1 : 2	25	72	N ₂	35	n/a
$[\text{Ru}(\text{H})_2(\text{N}_2)_2(\text{PCy}_3)_2]$	1 : 2	40	24	N ₂	52	6.0
$[\text{Ru}(\text{H})_2(\text{N}_2)_2(\text{PCy}_3)_2]$	1 : 2	40	5	Ar	50	1.6
$[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$	1 : 2	25	24	H ₂	0	n/a
$[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$	1 : 2	25	24	Ar	0	n/a
$[\text{Ru}(\text{H})_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$	1 : 4	25	24	Ar	0	n/a

^a Time taken for 25 % of **4a** to form in C–O cleavage reaction

Table S 5.1. Comparison of C–O cleavage reactions under different conditions.

5.3.8 Directing group



Reaction of **1 with **2d**:** In a dinitrogen glovebox, [Ru(H)₂(N₂)₂(PCy₃)₂] (**1**) (200 μL, 0.07 M, C₆D₆, 1 equiv), 1-(2-methoxyphenyl)-2,2-dimethyl-1-propanone (**2d**) (120 μL, 0.23 M, C₆D₆, 2 equiv) and ferrocene (80 μL, 0.17 M, C₆D₆, 1 equiv) were added by micropipette into a J. Young NMR tube and the solvent volume was made up to 600 μL with C₆D₆. The J. Young NMR tube was sealed and the reaction left at 25 °C for 3 days with a colour change from straw yellow to orange observed. The reaction was monitored by ¹H-NMR and ³¹P{¹H}-NMR spectroscopy and yields calculated against internal standards; ferrocene for ¹H-NMR.

In situ NMR data for **4d:** ¹H NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: −14.16 (t, *J*_{HP} = 26.2 Hz, 1H, RuH), 1.23 – 2.24 (m, 6H, Cy), 1.65 (s, 9H, C(CH₃)₃), 3.39 (s, 3H, OCH₃), 6.08 (d, *J*_{HH} = 7.8 Hz, 1H, ArH_m), 7.02 (t, *J*_{HH} = 7.9 Hz, 1H, ArH_p), 7.87 (d, *J*_{HH} = 7.3 Hz, 1H, ArH_m); ¹³C{¹H} NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 26.9 (C(CH₃)₃), 27.8 (m, Cy), 28.0 (s, Cy), 30.0 (s, Cy), 37.1 (m, Cy), 45.4 (C(CH₃)₃), 53.2 (OCH₃), 101.0 (C_m), 134.96 (C_p), 137.9 (C_m), 210.80 (C=O), 211.4 (Ru–C); ³¹P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ/ppm: 36.5.

In situ NMR data for **2d-H₂:** ¹H NMR (C₆D₆, 400 MHz, 298 K) δ/ppm: 1.04 (s, 9H, C(CH₃)₃), 3.23 (s, 3H, OCH₃), 4.88 (d, *J*_{HH} = 5.0 Hz, 1H, CH), 6.50 (d, *J*_{HH} = 8.2 Hz, 1H, ArH_m), 6.88 (m, 1H, ArH_m), 7.07 (m, 1H, ArH_p), 7.41 (dd, *J*_{HH} = 7.6 Hz and 1.6 Hz, 1H, ArH_o); ¹³C{¹H} NMR (C₆D₆, 125 MHz, 298 K) δ/ppm: 26.2 (C(CH₃)₃), 44.7 (C(CH₃)₃), 54.6 (OCH₃), 76.1 (CH), 111.1 (C_m), 120.4 (C_m), 129.6 (C_o), 155.7 (COCH₃).

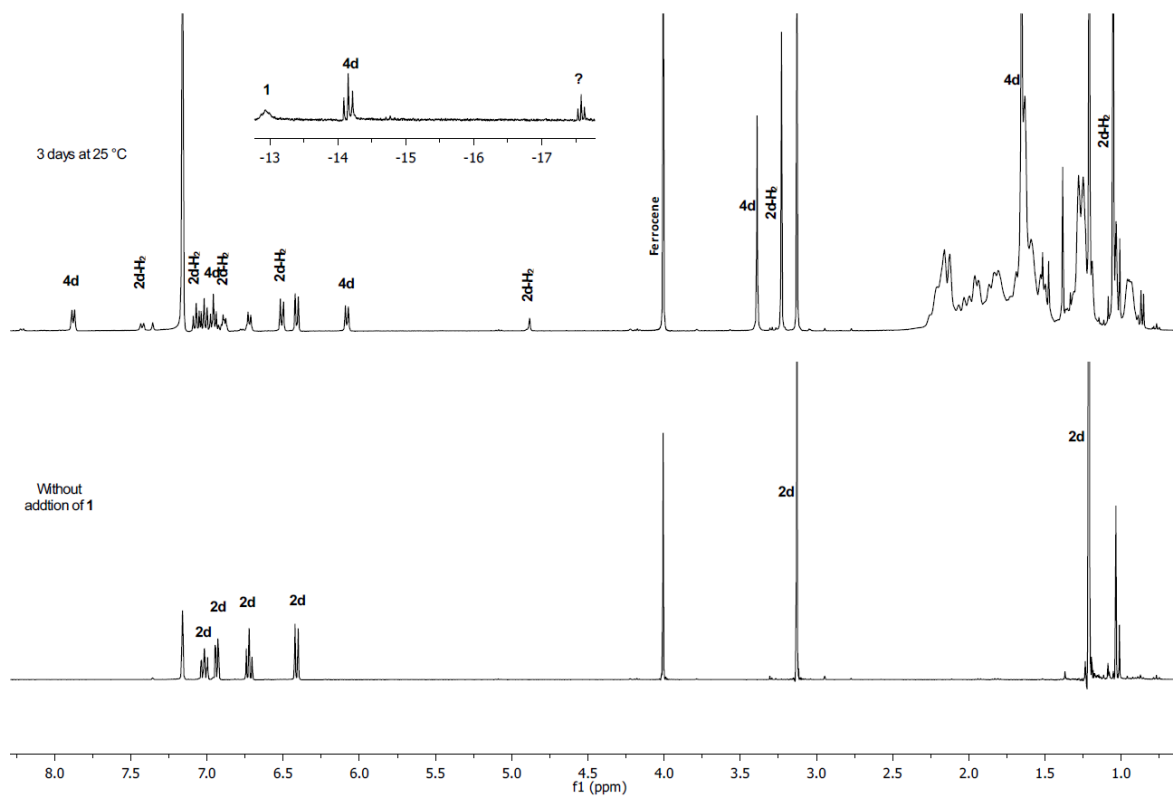


Figure S 5.19. ^1H NMR (C_6D_6 , 400 MHz, 298 K) stack plot for C–H activation of 1-(2-methoxyphenyl)-2,2-dimethyl-1-propanone

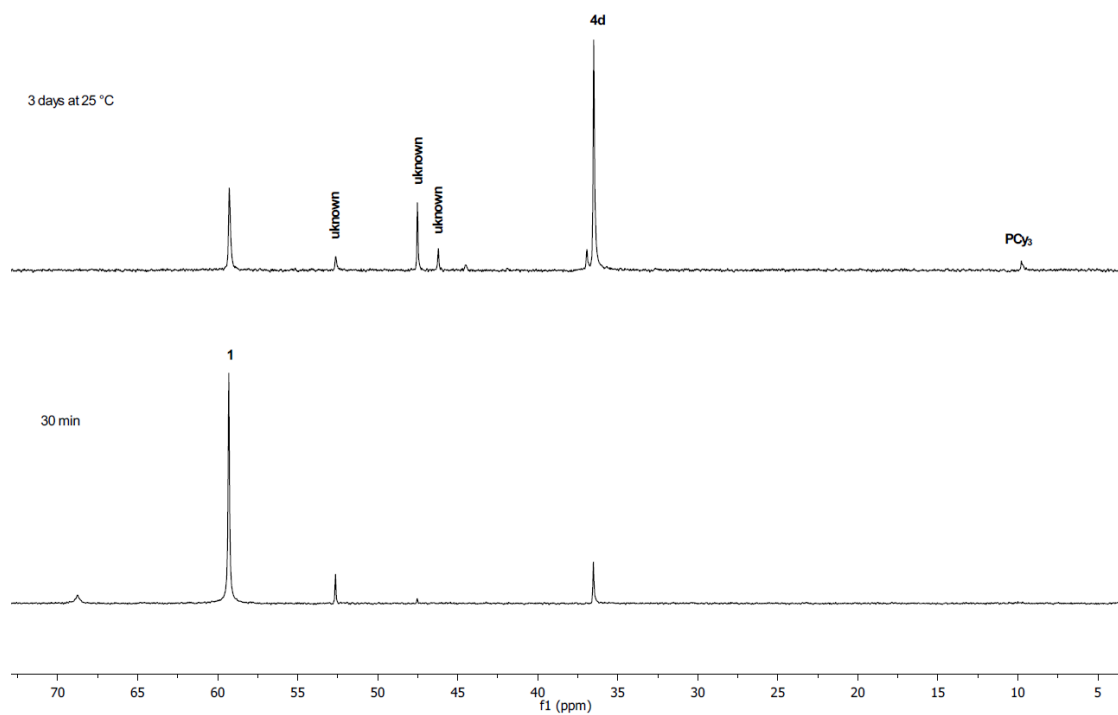
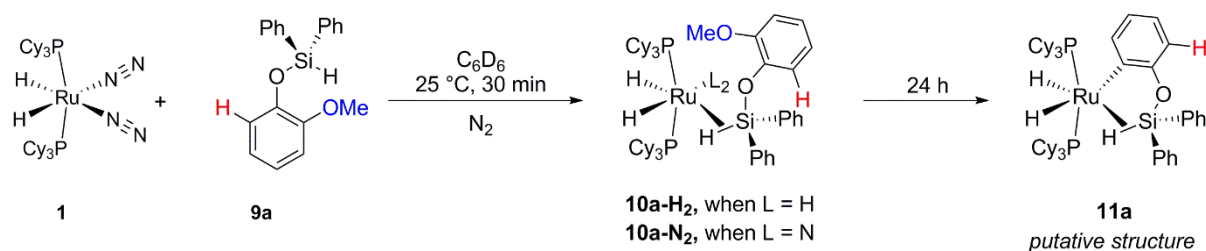


Figure S 5.20. ^{31}P $\{^1\text{H}\}$ NMR (C_6D_6 , 400 MHz, 298 K) stack plot for C–H activation of 1-(2-methoxyphenyl)-2,2-dimethyl-1-propanone



Reaction of 1 with 9a: In a dinitrogen glovebox, $[\text{Ru}(\text{H})_2(\text{N}_2)_2(\text{PCy}_3)_2]$ (**1**) (10 mg, 0.01 mmol), and (2-methoxyphenoxy)diphenylsilane (**9a**) (4.2 mg, 0.01 mmol) were dissolved in C_6D_6 (600 μL) and transferred into J. Young NMR tube. Reaction was left at 25 $^\circ\text{C}$ and monitored by ^1H and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy.

In situ NMR data for **10a-H₂**: ^1H NMR (Tol- D_8 , 400 MHz, 298 K) δ/ppm : -8.48 (br s, 3H, RuH and RuSiH), 0.88–1.97 (m, 66H, Cy), 3.52 (s, 3H, CH_3), 6.65 (m, 3H, ArH), 6.90 (d, $J_{\text{HH}} = 7.6$ Hz, 1H, ArH_m), 7.13 (m, 2H, Ph), 7.25 (m, 4H, Ph), 8.04 (m, 4H, Ph); $^{13}\text{C}\{^1\text{H}\}$ -NMR (Tol- D_8 , 125 MHz, 298 K) δ/ppm : 27.3 (Cy), 28.2 (Cy), 30.5 (Cy), 38.4 (Cy), 55.9 (CH_3), 113.2 (Ar), 119.6 (Ar), 121.2 (Ar), 121.4 (Ar), 127.1 (Ph), 127.5 (Ph), 135.3 (Ph), 148.1 (C(O)Si), 150.9 (SiC), 152.4 (C(OCH₃)); $^{31}\text{P}\{^1\text{H}\}$ NMR (Tol- D_8 , 162 MHz, 298 K) δ/ppm : 53.0; ^{29}Si (Tol- D_8 , 99 MHz, 298 K,) δ/ppm : 14.3. T_1 min (Tol- D_8 , 400 MHz) = 45.1 ms (Ru–H).

In situ ^1H NMR data for **10a-N₂** same as **10b-H₂**; $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz, 298 K) δ/ppm : 44.6

In situ NMR data for **11a**²: ^1H NMR (C_6D_6 , 400 MHz, 298 K) δ/ppm : -8.31 (td, 2H, $J_{\text{HP}} = 15.0$ Hz and $J_{\text{HH}} = 5.9$ Hz, RuH), -8.88 (br s, 1H, RuSiH); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz, 298 K) δ/ppm : 76.5; ^{29}Si (Tol- D_8 , 99 MHz, 298 K,) δ/ppm : 40.6.

² NMR data incomplete as product never isolated cleanly

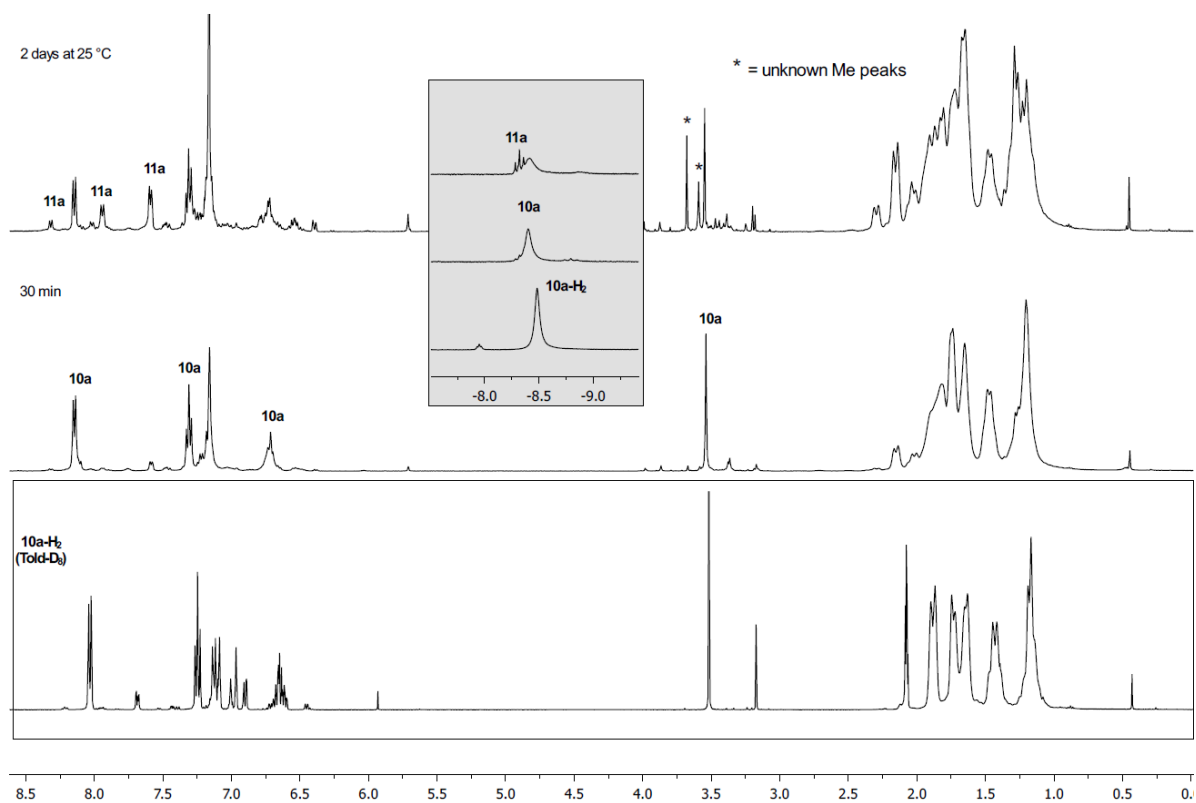


Figure S 5.21. ^1H NMR (C_6D_6 , 400 MHz, 298 K) (Bottom) 10a-H₂. (Top and middle) stack plot of reaction **1** with **9a**.

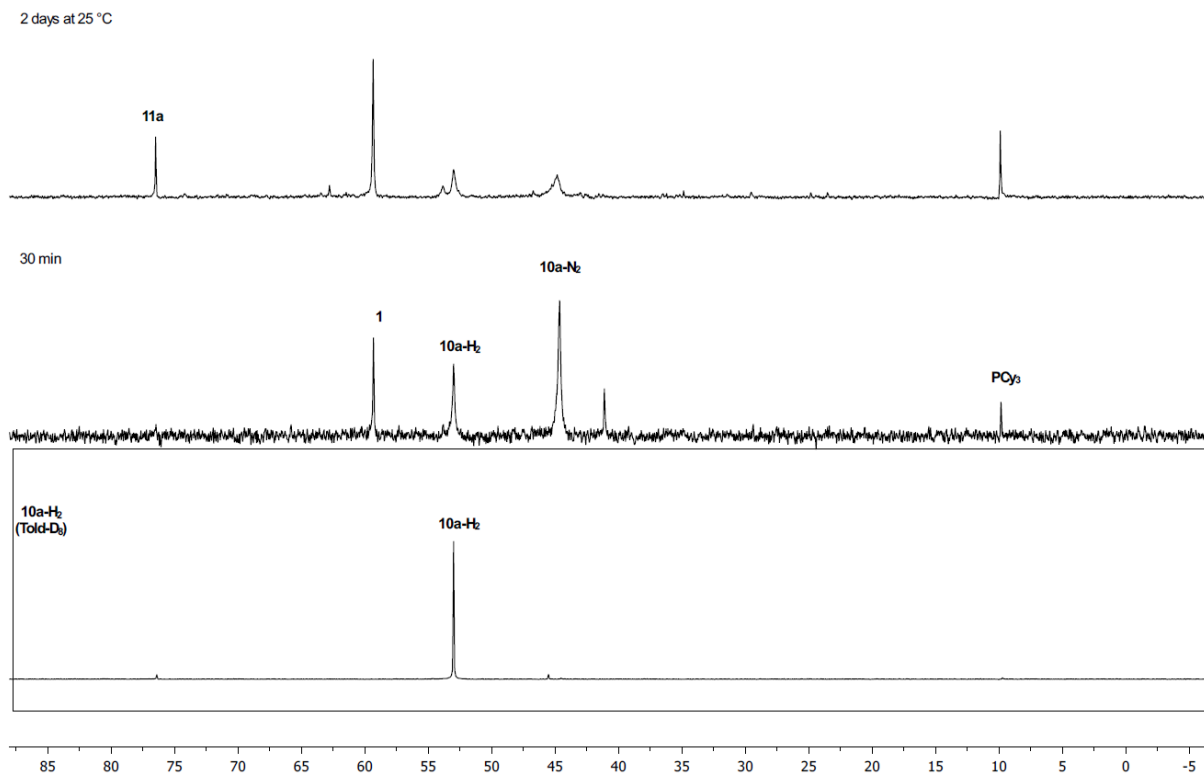
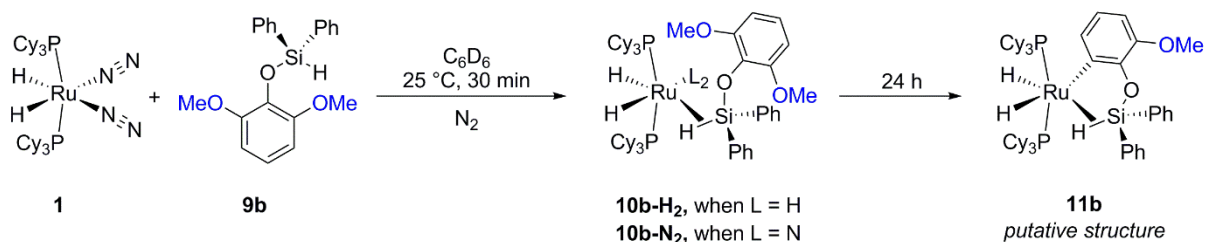


Figure S 5.22. ^{31}P $\{^1\text{H}\}$ NMR (C_6D_6 , 400 MHz, 298 K) (Bottom) 10a-H₂. (Top and middle) stack plot of reaction **1** with **9a**.



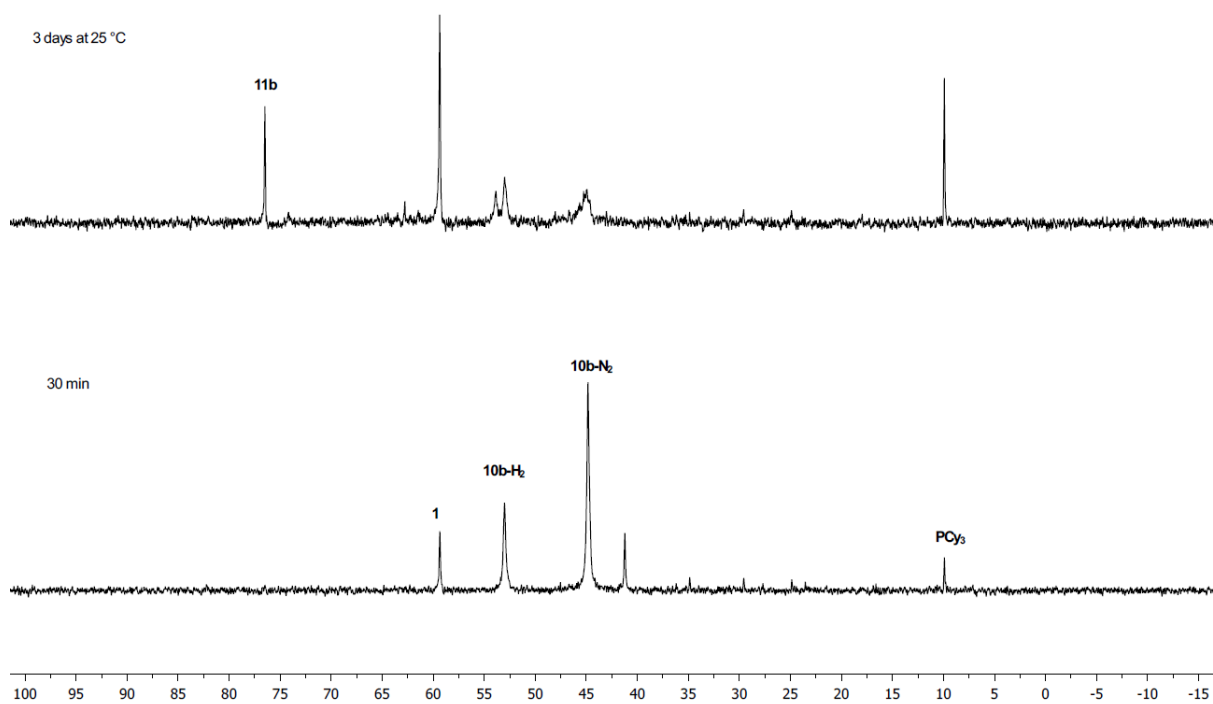
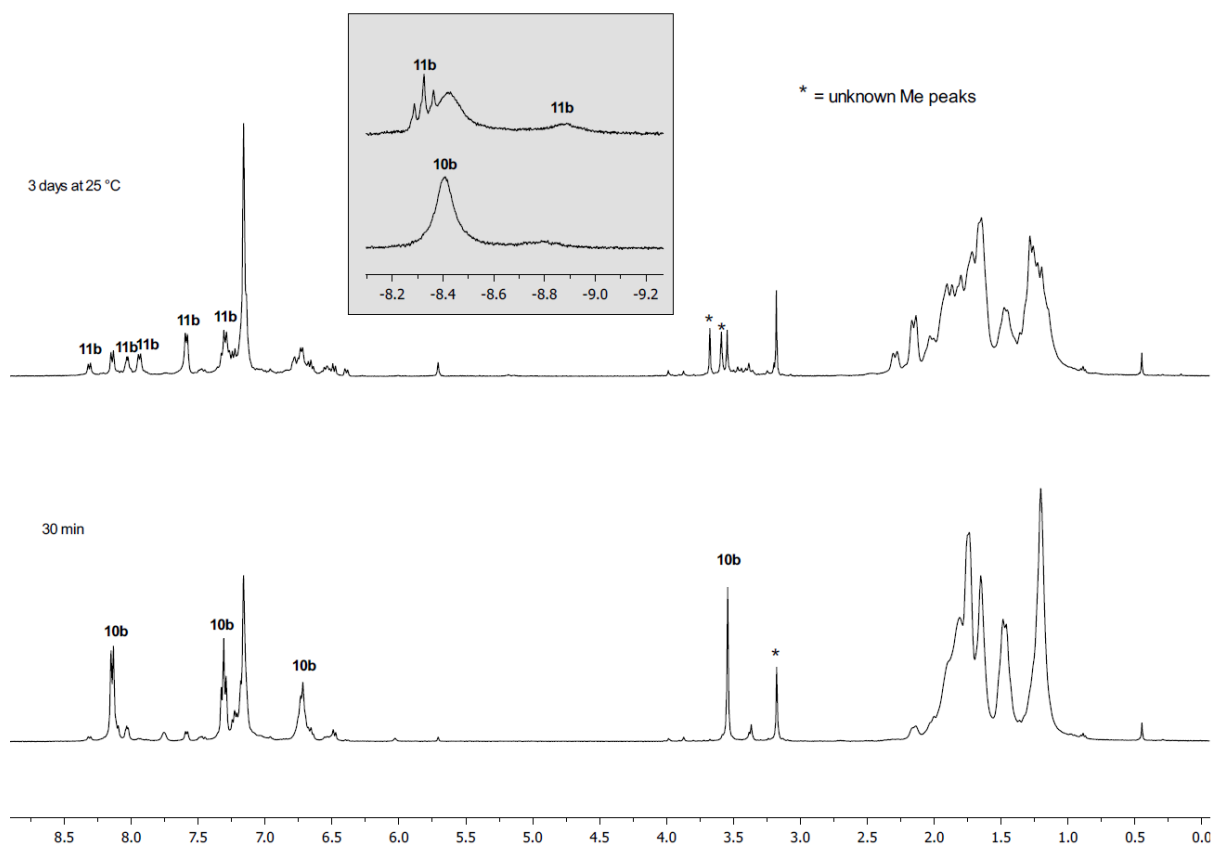
Reaction of 1 with 9b: In a dinitrogen glovebox, $[Ru(H)_2(N_2)_2(PCy_3)_2]$ (**1**) (10 mg, 0.01 mmol), and (2,6-dimethoxyphenoxy)diphenylsilane (**9b**) (4.7 mg, 0.01 mmol) were dissolved in C_6D_6 (600 μL) and transferred into J. Young NMR tube. Reaction was left at $25\text{ }^{\circ}\text{C}$ and monitored by ^1H and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy.

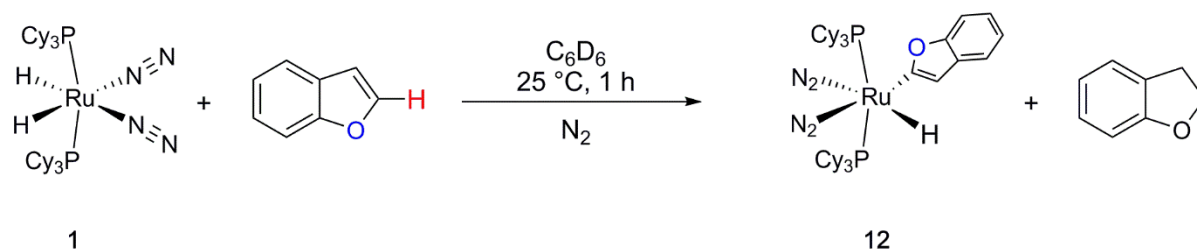
In situ NMR data for **10b-H₂**³: ^1H NMR (C_6D_6 , 400 MHz, 298 K) δ/ppm : -8.49 (br s, 3H, RuH and RuSiH), 0.96–2.08 (m, 66H, Cy), 3.27 (s, 6H, OCH₃), 6.37 (d, $J_{HH} = 8.2\text{ Hz}$, 2H, ArH_m), 6.73 (t, $J_{HH} = 7.1\text{ Hz}$, 1H, ArH_p), 7.30 (t, $J_{HH} = 7.4\text{ Hz}$, 4H, Ph), 7.87 (m, 2H, Ph), 8.12 (d, $J_{HH} = 7.4\text{ Hz}$, 4H, Ph); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz, 298 K) δ/ppm : 53.0.

In situ ^1H NMR data for **10b-N₂** same as **10b-H₂**; $^{31}\text{P}\{^1\text{H}\}$ NMR (Tol-D₈, 162 MHz, 298 K) δ/ppm : 44.7.

In situ NMR data for **11b**: ^1H -NMR (C_6D_6 , 400 MHz, 298 K) δ/ppm : -8.26 (td, 2H, $J_{HP} = 15.0\text{ Hz}$ and $J_{HH} = 2.9\text{ Hz}$, RuH), -8.49 (br s, 1H, RuSiH); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz, 298 K) δ/ppm : 77.4; ^{29}Si (Tol-D₈, 99 MHz, 298 K,) δ/ppm : 46.8.

³ NMR for both **10a** and **11b** incomplete





Reaction of **1 with benzofuran:** In a dinitrogen glovebox, [Ru(H)₂(N₂)₂(PCy₃)₂] (**1**) (10 mg, 0.01 mmol), and benzofuran (1.5 μ L, 0.01 mmol) were dissolved in C₆D₆ (600 μ L) and transferred into J. Young NMR tube. Reaction was left at 25 °C and monitored by ¹H and ³¹P{¹H}-NMR spectroscopy.

In situ NMR data for **12:** ¹H NMR (C₆D₆, 400 MHz, 298 K) δ /ppm: -15.58 (br s, 1H, RuH), 0.98–1.30 (m, 20H, Cy), 1.53–1.77 (m, 28H, Cy), 1.92–2.08 (m, 18H, Cy), 6.55 (s, 1H, CH), 7.01 (t, J_{HH} = 7.6 Hz, 1H, Ar_H), 7.06 (m, 1H, ArH), 7.51 (dd, J_{HH} = 7.6 and 2.3 Hz, 2H, ArH); ³¹P{¹H} NMR (C₆D₆, 162 MHz, 298 K) δ /ppm: 41.2.

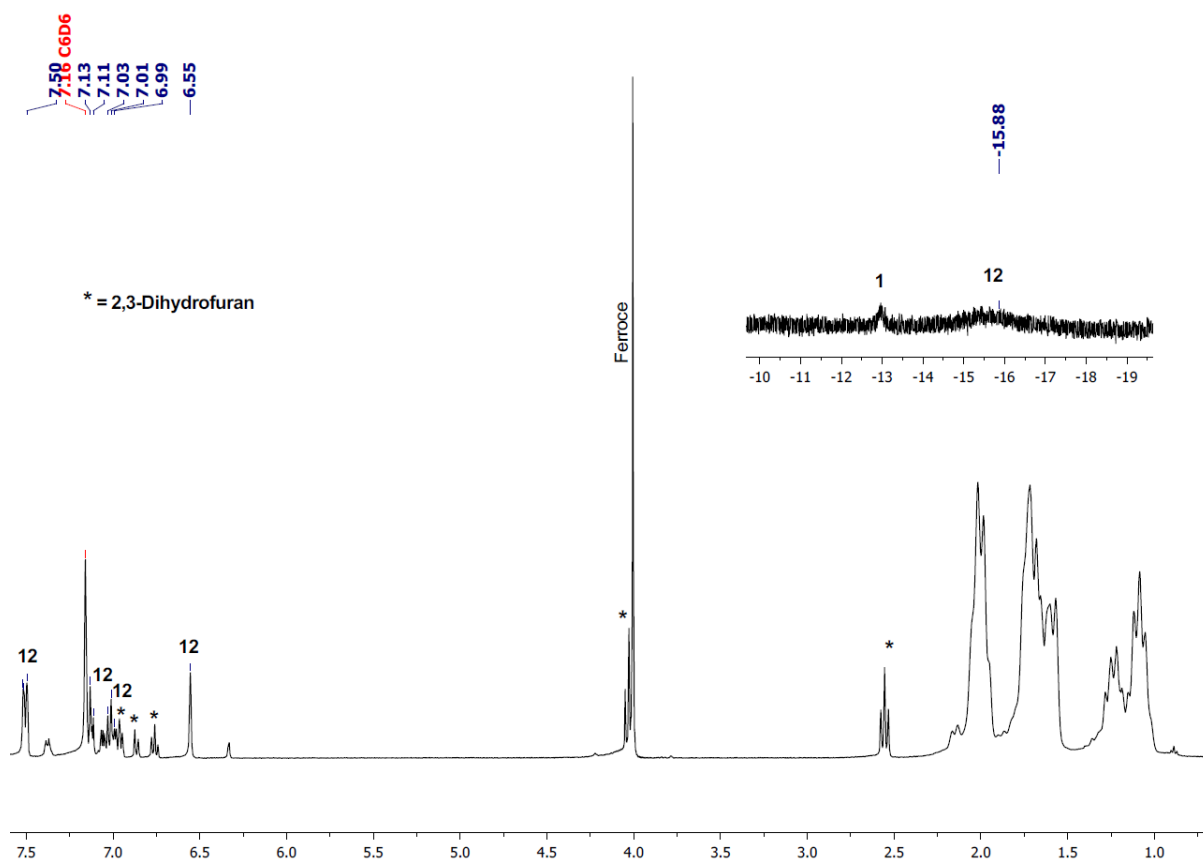


Figure S 5.25. ¹H NMR (C₆D₆, 400 MHz, 298 K) reaction of **1** with benzofuran

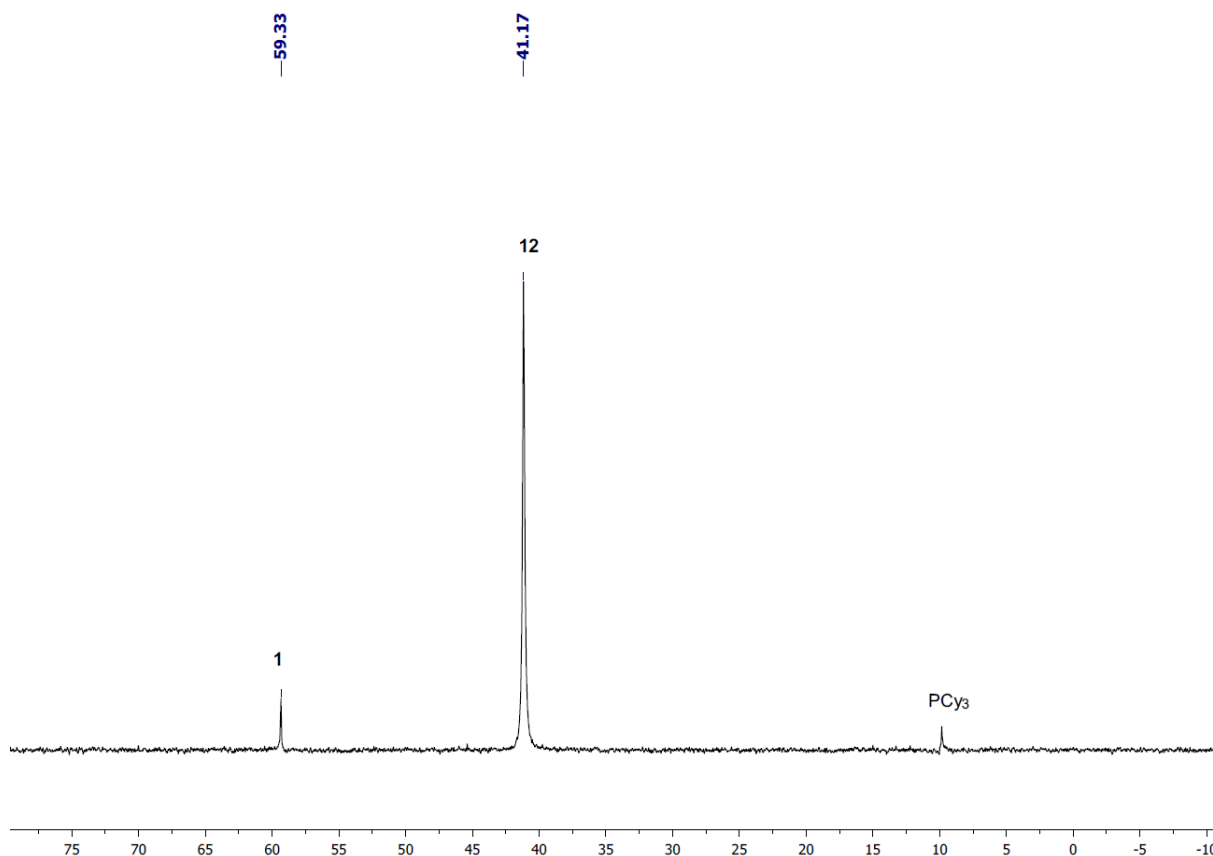
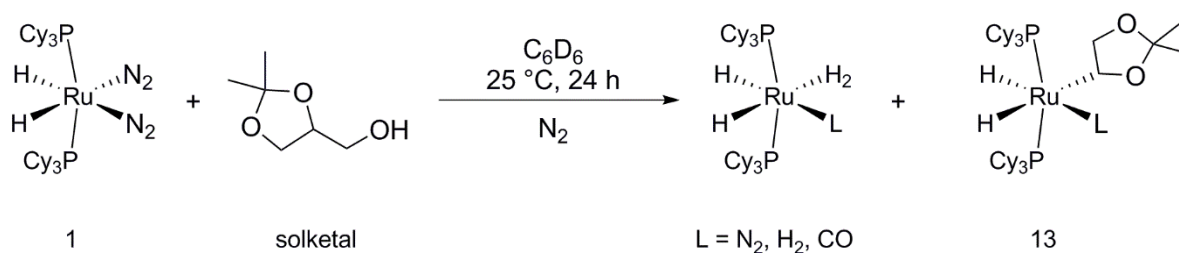


Figure S 5.26. ^{31}P $\{^1\text{H}\}$ NMR (C_6D_6 , 400 MHz, 298 K) reaction of **1** with benzofuran



Reaction of **1 with solketal:** In a dinitrogen glovebox, $[\text{Ru}(\text{H})_2(\text{N}_2)_2(\text{PCy}_3)_2]$ (**1**) (10 mg, 0.01 mmol), and solketal (2.0 μL , 0.01 mmol) were dissolved in C_6D_6 (600 μL) and transferred into J. Young NMR tube. Reaction was left at 25 $^\circ\text{C}$ and monitored by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

In situ NMR data for **13:** ^1H NMR (C_6D_6 , 400 MHz, 298 K) δ/ppm : -7.06 (br s, 2H, RuH), 1.12–2.24 (m, 66H, Cy), 2.08 (s, 6H, $\text{C}(\text{CH}_3)_2$), 3.52 (s, 2H, CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz, 298 K) δ/ppm : 71.9.

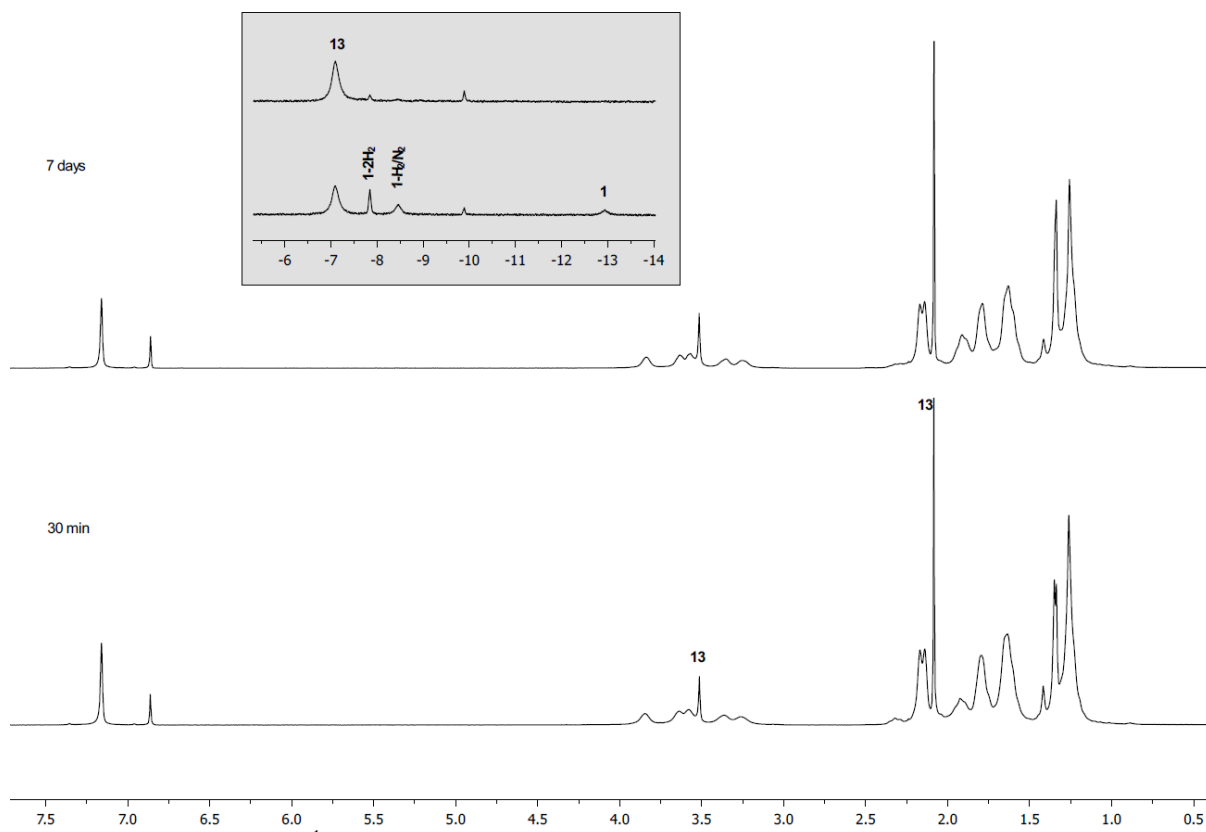


Figure S 5.27. ^1H NMR (C_6D_6 , 400 MHz, 298 K) stack plot of reaction **1** with solketal

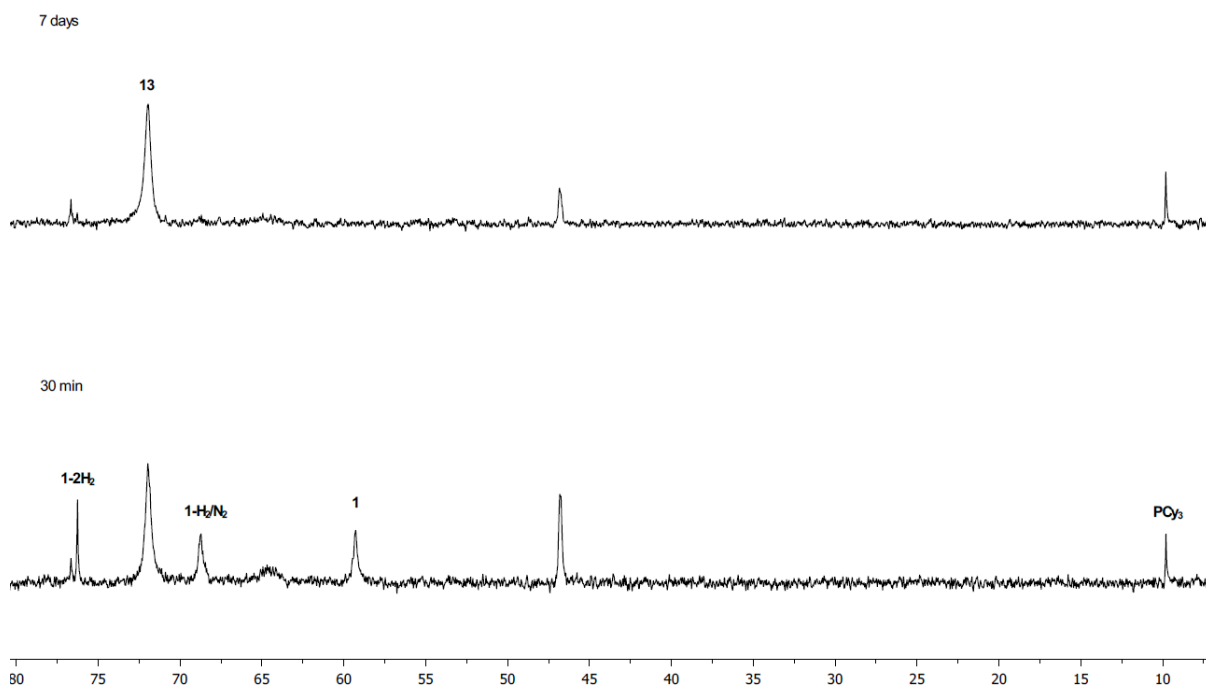


Figure S 5.28. ^{31}P $\{^1\text{H}\}$ NMR (C_6D_6 , 400 MHz, 298 K) stack plot of reaction **1** with solketal

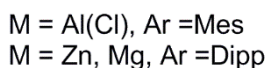
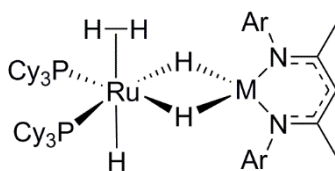
5.4 CHAPTER THREE: EXPERIMENTAL

5.4.1 Materials

The synthesis of the pro-ligands *Mes*BDIH¹² and *Dipp*BDIH,¹² and the series of β -diketiminate stabilised main group complexes: *Mes*BDIAl(H)(Cl),¹³ *Dipp*BDIMgH,¹⁴ *Dipp*BDIZnH¹⁵ and *Dipp*BDICaH¹⁶ were all prepared according to literature procedures. Solvents were freeze-pump-thaw degassed and stored over 3 Å molecular sieves prior to use. Chemicals purchased from Sigma Aldrich, Alfa Aesar and Fluorochem and used without further purification unless stated.

5.4.2 Synthesis of Heterobimetallics

1.1.1.3 M•Ru-H₂



Synthesis of M•Ru-H₂: In a dinitrogen glovebox, *Ar*BDIMH (Al = 56 mg, Zn = 67 mg, Mg = 62 mg, 0.14 mmol, 1 equiv) and **1** (100 mg, 0.14 mmol, 1 equiv) were weighed into a scintillation vial and dissolved in toluene (2 mL). The reaction mixture was left to stir overnight at 25 °C. The solvent was removed *in vacuo* to give an oily substance which was triturated with pentane (3 × 2 mL) until a solid was obtained. The solid was redissolved in toluene (600 μ L) and transferred into a J. Young NMR tube. The reaction mixture was subjected to freeze-pump-thaw procedure then H₂ (1 atm.) was added to the tube to cleanly form the **M•Ru-H₂** complexes.⁴ Solvent removed *in vacuo* and the resulting oil was triturated with cold pentane till a powdery solid was isolated (**Al**: 35 mg, 47 %; **Zn**: 42 mg; 52 % **Mg**; 42 mg, 54 %).

Al•Ru-H₂

¹H NMR (Tol-D₈, 400 MHz, 298K) δ /ppm: -10.85 (br s, 5H, Ru-H), 1.04–1.47 (m, 32H, Cy), 1.56 (s, 6H, CCH₃), 1.67–1.94 (m, 34H, Cy), 2.19 (s, 6H, *p*-ArCH₃), 2.37 (s, 6H, *o*-ArCH₃), 2.73 (s, 6H, *o*-ArCH₃), 5.33 (s, 1H, CH), 6.82 (s, 2H, ArH_m), 6.86 (s, 2H, ArH_m).

³¹P{¹H} NMR (Tol-D₈, 162 MHz, 298K) δ /ppm: δ 55.9 (br s).

⁴ Due to the sensitivity of **M•Ru-H₂** complexes, repeated attempts to acquire CHN analysis failed to provide satisfactory results

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 298 K, Tol-D₈) δ /ppm: 20.9 (*o*-ArCH₃), 21.1 (*p*-ArCH₃), 21.3 (*o*-ArCH₃), 23.9 (CCH₃), 27.2 (Cy), 28.4 (Cy), 30.9 (Cy), 38.8 (Cy), 101.9 (CH), 130.5 (C_m), 141.8 (C_p), 144.8 (C_o), 161.0 (C_i), 168.3 (NCCH₃).

T₁ minimum (Tol-D₈, 400 MHz, 273 K) = 36 ms (combined Ru–H and H–H).

Zn•Ru-H₂

^1H NMR (Tol-D₈, 400 MHz, 298K) δ /ppm: –10.32 (br s, 5H, Ru–H), 1.14–1.30 (m, 26H, Cy), 1.21 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, CH(CH₃)₂), 1.48 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, CH(CH₃)₂), 1.59 (s, 6H, CCH₃), 1.61–1.92 (m, 40H, Cy), 3.40 (hept, 4H, $^3J_{\text{HH}} = 6.7$ Hz, CH(CH₃)₂), 4.95 (s, 1H, CH), 7.15 (m, 6H, ArH).

$^{13}\text{C}\{^1\text{H}\}$ NMR (Tol-D₈, 126 MHz, 298K) δ /ppm : 23.5 (C(CH₃)₂), 25.3 (CCH₃), 25.4 (C(CH₃)₂), 27.4 (Cy), 28.7 (Cy), 29.1 (C(CH₃)₂), 29.9 (Cy), 39.8 (Cy), 96.7 (CH), 123.6 (C_m), 125.8 (C_p), 142.1 (C_o), 147.5 (C_i), 168.4 (CCH₃).

^{31}P NMR (Tol-D₈, 162 MHz, 298K) δ /ppm: δ 59.6 (s).

T₁ minimum (Tol-D₈, 400 MHz, 253 K) = 35 ms (combined Ru–H and H–H).

Mg•Ru-H₂

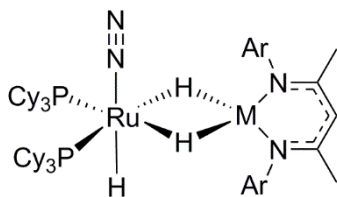
^1H NMR (Tol-D₈, 400 MHz, 298K) δ /ppm: –10.71 (br s, 5H, Ru–H), 1.13–1.27 (m, 26H, Cy), 1.21 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, CH(CH₃)₂), 1.50 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, CH(CH₃)₂), 1.57 (s, 6H, CCH₃), 1.63–1.93 (m, 40H, Cy), 3.33 (hept, 4H, $^3J_{\text{HH}} = 7.2$ Hz, CH(CH₃)₂), 4.91 (s, 1H, CH), 7.14 (m, 6H, ArH).

$^{13}\text{C}\{^1\text{H}\}$ NMR (Tol-D₈, 126 MHz, 298K) δ /ppm : 23.6 (C(CH₃)₂), 25.1 (CCH₃), 25.5 (C(CH₃)₂), 27.4 (Cy), 28.7 (Cy), 29.3 (C(CH₃)₂), 30.0 (Cy), 39.7 (Cy), 96.6 (CH), 123.6 (C_m), 125.7 (C_p), 142.0 (C_o), 147.2 (C_i), 169.7 (CCH₃).

^{31}P NMR (Tol-D₈, 162 MHz, 298K) δ /ppm: δ 60.0 (s).

T₁ minimum (Tol-D₈, 400 MHz, 193 K) = 52 ms (combined Ru–H and H–H).

1.1.1.4 M•Ru-N₂



M = Al(Cl), Ar = Mes
M = Zn, Mg, Ar = Dipp

Synthesis of **M•Ru-N₂**: In a dinitrogen glovebox, ^{Ar}*BDIMH* (Al = 56 mg, Zn = 67 mg, Mg = 62 mg, 0.14 mmol, 1 equiv) and **1** (100 mg, 0.14 mmol, 1 equiv) were weighed into a scintillation vial and dissolved in toluene (2 mL). The reaction mixture was left to stir overnight at 25 °C. The solvent was removed *in vacuo* to give an oily substance which was extracted with pentane (3 × 2 mL) until a solid was obtained. The solid was redissolved in mixture of toluene (1 mL) and pentane (1 mL) and filtered through micro-glass fibre into a scintillation vial then left to slowly evaporate in the glovebox atmosphere. Crystals suitable for X-ray crystallography were obtained as yellow blocks for **Zn•Ru-N₂** and **Mg•Ru-N₂** and as colourless blocks for **Al•Ru-N₂**. Clean formation and/or separation of **M•Ru-N₂** from **M•Ru-H₂** and **M•Ru** was unsuccessful after multiple methods of synthesis and attempts.⁵

Al•Ru-N₂

In situ ¹H NMR (C₆D₆, 400 MHz, 298K) δ/ppm: −15.81 (br s, 1H, Ru–H), −11.95 (br, 2H, Ru–H), 1.18–1.56 (m, 30H, Cy), 1.60 (s, 6H, CCH₃), 1.66 (m, 36H, Cy), 2.22 (s, 6H, ArCH₃), 2.45 (br s, 6H, ArCH₃), 2.80 (s, 6H, ArCH₃), 5.46 (s, 1H, CH), 6.87 (s, 2H, ArH), 6.90 (s, 2H, ArH).

In situ ³¹P-NMR (C₆D₆, 162 MHz, 298K) δ/ppm: δ 51.8 (br s), 38.5 (br s).

T₁ minimum (Tol-D₈, 400 MHz, 273 K) = 214 ms (Ru–H) and 232 ms (Ru–H).

FT-IR (ν/cm^{−1}) = 2160 (N≡N) and 1606 (Ru–H).

Zn•Ru-N₂

In situ ¹H NMR (Tol-D₈, 500 MHz, 273K) δ/ppm: −15.67 (tt, ²J_{HP} = 21.1 Hz and ²J_{HH} = 7.7 Hz, 1H, Ru–H), −11.35 (m, 2H, Ru–H); *In situ* ¹H NMR (Tol-D₈, 500 MHz, 298K) δ/ppm: −15.69 (m, 1H, Ru–H), −11.36 (m, 2H, Ru–H), 1.15–1.30 (m, 26H, Cy), 1.21 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 1.26 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 1.59 (s, 3H, CCH₃), 1.62 (s, 3H, CCH₃), 1.62–19.2 (m, 40H, Cy), 3.45 (m, 4H, CH(CH₃)₂), 4.88 (s, 1H, CH), 7.09–7.25 (m, 6H, ArH).

In situ ³¹P NMR (Tol-D₈, 162 MHz, 298K) δ/ppm: δ 46.6 (br s).

T₁ minimum (Tol-D₈, 400 MHz, 273 K) = 272 ms (Ru–H) and 347 ms (Ru–H).

FT-IR (ν/cm^{−1}) = 2135 (N≡N) and 1907 (Ru–H).

Mg•Ru-N₂

⁵ Unambiguous assignment of the ¹³C{¹H} NMR data was not possible as samples always contained a mixture of all three complexes.

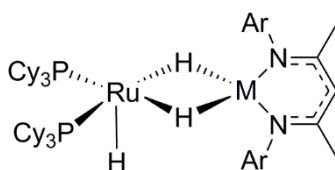
In situ ^1H NMR (Tol- D_8 , 500 MHz, 273K) δ/ppm : -15.17 (tt, $^2J_{\text{HP}} = 17.8$ Hz and $^2J_{\text{HH}} = 9.2$ Hz, 1H, Ru-H), -12.77 (m, 2H, Ru-H); **In situ ^1H NMR (Tol- D_8 , 400 MHz, 298K) δ/ppm :** -15.20 (tt, 1H, $^2J_{\text{HP}} = 17.9$ Hz and $^2J_{\text{HH}} = 9.4$ Hz, Ru-H), -11.40 (m, 2H, Ru-H), 1.19 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.19 – 1.23 (m, 26H, Cy), 1.25 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.50 (s, 6H, CCH_3), 1.58 – 2.03 (m, 40H, Cy), 3.40 (hept, 4H, $^3J_{\text{HH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 4.86 (s, 1H, CH), 7.08 – 7.20 (m, 6H, ArH).

In situ ^{31}P NMR (Tol- D_8 , 162 MHz, 298K) δ/ppm : δ 45.6 (s).

T_1 minimum (Tol- D_8 , 400 MHz, 273 K) = 371 ms (Ru-H) and 471 ms (Ru-H).

FT-IR (ν/cm^{-1}) = 2130 ($\text{N}\equiv\text{N}$) and 1854 (Ru-H).

1.1.1.5 M•Ru



M = Al(Cl), Ar = Mes
M = Zn, Mg, Ar = Dipp

Synthesis of 5: In a dinitrogen glovebox, *DippBDIMH* (Zn = 6.7 mg, Mg = 6.2 mg 0.01 mmol, 1 equiv) and **1** (10 mg, 0.01 mmol, 1 equiv) were weighed into a scintillation vial and dissolved in C_6D_6 (600 μL) and then transferred into J. Young NMR tube and left overnight at 25 $^\circ\text{C}$. Clean formation and/or separation of the intermediate **M•Ru** from **M•Ru-N₂** and **M•Ru-H₂** was unsuccessful after multiple methods of synthesis and attempts.⁶

Zn•Ru

In situ ^1H NMR (Tol- D_8 , 500 MHz, 298K) δ/ppm : -10.80 (br s, 3H, Ru-H), 4.89 (s, 1H, CH).

In situ ^{31}P NMR (Tol- D_8 , 162 MHz, 298K) δ/ppm : 64.5 (s).

T_1 minimum (Tol- D_8 , 400 MHz, 233 K) = 49 ms (Ru-H).

Mg•Ru

In situ ^1H NMR (Tol- D_8 , 400 MHz, 298K) δ/ppm : -11.10 (br s, 3H, Ru-H), 4.81 (s, 1H, CH).

⁶ Unambiguous assignment of the ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra data was not possible as samples always contained a mixture of all three complexes

In situ ^{31}P NMR (Tol- D_8 , 162 MHz, 298K) δ/ppm : δ 69.3 (s).

T_1 minimum (Tol- D_8 , 400 MHz, 213 K) = 100 ms (Ru-H).

The short T_1 minimum measurements acquired for **Zn•Ru** and **Mg•Ru** complexes is postulated to be the result of an equilibrium existing between **M•Ru** and **M•Ru-H₂** species thereby averaging a shorter T_1 time than expected and/or a fluxional process between the bridging and terminal hydrides *via* a mechanism that goes through a ruthenium dihydrogen intermediate.

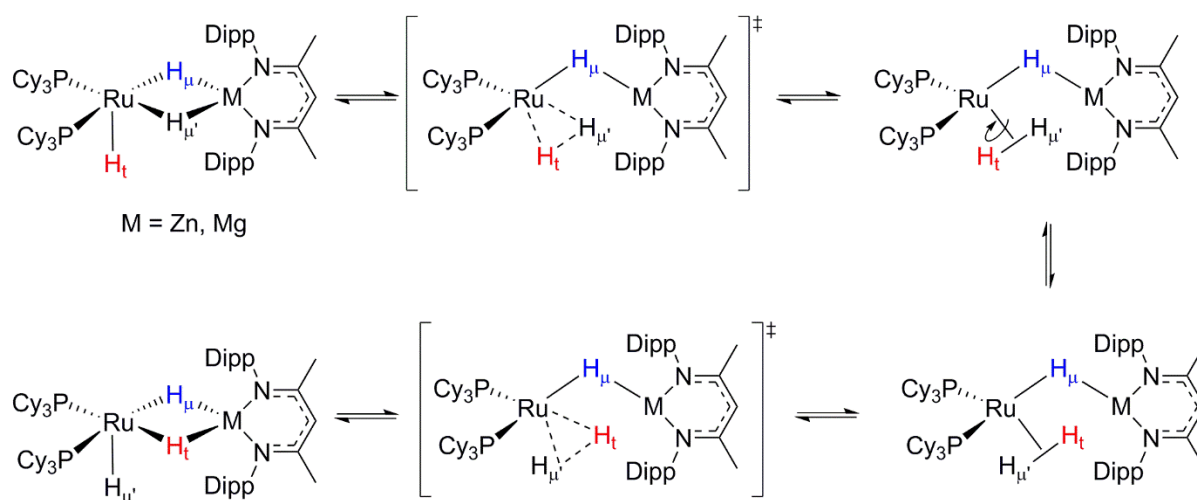
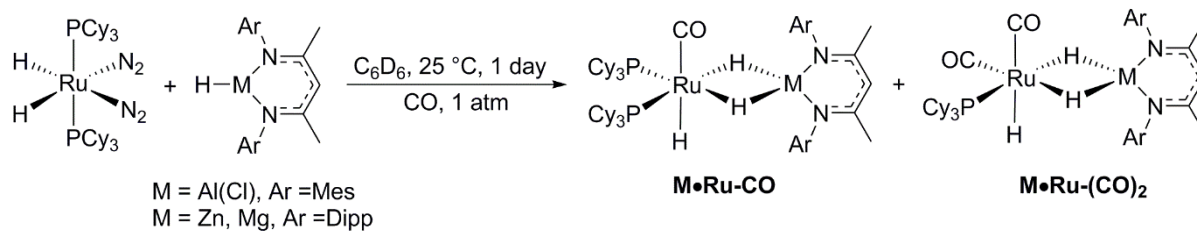


Figure S 5.29. Postulated exchange mechanism between the H_t and H_μ hydrides

5.4.3 Substitution reaction

1.1.1.6 CO



In dinitrogen glovebox **1** (200 μL , 0.07 M, C_6D_6) and $\text{BDI}^{\text{Ar}}\text{MH}$ (400 μl , 0.035 M, C_6D_6) were added into a J.Young NMR and left to react overnight at 25 °C. The reaction was checked to ensure all starting materials were consumed by NMR. Reaction was subjected to freeze-pump-thaw procedure $\times 3$ then

CO gas (1 atm) was added to the reaction. Formation of three new species observed in NMR: the previously reported $[\text{Ru}(\text{H})_2(\text{CO})_2(\text{PCy}_3)_2]$ ¹⁷ and complexes **M•Ru-CO** and **M•Ru(CO)₂**.⁷

Al•Ru-CO

In situ ¹H-NMR (C_6D_6 , 400 MHz, 298K) δ/ppm : -12.16 (m, 2H, Ru-H), -9.05 (s, Ru-H), 1.59 (s, 12H, C(CH_3)), 2.25 (s, 6H, CH_3), 2.80 (s, 6H, CH_3), 5.43 (s, 1H, CH), 6.93 (s, 4H, ArH).

In situ ³¹P-NMR (C_6D_6 , 162 MHz, 298K) δ/ppm : δ 59.2 (br s) and 40.9 (br s).

Al•Ru-(CO)₂

In situ ¹H NMR (C_6D_6 , 400 MHz, 298K) δ/ppm : -9.93 (br s, 2H, Ru-H), -9.39 (br d, ² J_{HP} = 55.6 Hz, 1H, Ru-H), 1.67 (s, 12H, C(CH_3)), 2.39 (s, 6H, CH_3), 2.74 (s, 6H, CH_3), 5.22 (s, 1H, CH), 6.89 (m, 4H, ArH).

In situ ³¹P NMR (C_6D_6 , 162 MHz, 298K) δ/ppm : δ 59.2 (s).

Zn•Ru-CO

In situ ¹H NMR (C_6D_6 , 400 MHz, 298K) δ/ppm : -12.08 (m, 2H, Ru-H), -9.13 (tt, ² J_{HP} = 21.1 Hz and ² J_{HH} = 8.0 Hz, 1H, Ru-H), 3.41 (m, 4H, CH(CH_3)₂), 4.96 (s, 1H, CH).

In situ ³¹P NMR (C_6D_6 , 162 MHz, 298K) δ/ppm : δ 51.3 (s).

Zn•Ru-(CO)₂

In situ ¹H NMR (C_6D_6 , 400 MHz, 298K) δ/ppm : -9.73 (dt, ² J_{HP} = 43.5 Hz and ² J_{HH} = 7.4 Hz, 1H, Ru-H), -9.52 (m, 2H, Ru-H), 3.35 (m, 4H, CH(CH_3)₂), 5.02 (s, 1H, CH).

In situ ³¹P NMR (C_6D_6 , 162 MHz, 298K) δ/ppm : δ 63.6 (s).

⁷ ¹H-NMR and ¹³C-NMR spectra assignment incomplete as sample always contained a mixture of heterobimetallic complexes

Mg•Ru-CO

***In situ* ^1H NMR (C_6D_6 , 400 MHz, 298K) δ/ppm :** -13.46 (m, 2H, Ru-*H*), -8.96 (td, $^2J_{\text{HP}} = 16.1$ Hz and $^2J_{\text{HH}} = 8.6$ Hz, 1H, Ru-H), 3.43 (m, 4H, CH(CH₃)₂), 4.92 (s, 1H, CH).

***In situ* ^{31}P NMR (C_6D_6 , 162 MHz, 298K) δ/ppm :** δ 49.3 (s).

Mg•Ru-(CO)₂

***In situ* ^1H NMR (C_6D_6 , 400 MHz, 298K) δ/ppm :** -10.85 (dt, $^2J_{\text{HP}} = 56.9$ Hz and $^2J_{\text{HH}} = 9.1$ Hz, 1H, Ru-*H*), -10.23 (m, 2H, Ru-H), 3.32 (m, 4H, CH(CH₃)₂), 5.00 (s, 1H, CH).

***In situ* ^{31}P NMR (C_6D_6 , 162 MHz, 298K) δ/ppm :** δ 63.8 (s).

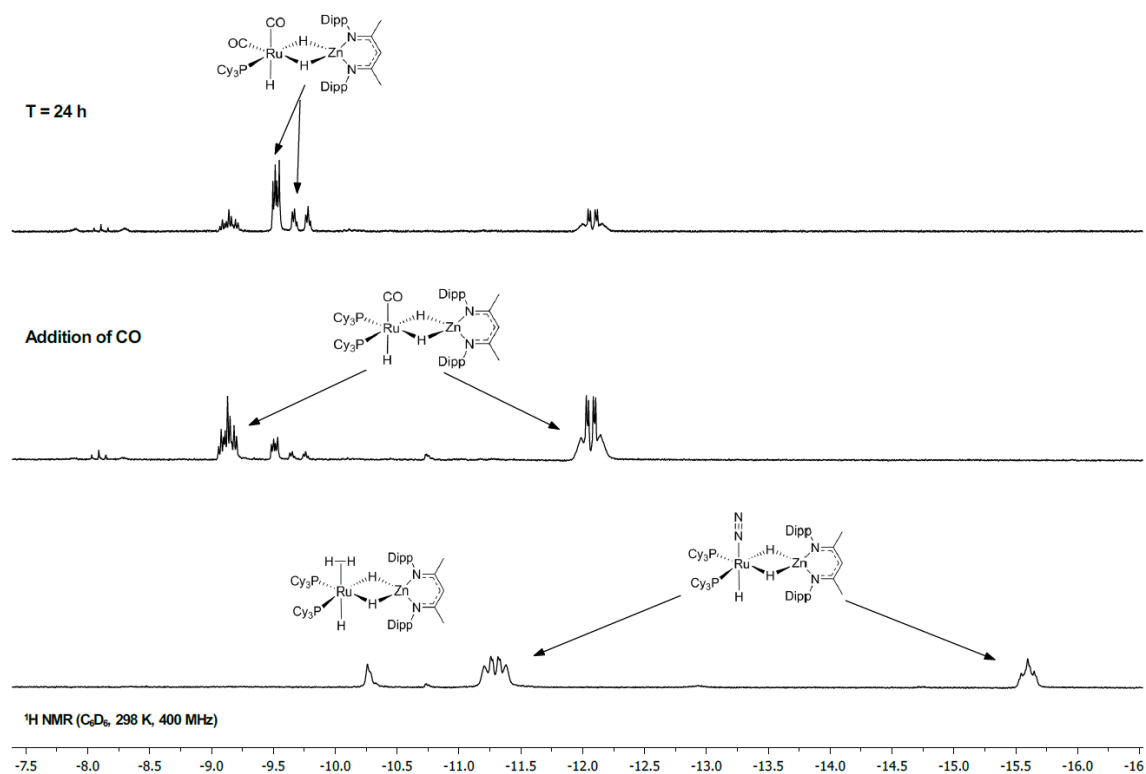


Figure S 5.30. ^1H NMR spectra stack plot of reaction of **Zn•Ru** heterobimetallic complexes with CO. Only Ru–H region shown for clarity.

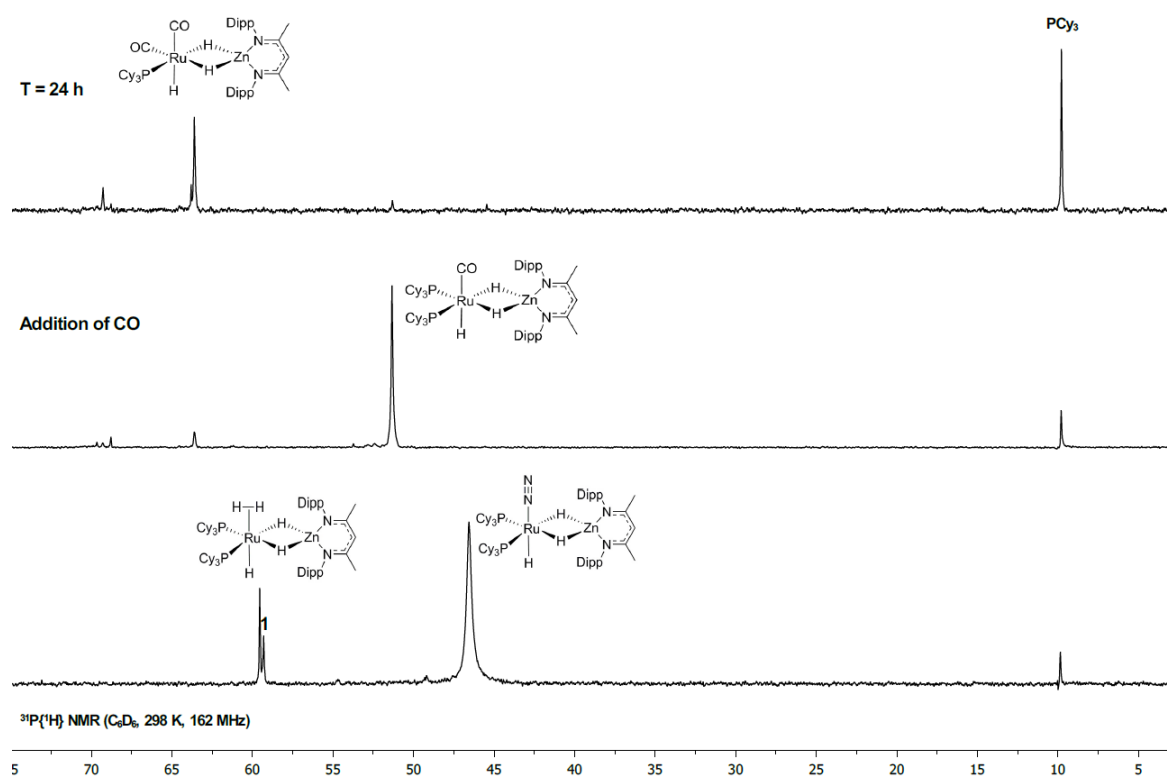


Figure S 5.31. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra stack plot of reaction of **Zn•Ru** heterobimetallic complexes with CO

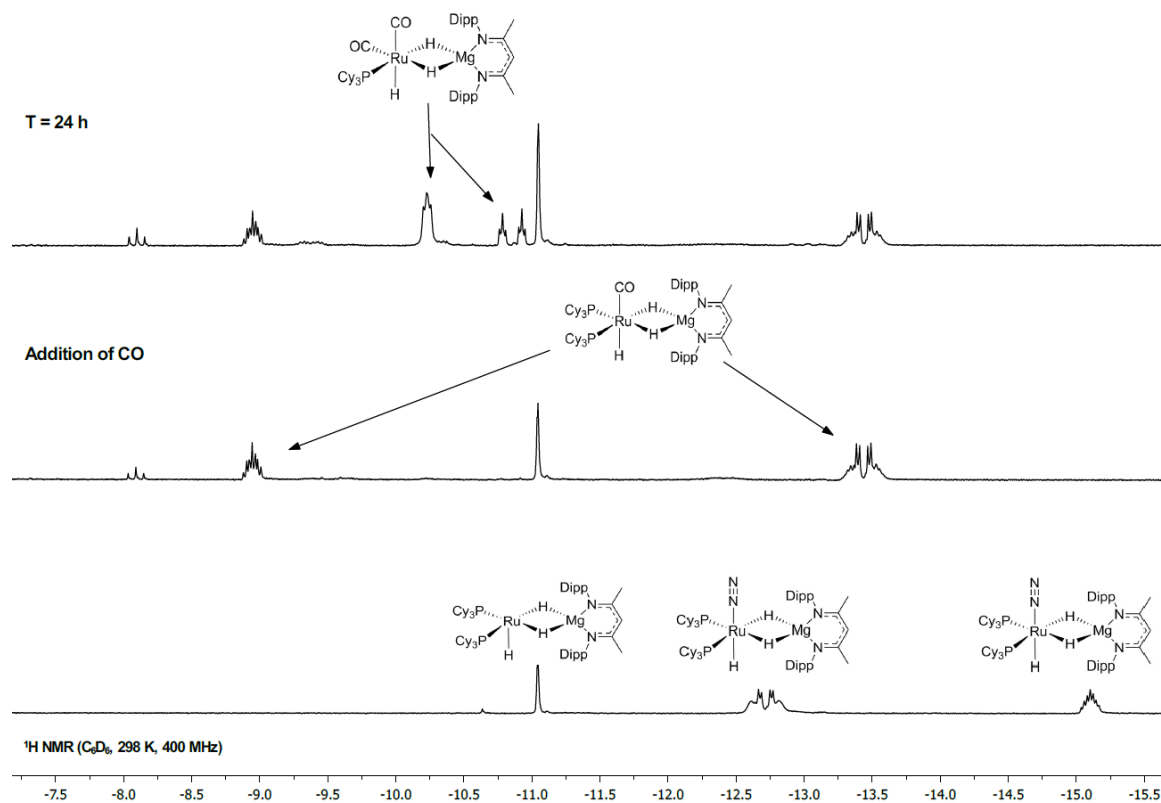


Figure S 5.32. ^1H NMR spectra stack plot of reaction of $\text{Mg}\cdot\text{Ru}$ heterobimetallic complexes with CO. Only Ru-H region shown for clarity.

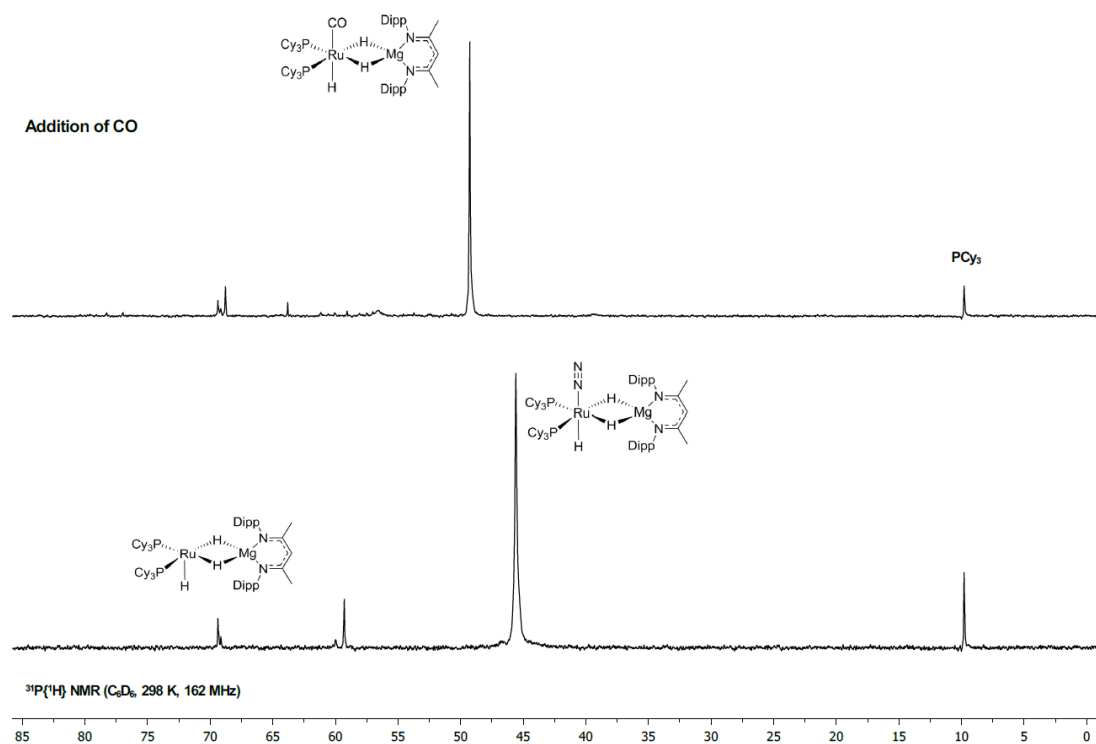
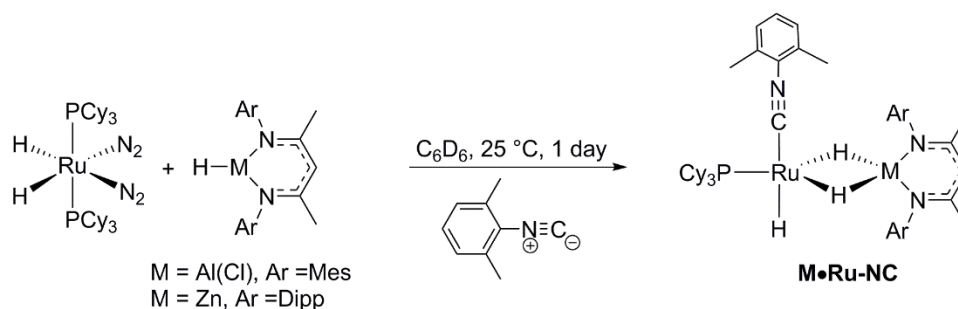


Figure S 5.33. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra stack plot of reaction of $\text{Mg}\cdot\text{Ru}$ heterobimetallic complexes with CO

1.1.1.7 Isonitrile



In dinitrogen glovebox **1** (200 μL , 0.07 M, C_6D_6) and $\text{BDI}^{\text{Ar}}\text{MH}$ (400 μl , 0.035 M, C_6D_6) were added into a J.Young NMR and left to react overnight at 25 $^\circ\text{C}$. The reaction was checked to ensure all starting materials were consumed by NMR. 2,6-dimethylphenylisonitrile (1.8 mg, 0.01 mmol) was added to the reaction mixture. Retention of **M•Ru-H₂** and **M•Ru** in the reaction and formation of **M•Ru-NC**.⁸

Al•Ru-NC

In situ ^1H NMR (C_6D_6 , 400 MHz, 298K) δ/ppm : -10.26 (br s, 2H, Ru-H), -9.60 (br d, $^2J_{\text{HP}} = 56.1$ Hz, 1H, Ru-H), 5.29 (s, 1H, CH).

In situ ^{31}P NMR (C_6D_6 , 162 MHz, 298K) δ/ppm : δ 62.2 (s).

Zn•Ru-NC

In situ ^1H NMR (C_6D_6 , 400 MHz, 298K) δ/ppm : -9.84 (dd, $^2J_{\text{HP}} = 13.5$ Hz and $^2J_{\text{HH}} = 6.7$ Hz, 2H, Ru-H), -9.56 (dt, $^2J_{\text{HP}} = 47.2$ Hz and $^2J_{\text{HH}} = 6.7$ Hz, 1H, Ru-H), 3.49 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 5.02 (s, 1H, CH).

In situ ^{31}P NMR (C_6D_6 , 162 MHz, 298K) δ/ppm : δ 64.6 (s).

⁸ ^1H -NMR and ^{13}C -NMR spectra assignment incomplete as sample always contained a mixture of heterobimetallic complexes

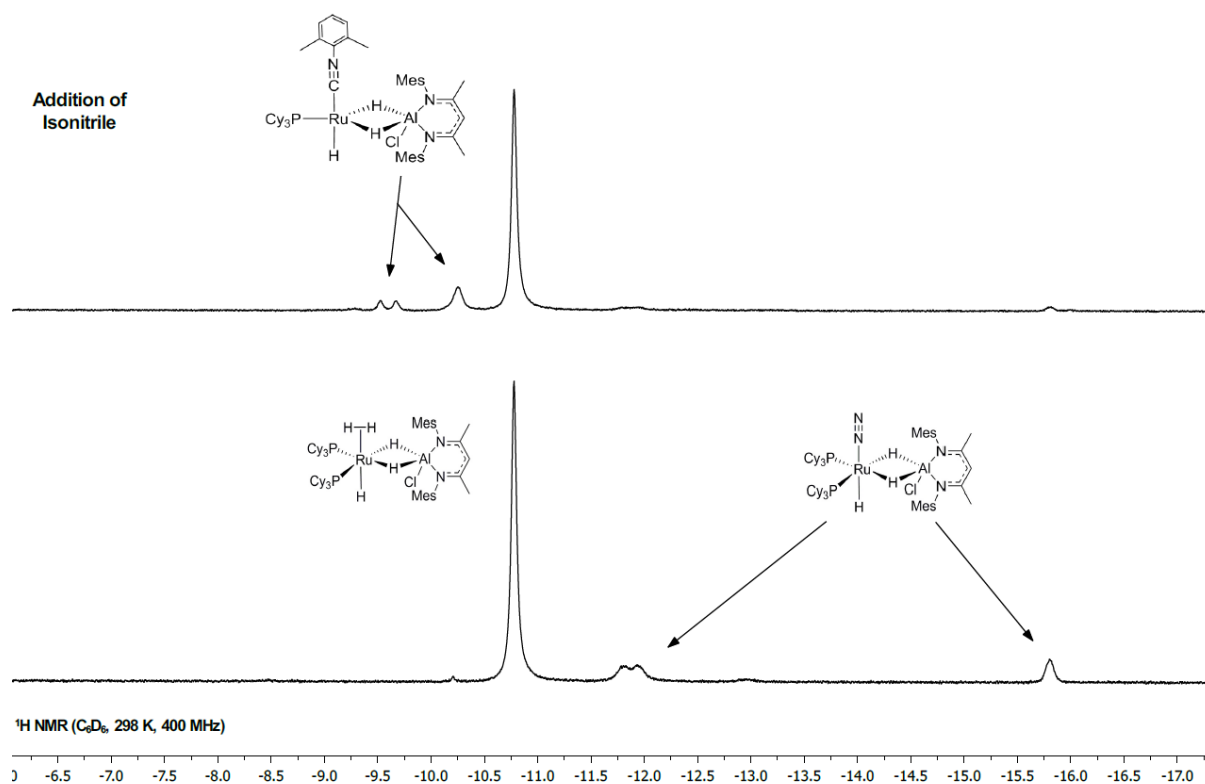


Figure S 5.34. ^1H NMR spectra stack plot of reaction of **Al•Ru** heterobimetallic complexes with 2,6-dimethylphenylisonitrile. Only Ru–H region shown for clarity

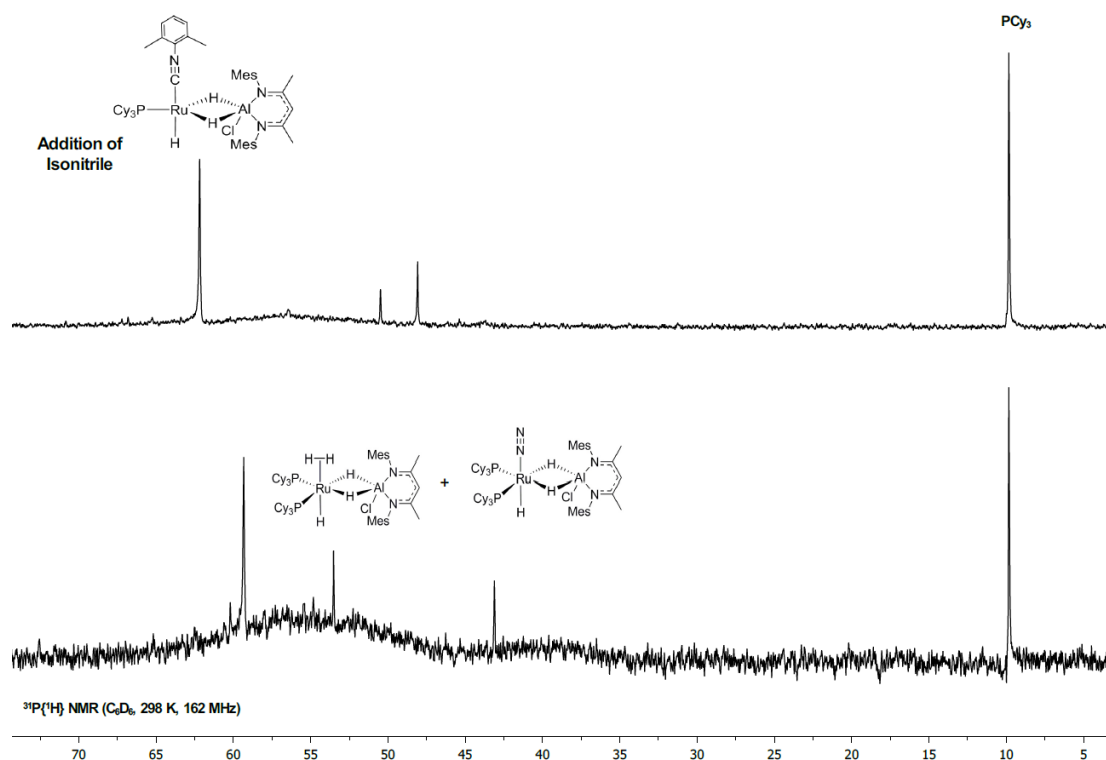


Figure S 5.35. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra stack plot of reaction of **Al•Ru** heterobimetallic complexes with 2,6-dimethylphenylisonitrile

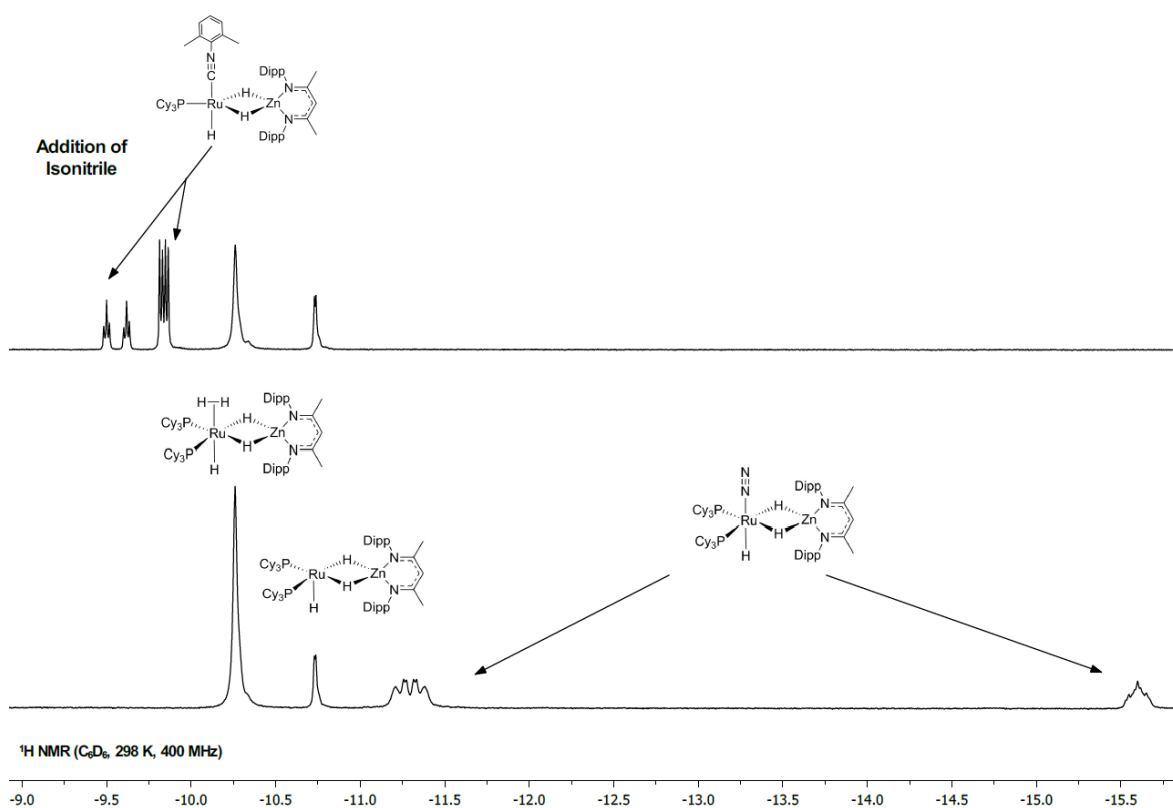


Figure S 5.36. ^1H NMR spectra stack plot of reaction of $\text{Zn}\cdot\text{Ru}$ heterobimetallic complexes with 2,6-dimethylphenylisonitrile. Only Ru-H region shown for clarity.

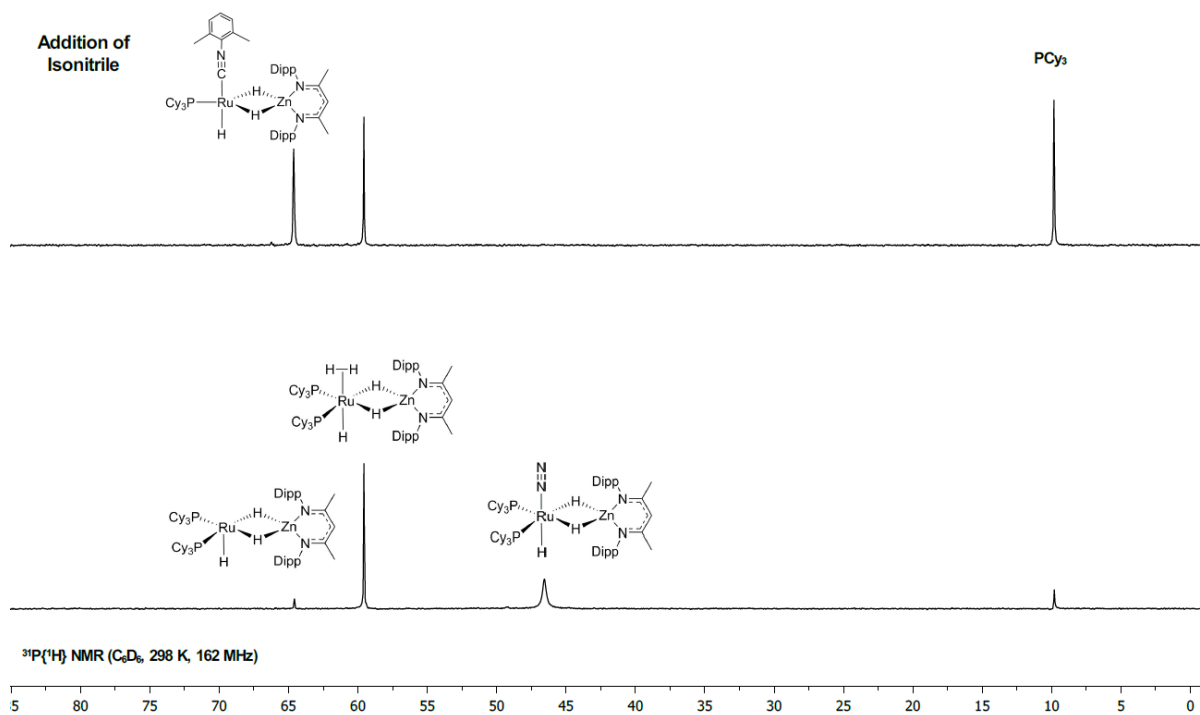


Figure S 5.37. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra stack plot of reaction of $\text{Zn}\cdot\text{Ru}$ heterobimetallic complexes with 2,6-dimethylphenylisonitrile

5.4.4 Variable Temperature NMR data

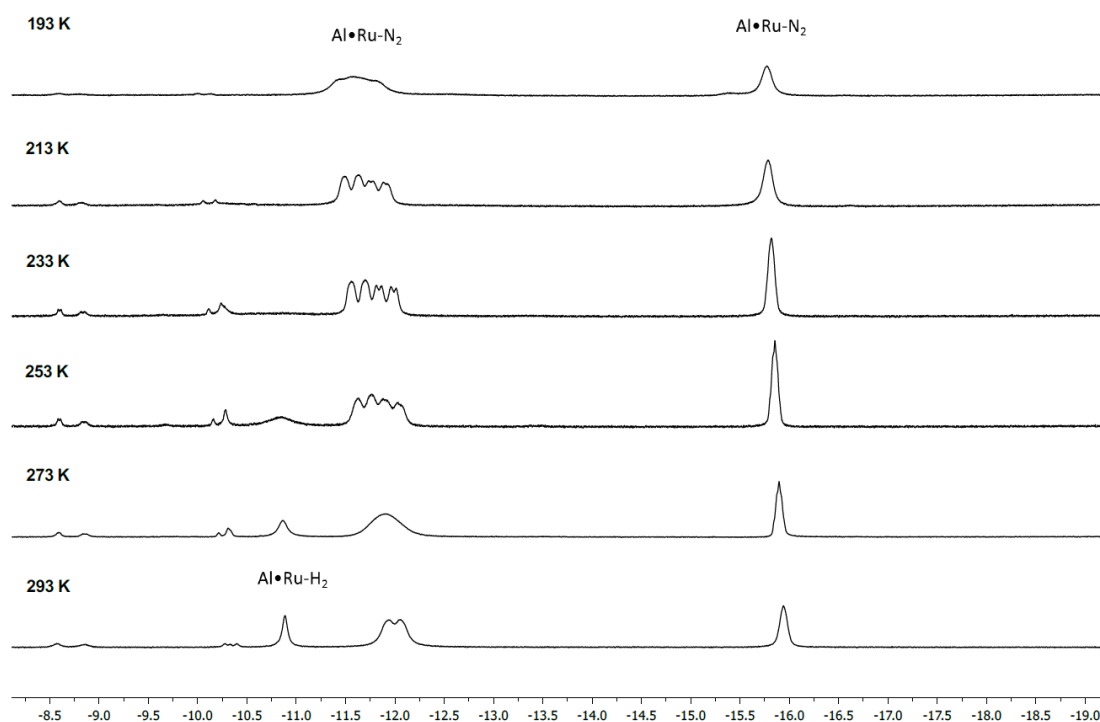


Figure S 5.38. VT ^1H NMR spectra on sample containing $\text{Al}\cdot\text{Ru-N}_2$ (major product) and $\text{Al}\cdot\text{Ru-H}_2$ (minor product) complexes. Only Ru-H region shown for clarity.

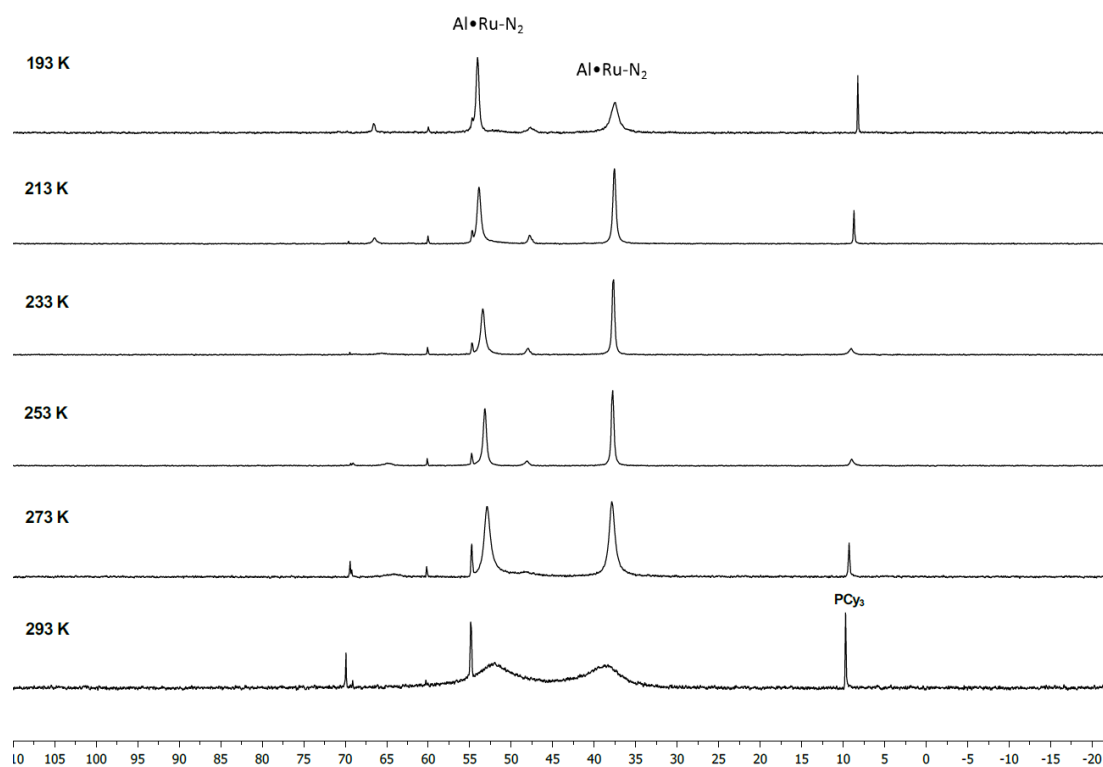


Figure S 5.39. VT $^{31}\text{P}\{^1\text{H}\}$ NMR spectra on sample containing $\text{Al}\cdot\text{Ru-N}_2$ (major product) and $\text{Al}\cdot\text{Ru-H}_2$ (minor product) complexes.

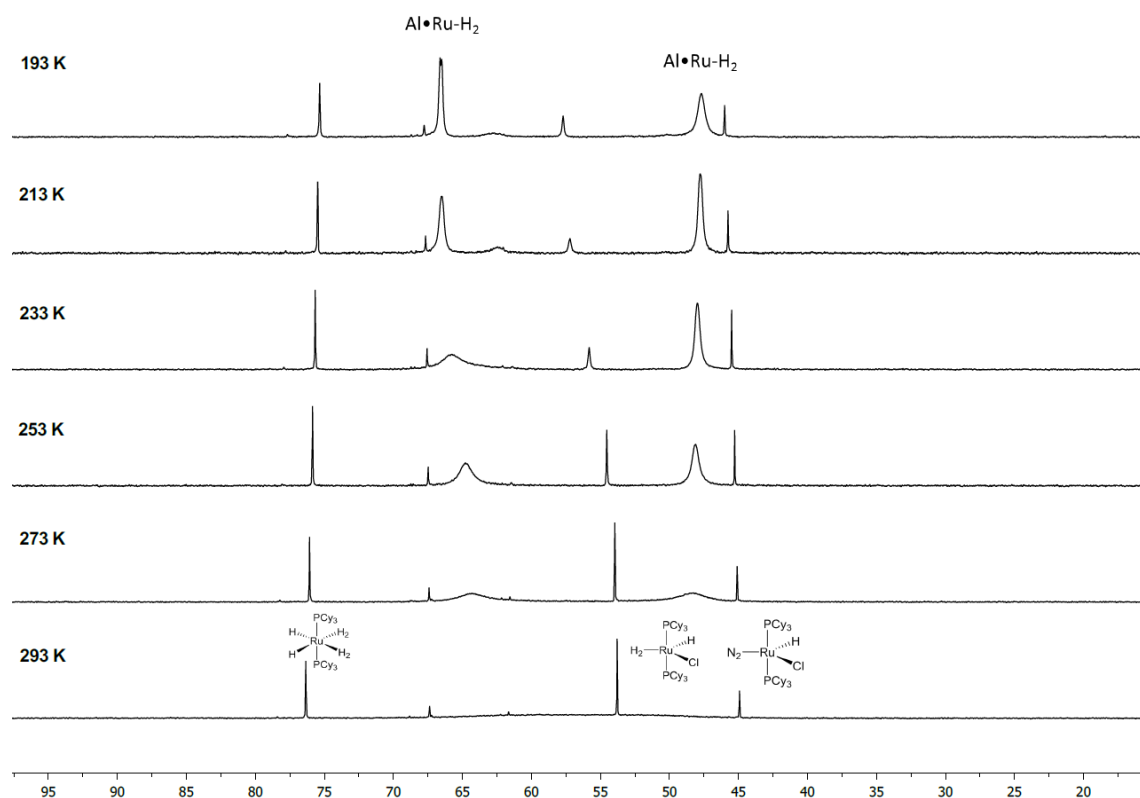


Figure S 5.40. VT $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of sample containing just the $\text{Al}\cdot\text{Ru}\text{-H}_2$ heterobimetallic complex as well as the by-product of the reaction of **1** with $^{\text{Mes}}\text{BDIAl(H)(Cl)}$.

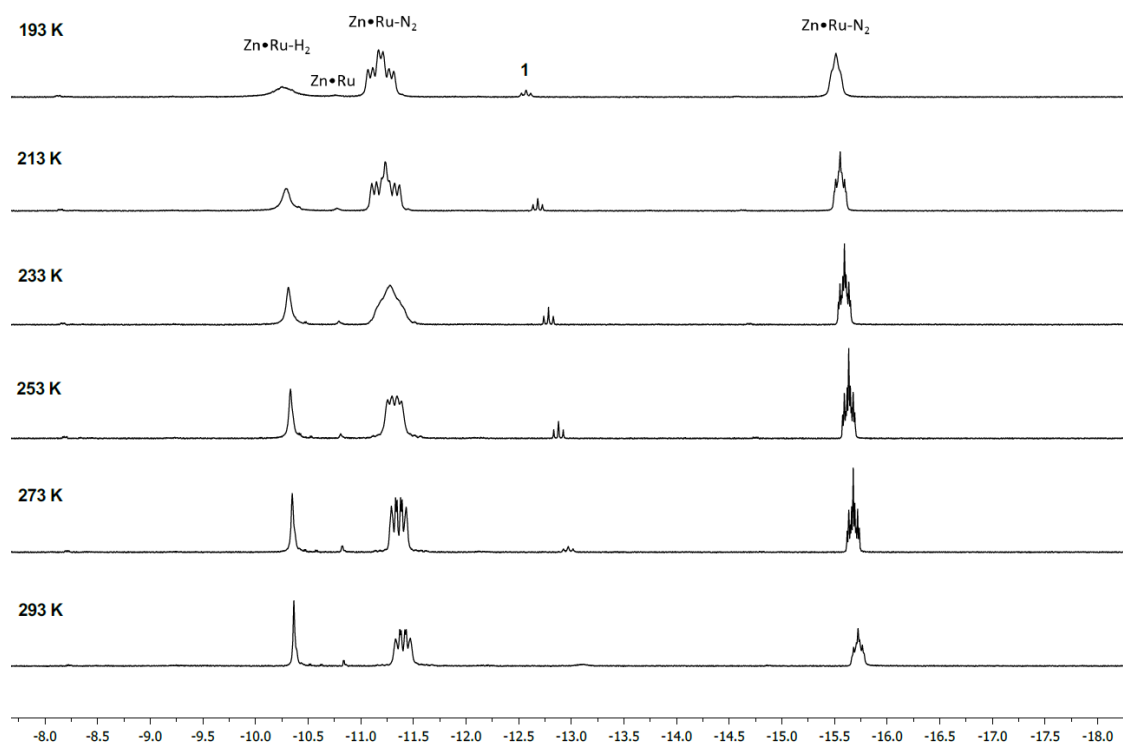


Figure S 5.41. VT ^1H NMR spectra on sample containing $\text{Zn}\cdot\text{Ru}\text{-H}_2$, $\text{Zn}\cdot\text{Ru}\text{-N}_2$ and $\text{Zn}\cdot\text{Ru}$ (minor) complexes. Only Ru-H region shown for clarity

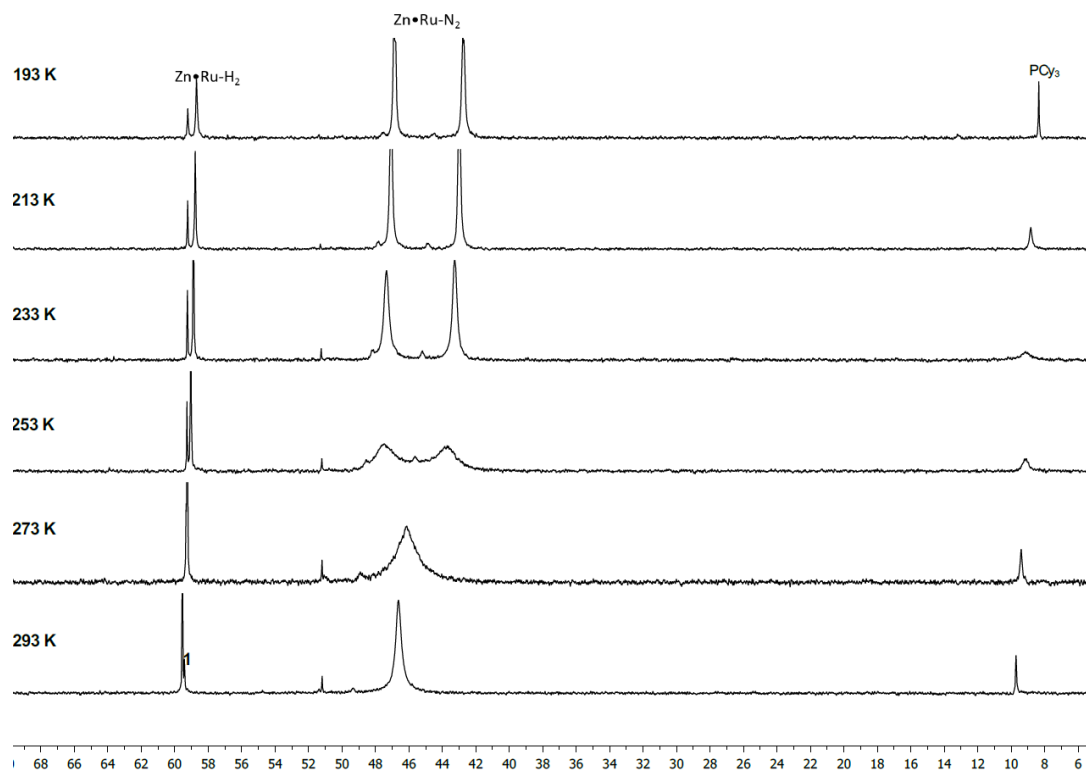


Figure S 5.42. VT $^{31}\text{P}\{^1\text{H}\}$ NMR spectra on sample containing $\text{Zn}\cdot\text{Ru}\text{-H}_2$ and $\text{Zn}\cdot\text{Ru}\text{-N}_2$ complexes.

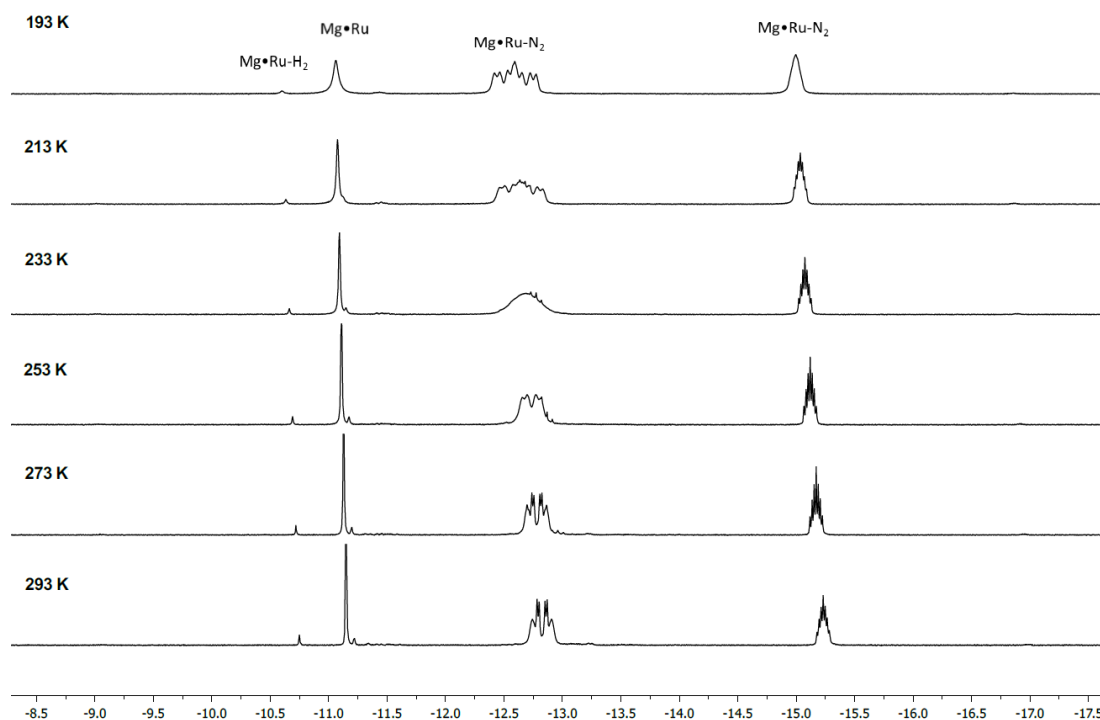


Figure S 5.43. VT ^1H NMR spectra on sample containing $\text{Mg}\cdot\text{Ru}\text{-H}_2$ (minor product), $\text{Mg}\cdot\text{Ru}\text{-N}_2$ and $\text{Mg}\cdot\text{Ru}$ complexes. Only Ru-H region shown for clarity

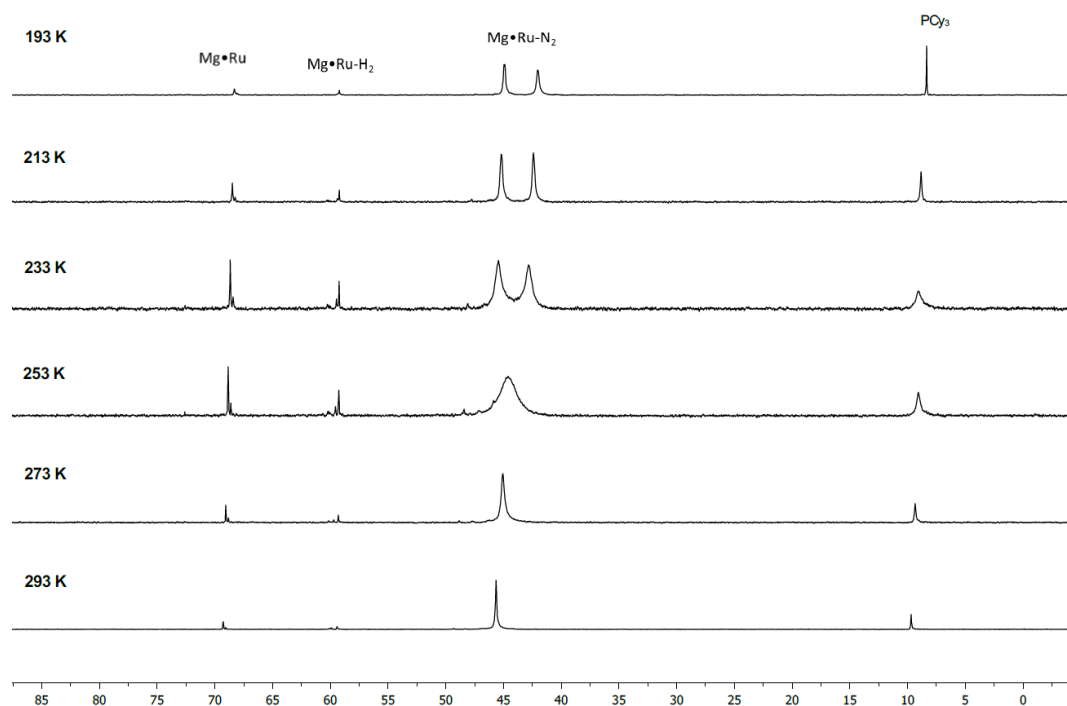


Figure S 5.44. VT $^{31}\text{P}\{^1\text{H}\}$ NMR spectra on sample containing **Mg•Ru-H₂** (minor), **Mg•Ru-N₂** and **Mg•Ru** complexes.

VT NMR data was fitted using line shape analysis with the DNMR programme integrated into Topsin v3.1. The ^1H and ^{31}P resonances of **Mg•Ru-N₂** and **Zn•Ru-N₂** were fitted over the 213 to 293 K range with an initial line broadening factor of 20 Hz for ^{31}P NMR. Fits for k were optimized to the experimental data with reasonable accuracy and the modelled data are presented below.

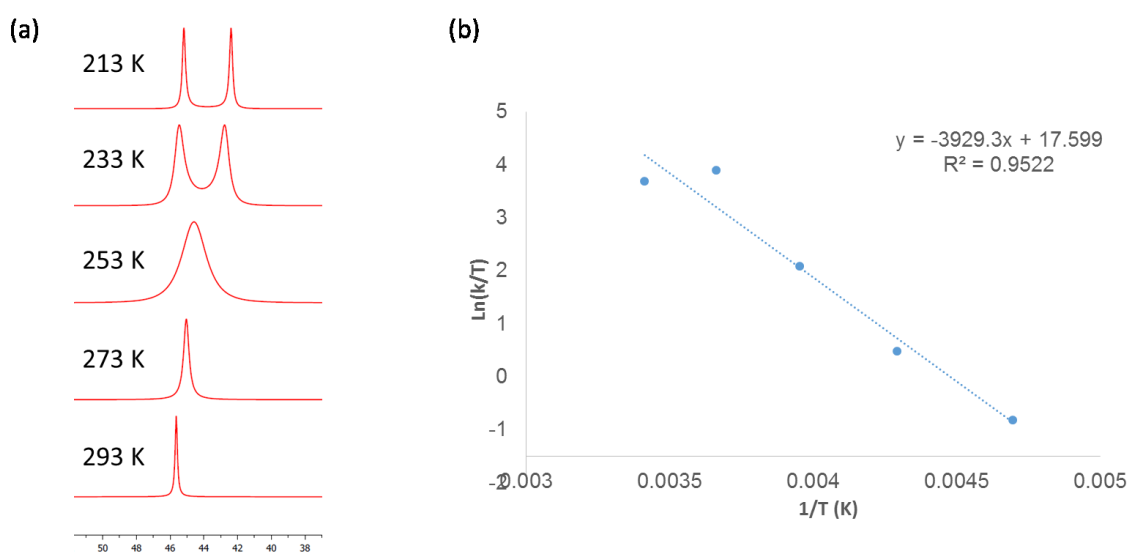


Figure S 5.45. (a) Modelled VT $^{31}\text{P}\{^1\text{H}\}$ NMR on a sample of **Mg•Ru-N₂** (b) Eyring analysis of the modelled VT $^{31}\text{P}\{^1\text{H}\}$ NMR data

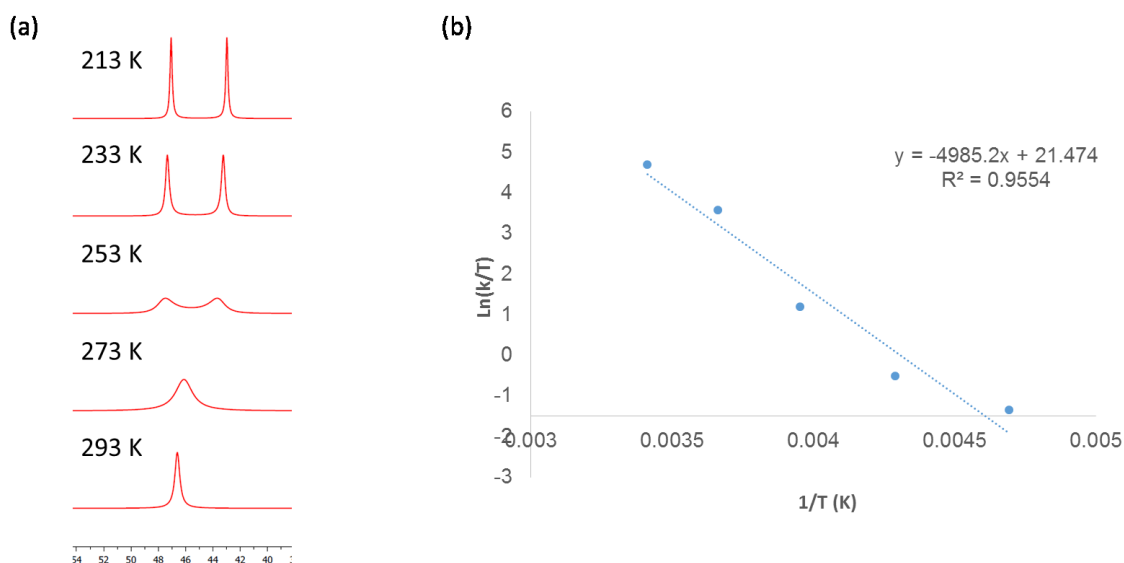


Figure S 5.46. (a) Modelled VT ^{31}P $\{^1\text{H}\}$ NMR on a sample of **Zn•Ru-N₂** (b) Eyring analysis of the modelled VT $^{31}\text{P}\{^1\text{H}\}$ NMR data

The calculated activation parameters for the exchange process are as follows:

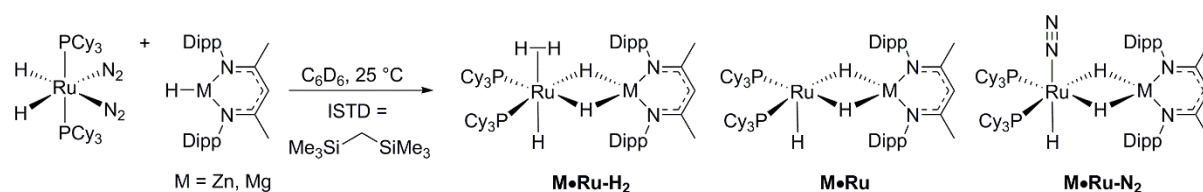
Mg•Ru-N₂

$$\Delta H^\ddagger = 45 \pm 17 \text{ kJ mol}^{-1}, \Delta S^\ddagger = +28 \pm 62 \text{ J K}^{-1} \text{ mol}^{-1}, \Delta G^\ddagger_{298\text{K}} = 37 \pm 1.8 \text{ kJ mol}^{-1}.$$

Zn•Ru-N₂

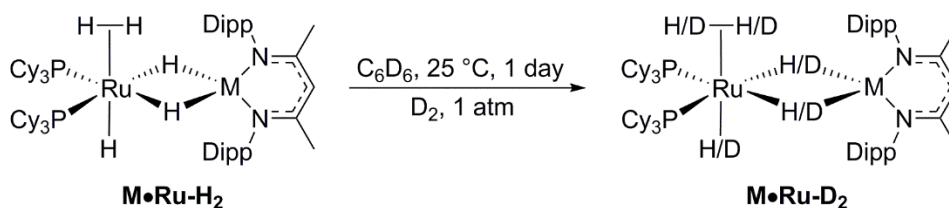
$$\Delta H^\ddagger = 45 \pm 8.8 \text{ kJ mol}^{-1}, \Delta S^\ddagger = +28 \pm 26 \text{ J K}^{-1} \text{ mol}^{-1}, \Delta G^\ddagger_{298\text{K}} = 37 \pm 1.1 \text{ kJ mol}^{-1}.$$

5.4.5 Kinetic Experiments



In dinitrogen glovebox **1** (200 μL , 0.07 M, C_6D_6) was added into a J.Young NMR and the solution was frozen. Whilst the solution was still frozen BDI^{4r}MH (400 μL , 0.035 M, C_6D_6) and $[(\text{SiMe}_3)_2]\text{CH}_2$ (1.5 μL , 0.007 mmol) was added to the J.Young tube NMR and the whole solution was frozen. The reaction mixture was left to thaw whilst in the spectrometer. (**Mg**: 60 scan/h for 2 h, 6 scan/h for 2h, 2 scan/h for 8h (Run #2); **Zn**: 60 scan/h for 3 h).

5.4.6 D₂ Labelling Experiments



In a dinitrogen glovebox, *Dipp*BDIMH (Zn = 6.7 mg, Mg = 6.2 mg, 0.01 mmol, 1 equiv) and **1** (10 mg, 0.01 mmol, 1 equiv) were weighed into a scintillation vial and dissolved in C₆D₆ (600 μL). The reaction mixture was left to react overnight at 25 °C. Reaction was subjected to freeze-pump-thaw procedure × 3 then H₂ (1 atm.) was added to the tube to cleanly form the **M•Ru-H₂** complexes. The reaction was then again subjected to freeze-pump-thaw procedure × 3 then D₂ (1 atm.) was added to the tube to cleanly form a mixture of isotopomers of the dihydrogen heterobimetallic hydride complexes.

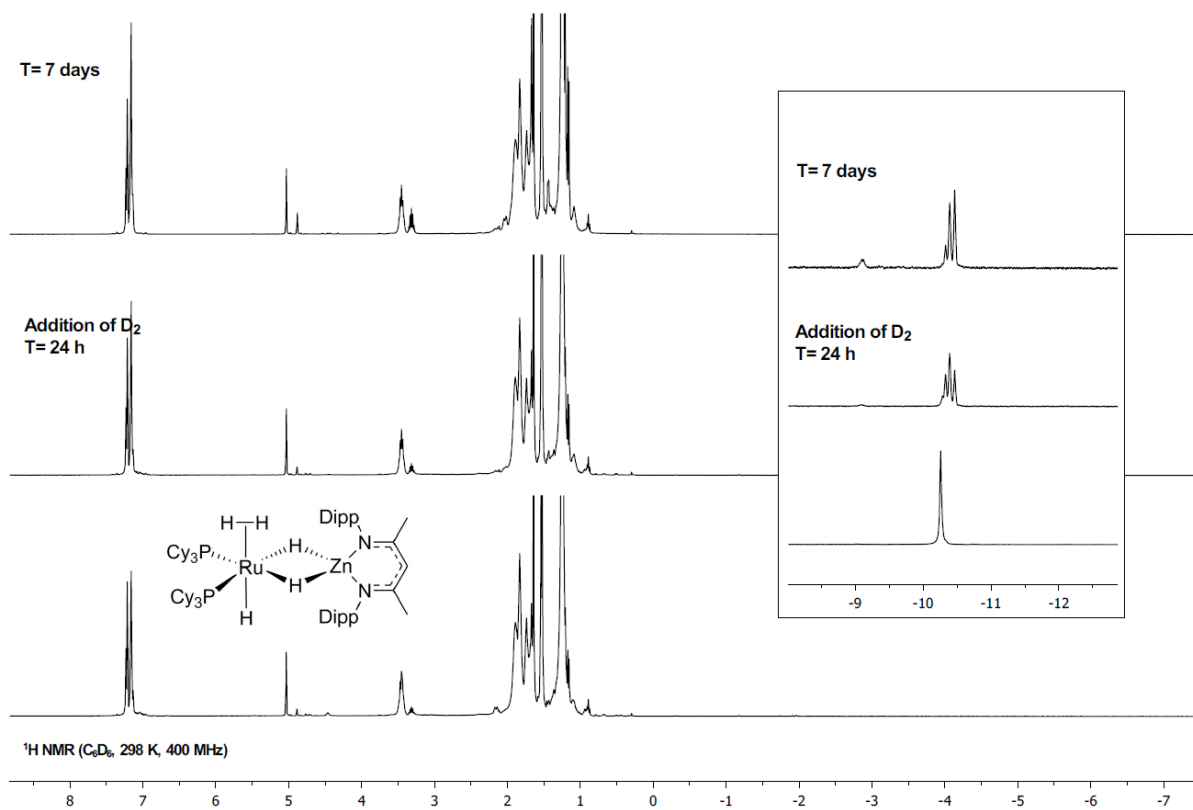
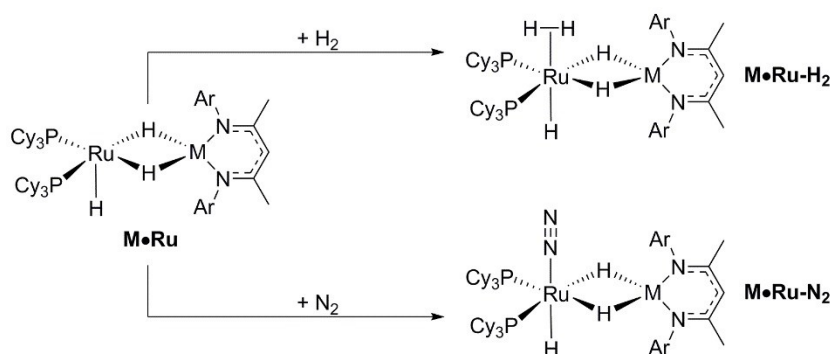


Figure S 5.47. ¹H NMR spectra stacked plot of D₂ labelling experiment of **Zn•Ru-H₂**

5.4.7 DFT and QTAIM

Calculations were conducted in Gaussian09 suite.¹⁸ All minima were confirmed by frequency calculations and solid-state data were used as an input for the atom coordinates. NBO calculations were run using NBO v5.9 within g09.^{19,20} The functional ω B97x-D²¹ was employed, Ru, Al, Mg and Zn centres were described with Stuttgart SDDAll RECPs and associated basis sets.^{22–24} 6-31++G(d,3pd) basis set was used for all hydrides, 6-31G* basis set was used to describe C and H atoms and 6-311+G* basis set was used to describe N, P and Cl atoms.^{25–27} The topology of the electron density for selected systems within the QTAIM framework was carried out using the AIMALL software.^{28–30}

1.1.1.8 Thermodynamic Parameter

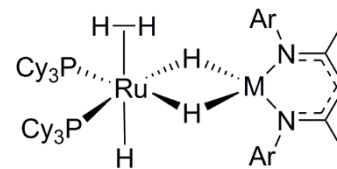


		M•Ru	M•Ru-H ₂	M•Ru-N ₂
Al	ΔG	0	−12.1	−6.1
Zn	ΔG	0	−8.1	−3.8
Mg	ΔG	0	−15.8	−12.4

Table S 5.2. Calculated Gibbs free energy (kcal mol^{−1}) of the complexes

1.1.1.9 NBO and QTAIM analysis

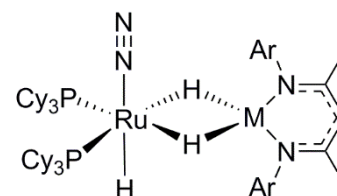
		WBI		ρ		∇^2	
		Ru	M	Ru	M	Ru	M
Al	H_μ	0.42	0.24	0.12	-	-1.22	-
		0.43	0.26	0.12	-	-1.17	-
	H_t	0.47	0.22	0.12	-	-1.17	-
Zn	H_μ	0.43	0.16	0.11	0.07	-1.08	-0.47
		0.44	0.14	0.10	0.06	-0.98	-0.43
	H_t	0.57		0.13		-1.36	
Mg	H_μ	0.47	0.07	0.12	-	-1.12	-
		0.47	0.06	0.11	-	-1.05	-
	H_t	0.55		0.12		-1.17	



M = Al(Cl), Ar = Mes
M = Zn, Mg, Ar = Dipp

Table S 5.3. NBO analysis: Wiberg Bond Indices (WBI) and QTAIM analysis: Rho (ρ) and Laplacian squared (∇^2) of $M\cdots Ru\ H_2$

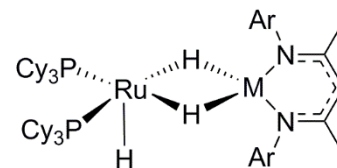
		WBI		ρ		∇^2	
		Ru	M	Ru	M	Ru	M
Al	H_μ	0.42	0.26	0.12	-	-1.13	-
		0.43	0.26	0.12	-	-1.21	-
	H_t	0.50		0.12		-1.24	
Zn	H_μ	0.43	0.15	0.11	0.06	-0.99	-0.39
		0.44	0.15	0.11	0.07	-1.07	-0.49
	H_t	0.57		0.14		-1.42	
Mg	H_μ	0.46	0.08	0.11	0.03	-1.07	-0.02
		0.47	0.07	0.11	0.03	-1.10	-0.02
	H_t	0.57		0.12		-1.25	



M = Al(Cl), Ar = Mes
M = Zn, Mg, Ar = Dipp

Table S 5.4. NBO analysis: Wiberg Bond Indices (WBI) and QTAIM analysis: Rho (ρ) and Laplacian squared (∇^2) of $M\cdots Ru-N_2$

		WBI		ρ		∇^2	
		Ru	M	Ru	M	Ru	M
Zn	H_μ	0.44	0.17	0.10	0.07	-0.94	-0.48
		0.44	0.16	0.11	0.07	-1.01	-0.46
	H_t	0.76		0.16		-1.89	
Mg	H_μ	0.48	0.09	0.10	-	-0.96	-
		0.49	0.07	0.11	-	-1.10	-
	H_t	0.77		0.15		-1.74	



M = Al(Cl), Ar = Mes
M = Zn, Mg, Ar = Dipp

Table S 5.5. NBO analysis: Wiberg Bond Indices (WBI) and QTAIM analysis: Rho (ρ) and Laplacian squared (∇^2) of $M\bullet Ru$

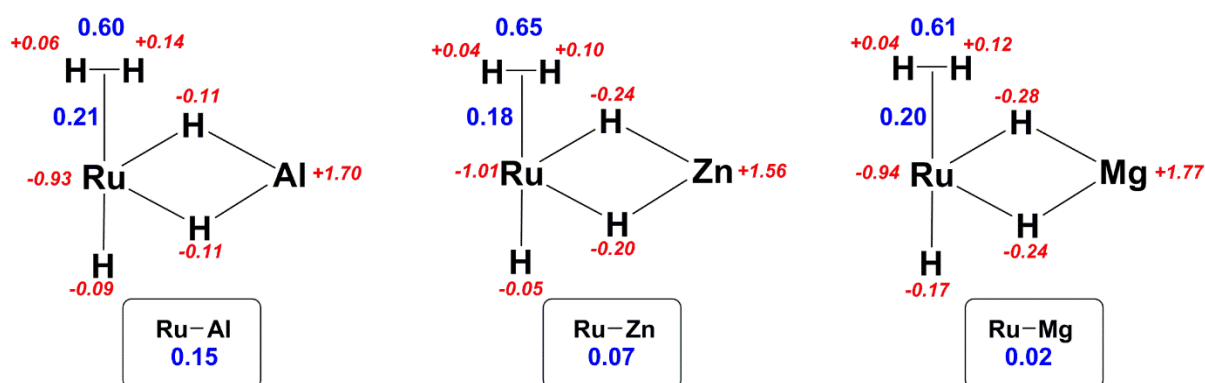


Figure S 5.49. NBO analysis of $M\bullet Ru-H_2$: (Red) NPA charge, (Blue) Wiberg Bond Index

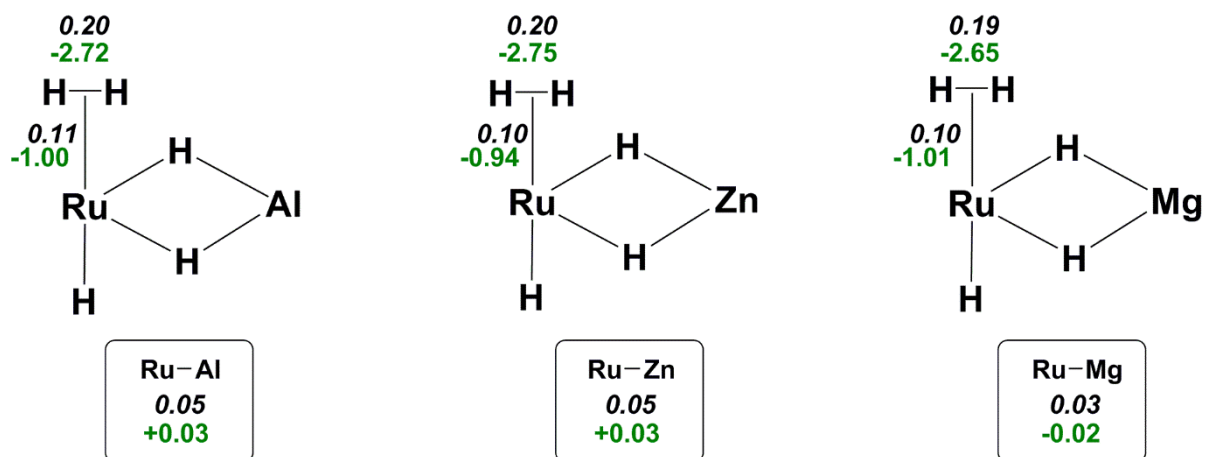


Figure S 5.50. QTAIM analysis: of $M\bullet Ru-H_2$. (Black) ρ , (Green) ∇^2

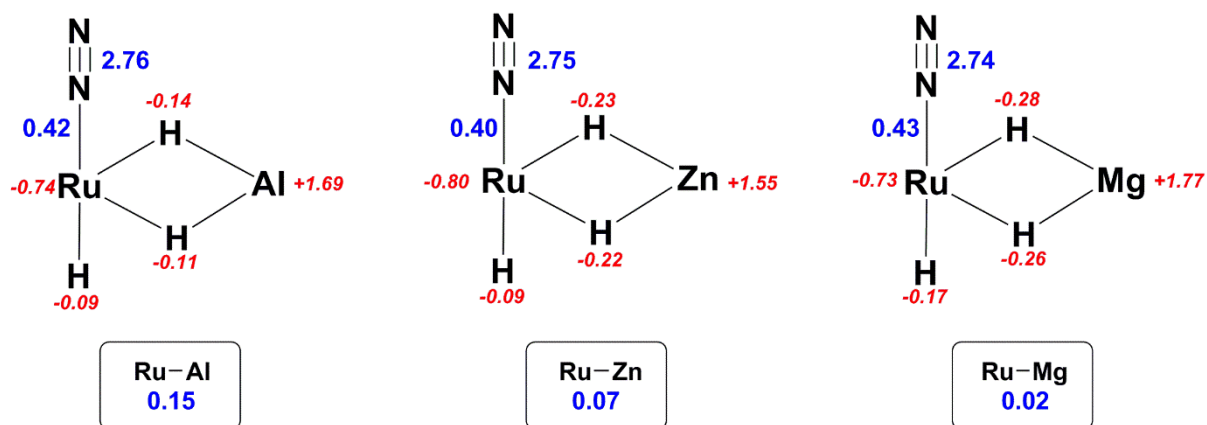


Figure S 5.51. NBO analysis of $\mathbf{M}\cdot\mathbf{Ru}-\mathbf{N}_2$: (Red) NPA charge, (Blue) Wiberg Bond Index

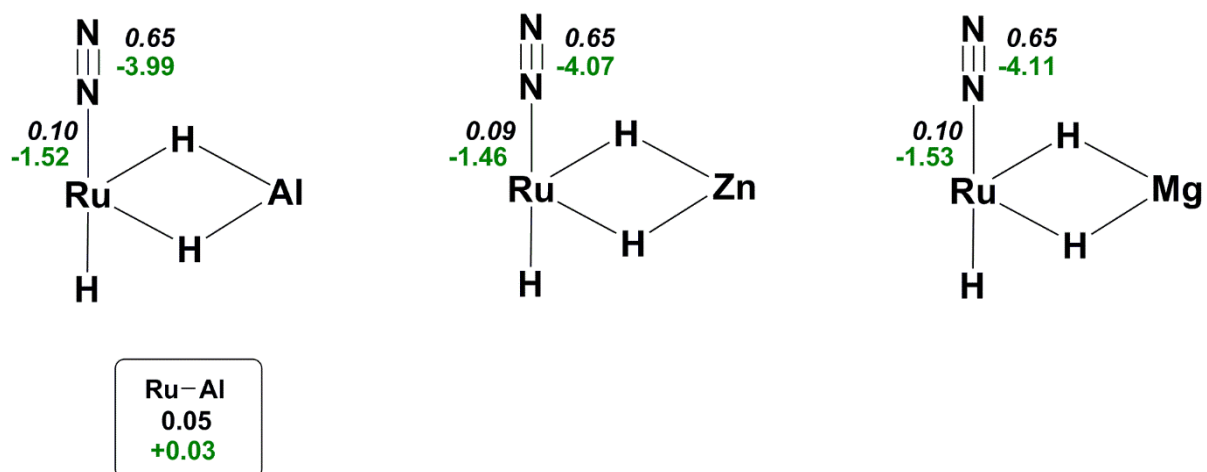


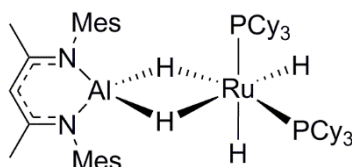
Figure S 5.52. QTAIM analysis: of $\mathbf{M}\cdot\mathbf{Ru}-\mathbf{N}_2$. (Black) ρ , (Green) ∇^2

5.5 CHAPTER FOUR: EXPERIMENTAL

5.5.1 Materials

Solvents were freeze-pump-thaw degassed and stored over 3 Å molecular sieves prior to use. Chemicals were purchased from Sigma Aldrich, Alfa Aesar and Fluorochem and used without further purification unless stated. The synthesis of the pro-ligands ^{Mes}BDIH,¹² ^{Dipp}BDIH,¹² ^{2,6-Xylyl}BDIH,¹² ^{3,5-Xylyl}BDIH³¹ and ^{Ph}BDIH,³¹ the series of β-diketiminato stabilised aluminium complexes: ^{Mes}BDIAL(H)₂,¹³ ^{Dipp}BDIAL(H)₂,³² ^{Dipp}BDIAL(I),³³ ^{3,5-Xylyl}BDIAL(H)₂¹³ and ^{Ph}BDIAL(H)₂¹³ were all prepared according to literature procedures.

5.5.2 Synthesis of Al•Ru heterobimetallic hydride complexes



Synthesis of ^{Mes}Al•Ru: In a dinitrogen glovebox ^{Mes}BDIAL(H)₂ (5.0 mg, 0.01 mmol) and [Ru(H)₂(N₂)₂(PCy₃)₂] (10 mg, 0.01 mmol) were weighed into a scintillation vial and dissolved in C₆D₆ (600 μL) and then transferred into a J. Young NMR tube. Effervescence was observed along with a colour change from faint yellow to orange. Isolation of ^{Mes}Al•Ru failed as this complex dimerised to form ^{Mes}Al₂•Ru₂ at 25 °C.

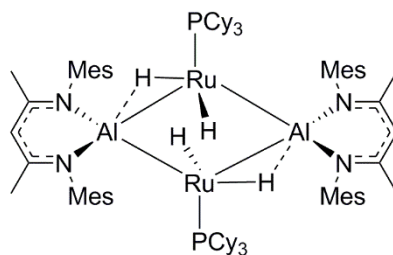
In situ ¹H NMR (Tol-D₈, 500 MHz, 213K) δ/ppm: –13.86 (br s, 1H, Ru–H_μ), –12.45 (br s, 1H, Ru–H_μ), –9.91 (br s, 1H, Ru–H_t), –9.32 (br s, 1H, Ru–H_t). **In situ ¹H NMR (Tol-D₈, 500 MHz, 298K) δ/ppm:** –8.78 – –14.61 (br s, 4H, Ru–H), 1.33–1.16 (m, 18H, Cy), 1.37 (s, 6H, CCH₃), 1.51–1.45 (m, 12H, Cy), 1.77–1.70 (m, 6H, Cy), 1.89–1.81 (m, 12H, Cy), 2.11–2.02 (m, 18H, Cy), 2.20 (s, 6H, ArCH₃), 2.32 (s, 12H, ArCH₃), 4.98 (s, 1H, CH), 6.84 (s, 4H, ArH).

In situ ¹³C{¹H} NMR (C₆D₆, 126 MHz, 298K) δ/ppm: 20.1 (ArCH₃), 21.11 (ArCH₃), 24.1 (CCH₃), 27.7 (Cy), 28.9 (Cy), 30.7 (Cy), 40.9 (Cy), 100.3 (CH), 130.0 (C_m), 133.1 (C_o), 135.3 (C_i), 142.8 (C_p), 170.5 (CCH₃).

In situ ³¹P{¹H} NMR (Tol-D₈, 162 MHz, 213K) δ/ppm: 70.7 and 66.2. **In situ ³¹P{¹H} NMR (Tol-D₈, 162 MHz, 298K) δ/ppm:** 69.9.

Elemental analysis: Due to sensitivity of this complex repeated attempts to acquire CHN analysis failed to provide satisfactory results.

T₁(min)(Tol-D₈, 313 K, 400 MHz) = 247 ms (Ru–H).



Synthesis of $^{\text{Mes}}\text{Al}_2\cdot\text{Ru}_2$: In a dinitrogen glovebox, $^{\text{Mes}}\text{BDIAl(H)}_2$ (25 mg, 0.07 mmol) and $[\text{Ru(H)}_2(\text{N}_2)_2(\text{PCy}_3)_2]$ (50 mg, 0.07 mmol) were weighed into an ampoule and dissolved in toluene (2 mL) and sealed up. Immediate colour change from yellow to deep orange was observed along with effervescent. The mixture was left to stir at 40 °C for 24 h. The solvent was removed *in vacuo* leaving an orange/red solid. The solid was dissolved in pentane and filtered through micro-glass fibre into a small scintillation vial. Slow diffusion of the solvent resulted in formation of orange crystals (32 mg, 61 %).

^1H NMR (Tol- D_8 , 500 MHz, 298K) δ /ppm: –14.20 (br s, 4H, Ru–H), 1.24–1.40 (m, 28H, Cy), 1.50 (s, 12H, CCH_3), 1.62–1.92 (m, 38H, Cy), 2.22–2.41 (m, 36H, ArCH_3), 5.28 (s, 2H, CH), 6.83 (s, 8H, ArH).

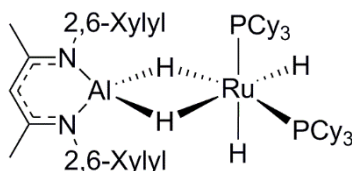
$^{13}\text{C}\{^1\text{H}\}$ NMR (Tol- D_8 , 126 MHz, 298K) δ /ppm : 21.0 (ArCH_3), 22.2 (ArCH_3), 23.7 (CCH_3), 27.3 (Cy), 28.6 (Cy), 29.7 (Cy), 39.2 (Cy), 102.2 (CH), 129.6 (C_m), 133.7 (C_o), 134.3 (C_i), 143.8 (C_p), 168.9 (CCH_3).

$^{31}\text{P}\{^1\text{H}\}$ NMR (Tol- D_8 , 162 MHz, 298K) δ /ppm: δ 74.0.

AT-IR (v/cm-1): 1610 – 1654 (Ru–H–Al).

Elemental Analysis Calc. for $\text{C}_{82}\text{H}_{134}\text{Al}_2\text{N}_2\text{P}_2\text{Ru}_2$: C, 66.19; H, 8.67; N, 3.77 found C, 65.93; H, 8.69; N, 3.60.

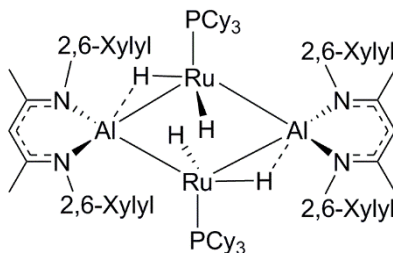
$T_1(\text{min})$ (Tol- D_8 , 273 K, 400 MHz) = 221 ms (Ru–H).



Synthesis of $^{2,6\text{-Xylyl}}\text{Al}\cdot\text{Ru}$: In a dinitrogen glovebox $^{2,6\text{-Xylyl}}\text{BDIAL}(\text{H})_2$ (4.4 mg, 0.01 mmol) and $[\text{Ru}(\text{H})_2(\text{N}_2)_2(\text{PCy}_3)_2]$ (10 mg, 0.01 mmol) were weighed into a scintillation vial and dissolved in C_6D_6 (600 μL) and then transferred into a J. Young NMR tube. Effervescence was observed along with a colour change from faint yellow to orange. Isolation of $^{2,6\text{-Xylyl}}\text{Al}\cdot\text{Ru}$ failed as this complex dimerised to form $^{2,6\text{-Xylyl}}\text{Al}_2\cdot\text{Ru}_2$ at 25 $^\circ\text{C}$.⁹

***In situ* ^1H NMR (Tol- D_8 , 500 MHz, 298K) δ/ppm :** $-9.32 - -14.14$ (br s, 4H, Ru- H), $1.20 - 1.39$ (br s, 18H, Cy), 1.33 (s, 6H, CCH_3), $1.42 - 2.23$ (m, 48H, Cy), 2.36 (s, 12H, ArCH_3), 4.95 (s, 1H, CH), $6.96 - 7.10$ (m, 6H, ArH).

***In situ* $^{31}\text{P}\{^1\text{H}\}$ NMR (Tol- D_8 , 162 MHz, 298K) δ/ppm :** 70.0.



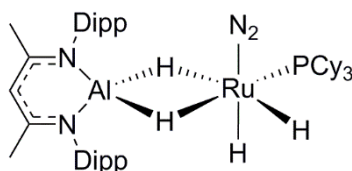
Synthesis of $^{2,6\text{-Xylyl}}\text{Al}_2\cdot\text{Ru}_2$: In a dinitrogen glovebox $^{2,6\text{-Xylyl}}\text{BDIAL}(\text{H})_2$ (6.2 mg, 0.02 mmol) and $[\text{Ru}(\text{H})_2(\text{N}_2)_2(\text{PCy}_3)_2]$ (16 mg, 0.02 mmol) were weighed into a scintillation vial and dissolved in C_6D_6 (600 μL) and then transferred into a J. Young NMR tube. Effervescence was observed along with a colour change from faint yellow to orange. Reaction was left at 25 $^\circ\text{C}$ for 1 week. Clean formation and/or separation of $^{2,6\text{-Xylyl}}\text{Al}_2\cdot\text{Ru}_2$ from $^{2,6\text{-Xylyl}}\text{Al}\cdot\text{Ru}$ was unsuccessful as full conversion of the monomer to the dimer was incomplete.¹⁰

***In situ* ^1H NMR (Tol- D_8 , 500 MHz, 298K) δ/ppm :** -14.19 (br s, 4H, Ru- H), 1.45 (s, 12H, CCH_3), $1.51 - 1.45$ (m, 12H, Cy), 2.21 (m, 24H, ArCH_3), 5.27 (s, 2H, CH), $6.97 - 7.10$ (m, 12H, ArH).

***In situ* $^{31}\text{P}\{^1\text{H}\}$ NMR (Tol- D_8 , 162 MHz, 298K) δ/ppm :** 74.4.

⁹ No $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum was acquired for this sample and no further spectroscopic analysis were performed

¹⁰ Unambiguous assignment of ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra data was not possible as sample contained a mixture of $^{2,6\text{-Xylyl}}\text{Al}_2\cdot\text{Ru}_2$ and $^{2,6\text{-Xylyl}}\text{Al}\cdot\text{Ru}$



Synthesis of $\text{DippAl}\cdot\text{Ru}$: In dinitrogen glovebox DippBDIAI(H)_2 (32 mg, 0.07 mmol) and $[\text{Ru(H)}_2(\text{N}_2)_2(\text{PCy}_3)_2]$ (50 mg, 0.07 mmol) were weighed into a scintillation vial and dissolved in toluene (2 mL) then left to stir at 25 °C overnight. Solvent was removed *in vacuo* to give an oily residue which was washed with pentane and dried until a yellow powder was obtained. Solid was re-dissolved in a mixture of toluene (1 mL) and hexane (1 mL) then filtered through micro-glass fibre and left in the glovebox freezer (−35 °C) overnight to give orange solid as product $\text{DippAl}\cdot\text{Ru}$ (24 mg, 40 %).

^1H NMR (C_6D_6 , 400 MHz, 298 K) δ/ppm : −16.12 (d, $^2J_{\text{HP}} = 15.8$ Hz, 1H, Ru−H), −9.73 (d, $^2J_{\text{HP}} = 41.6$ Hz, 1H, Ru−H), −9.05 (br s, 2H, Ru−H), 1.09 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.18–1.35 (m, 19H, Cy), 1.54 (s, 6H, CCH_3), 1.58 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.69–1.80 (m, 8H, Cy), 1.94–2.04 (m, 6H, Cy), 3.18 (hept, $^3J_{\text{HH}} = 6.7$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 5.02 (s, 1H, CH), 7.14 (m, 6H, ArH).

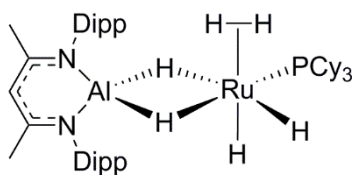
^{13}C $\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz, 298 K) δ/ppm : 24.3 (CCH_3), 24.7 ($\text{CH}(\text{CH}_3)_2$), 25.0 ($\text{CH}(\text{CH}_3)_2$), 27.2 (Cy), 28.5 (Cy), 29.3 ($\text{CH}(\text{CH}_3)_2$), 30.4 (Cy), 37.8 (d, $^1J_{\text{CP}} = 17.2$ Hz, $\text{C}_{\text{y}}\text{i}$), 99.1 (CH), 124.7 (ArH), 140.0 (NC_i), 143.7 (C_o), 171.5 (CCH_3).

^{31}P $\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz, 298 K) δ/ppm : 73.6.

AT-IR (v/cm^{-1}): 2135 ($\text{N}\equiv\text{N}$), 1908 and 1872 (Ru−H).

Elemental Analysis Calc. for $\text{C}_{65}\text{H}_{111}\text{AlN}_2\text{P}_2\text{Ru}$: C, 65.78; H, 9.16; N, 6.53 found C, 66.46; H, 8.75; N, 5.69.

$\text{T}_1(\text{min})(\text{Tol}-\text{D}_8, 233 \text{ K}, 400 \text{ MHz})$ = 198 ms ($\delta_{\text{H}} = -7.83$ ppm), 224 ms ($\delta_{\text{H}} = -9.66$ ppm), 220 ms ($\delta_{\text{H}} = -10.49$ ppm) and 246 ms ($\delta_{\text{H}} = -16.07$ ppm).



Synthesis of $\text{DippAl}\cdot\text{Ru-H}_2$: In dinitrogen glovebox $\text{DippAl}\cdot\text{Ru}$ (14 mg, 0.02 mmol) was weighed and dissolved in Tol- D_8 (600 μL). The reaction was subjected to freeze-pump-thaw procedure $\times 1$ then H_2 gas (1 atm.) was added to the reaction vessel. The reaction was monitored by multinuclear NMR spectroscopy.

^1H NMR (Tol- D_8 , 400 MHz, 298 K) δ/ppm : -9.67 (br s, 6H, Ru- H), 1.09 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.52 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.56 (s, 6H, $\text{CH}(\text{CH}_3)_2$), 1.00 – 1.23 (m, 19H, Cy), 1.59 – 1.69 (m, 8H, Cy), 1.75 – 1.85 (m, 6H, Cy), 3.11 (hept, $^3J_{\text{HH}} = 6.8$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 5.01 (s, 1H, CH), 7.11 (m, 6H, ArH).

^{13}C $\{^1\text{H}\}$ NMR (Tol- D_8 , 125 MHz, 298 K) δ/ppm : 24.4 (CCH_3), 24.7 ($\text{CH}(\text{CH}_3)_2$), 25.2 ($\text{CH}(\text{CH}_3)_2$), 27.2 (Cy), 27.8 (Cy), 28.5 (Cy), 29.2 ($\text{CH}(\text{CH}_3)_2$), 30.3 (Cy), 99.1 (CH), 124.5 (C_m), 126.3 (C_p), 140.5 (NC_i), 143.8 (C_o), 171.3 (CCH_3).

^{31}P $\{^1\text{H}\}$ NMR (Tol- D_8 , 162 MHz, 298 K) δ/ppm : 81.5 .

$T_1(\text{min})$ (Tol- D_8 , 253 K, 400 MHz) = 53 ms (Ru-H).

5.5.3 Variable Temperature NMR Data

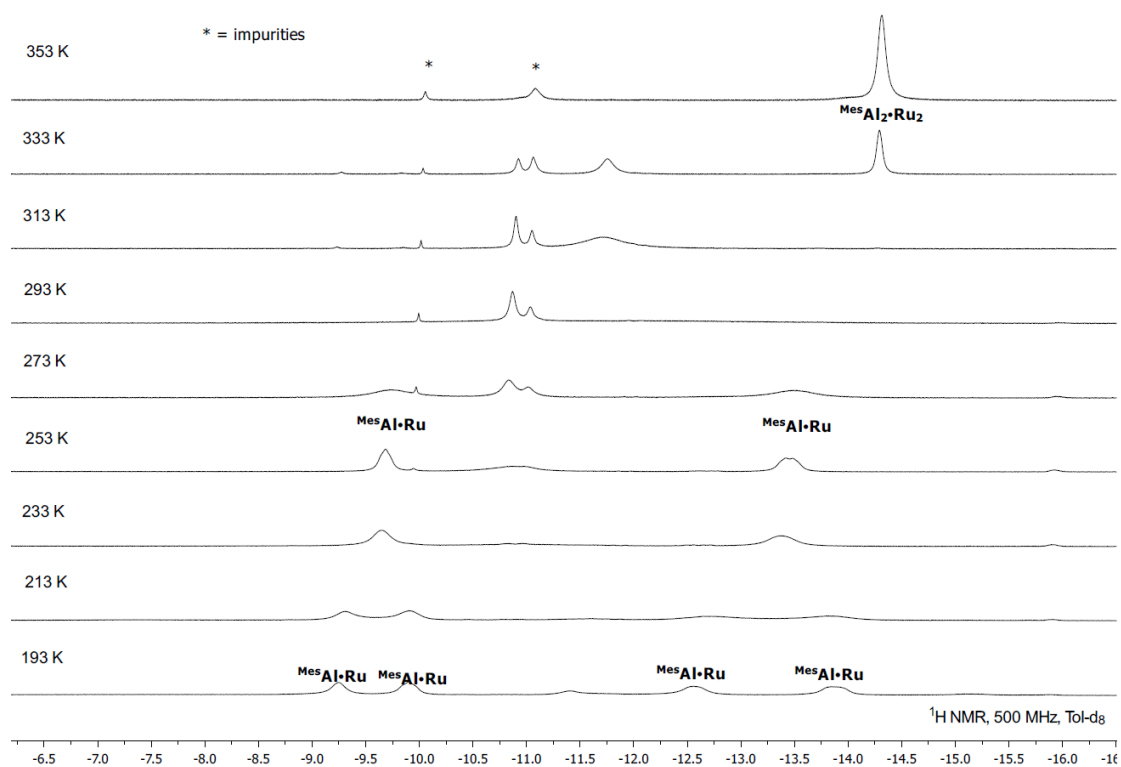


Figure S 5.53. VT ^1H NMR on a sample of MesAlRu freshly generated from the reaction of $\text{MesBDIAL}(\text{H})_2$ with **1** in Tol- d_8 . Only Ru-H region shown for clarity.

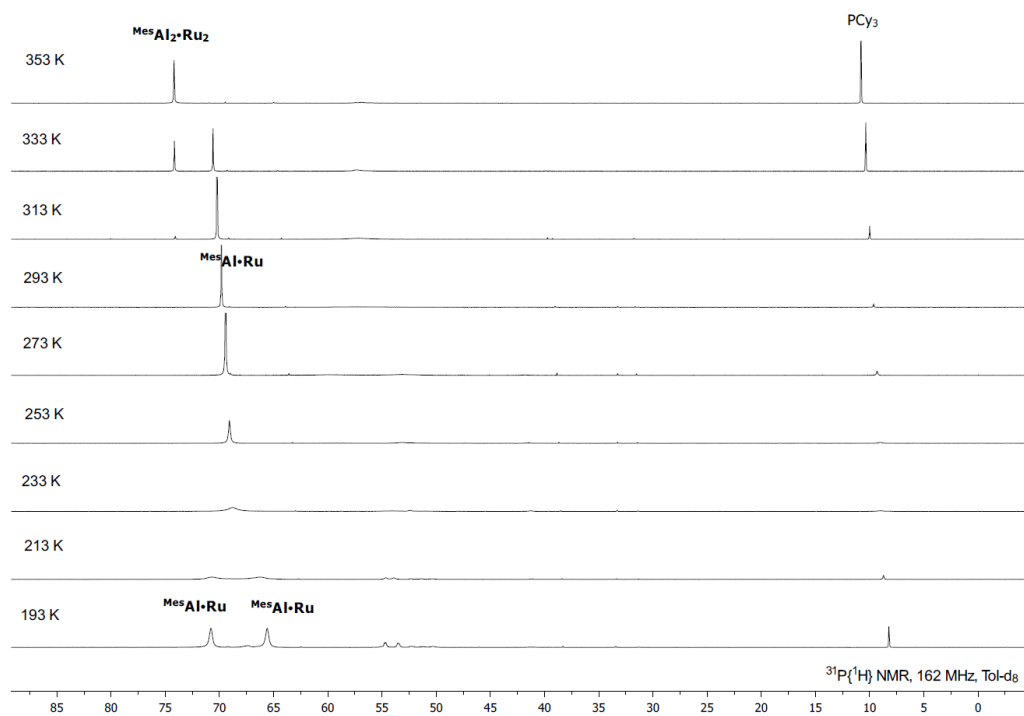


Figure S 5.54. VT $^{31}\text{P}\{^1\text{H}\}$ NMR on a sample of MesAlRu freshly generated from the reaction of $\text{MesBDIAL}(\text{H})_2$ with **1** in Tol- d_8 .

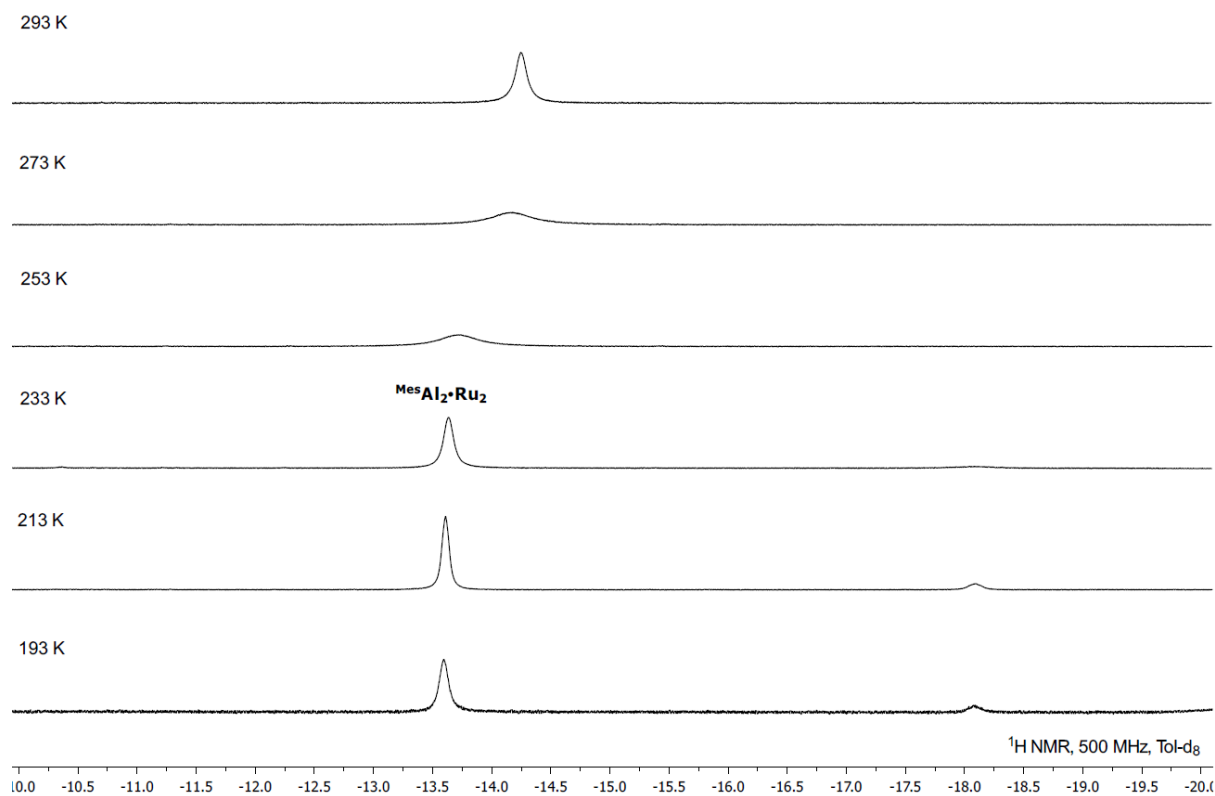


Figure S 5.55. VT ^1H NMR on a sample containing $\text{MesAl}_2\cdot\text{Ru}_2$ in Tol-d_8 . Only Ru–H region shown for clarity.

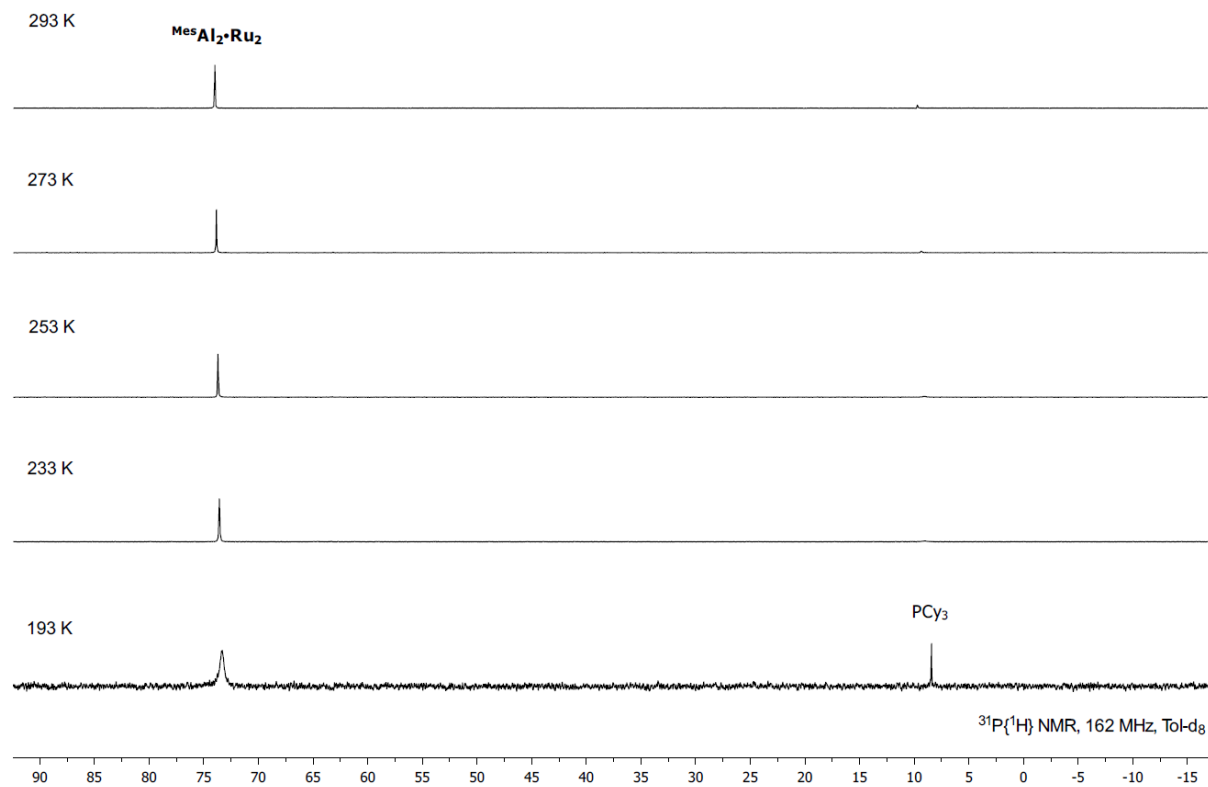


Figure S 5.56. VT $^{31}\text{P}\{^1\text{H}\}$ NMR on a sample containing $\text{MesAl}_2\cdot\text{Ru}_2$ in Tol-d_8 .

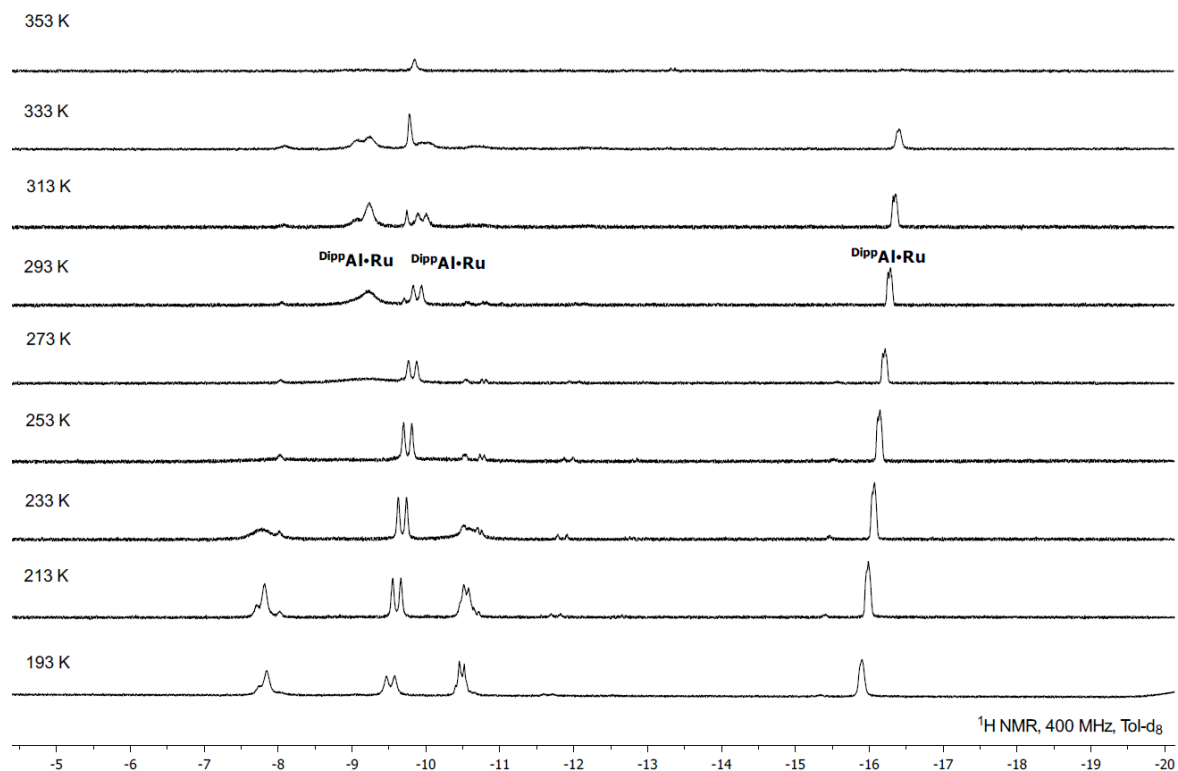


Figure S 5.57. VT ^1H NMR on a sample containing $\text{DippAl}\cdot\text{Ru}$ in Tol-d_8 . Only Ru–H region shown for clarity.

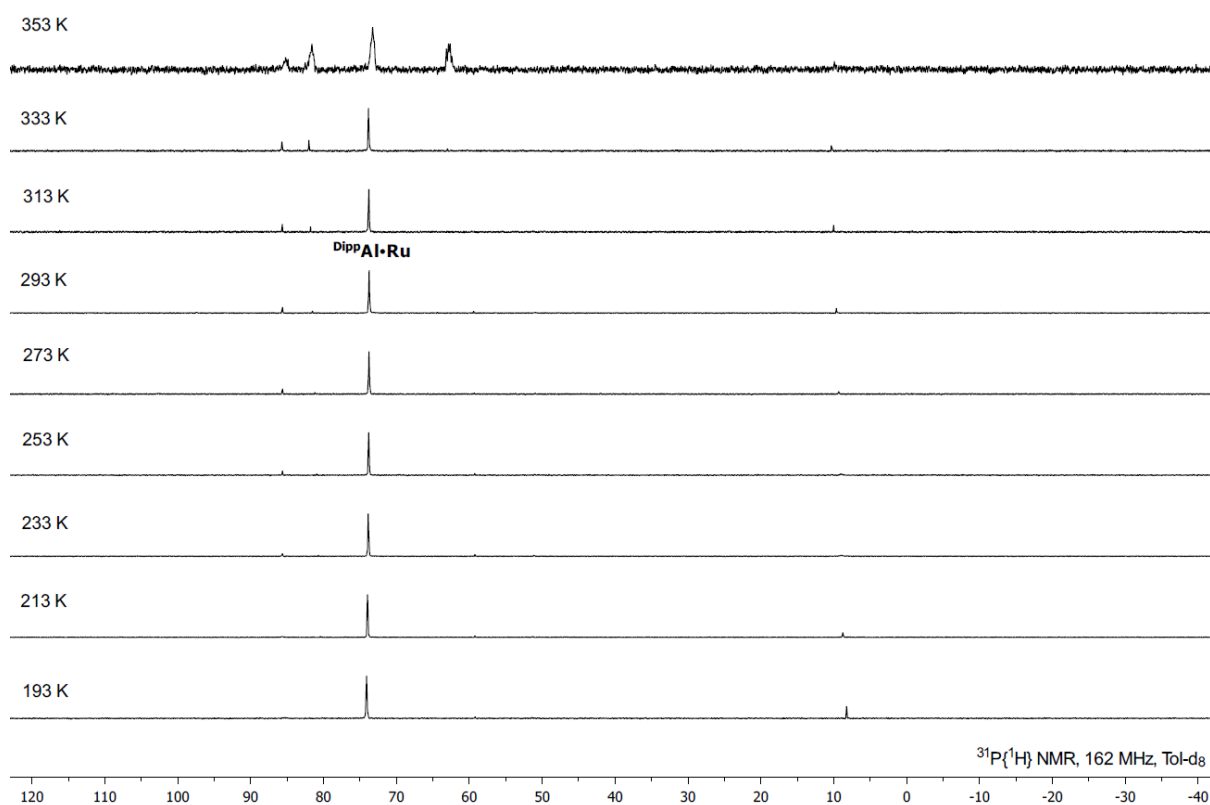


Figure S 5.58. VT $^{31}\text{P}\{^1\text{H}\}$ NMR on a sample containing $\text{DippAl}\cdot\text{Ru}$ in Tol-d_8 .

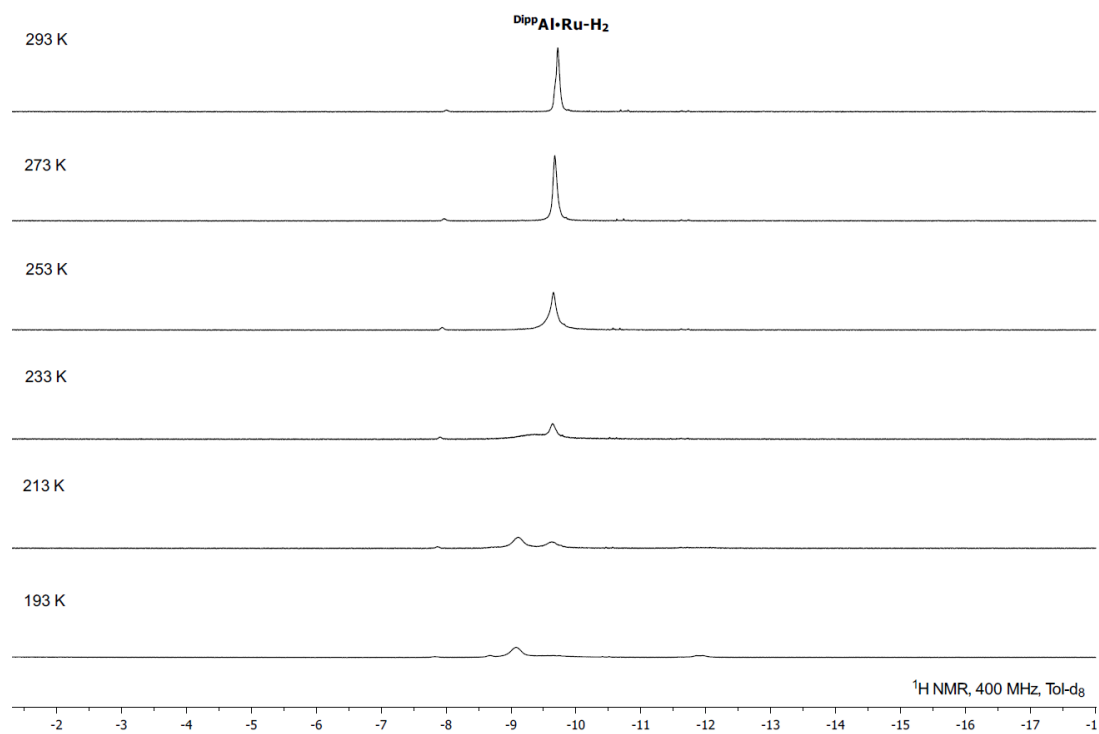


Figure S 5.59. VT ^1H NMR on a sample containing $\text{DippAl}\cdot\text{Ru-H}_2$ in Tol-d_8 . Only Ru–H region shown for clarity.

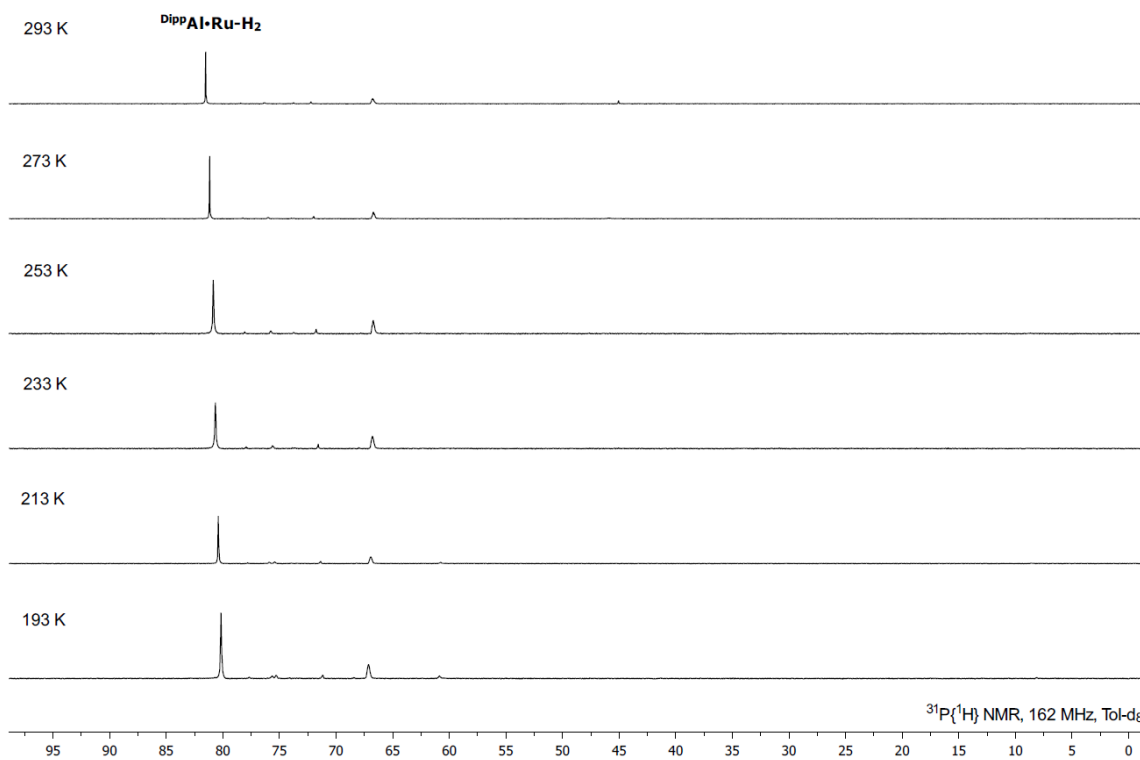


Figure S 5.60 VT $^{31}\text{P}\{^1\text{H}\}$ NMR on a sample containing $\text{DippAl}\cdot\text{Ru-H}_2$ in Tol-d_8

VT NMR data was fitted using line shape analysis with the DNMR programme integrated into Topsin v3.1. The ^1H and ^{31}P resonances of $^{\text{Mes}}\text{Al}\cdot\text{Ru}$ were fitted over the 193 to 253 K range with an initial line broadening factor of 20 Hz for ^{31}P NMR and 2 Hz for ^1H . Fits for k were optimized to the experimental data with reasonable accuracy and the modelled data are presented below, a minor unassigned species observable was not included in the model. The activation parameters for the exchange process are as follows:

$$^{31}\text{P} \quad \Delta H^\ddagger = 45 \pm 4.8 \text{ kJ mol}^{-1}, \Delta S^\ddagger = +28 \pm 22 \text{ J K}^{-1} \text{ mol}^{-1}, \Delta G^\ddagger_{298\text{K}} = 37 \pm 11 \text{ kJ mol}^{-1}.$$

$$^1\text{H} \quad \Delta H^\ddagger = 45 \pm 3.5 \text{ kJ mol}^{-1}, \Delta S^\ddagger = +26 \pm 30 \text{ J K}^{-1} \text{ mol}^{-1}, \Delta G^\ddagger_{298\text{K}} = 37 \pm 12 \text{ kJ mol}^{-1}.$$

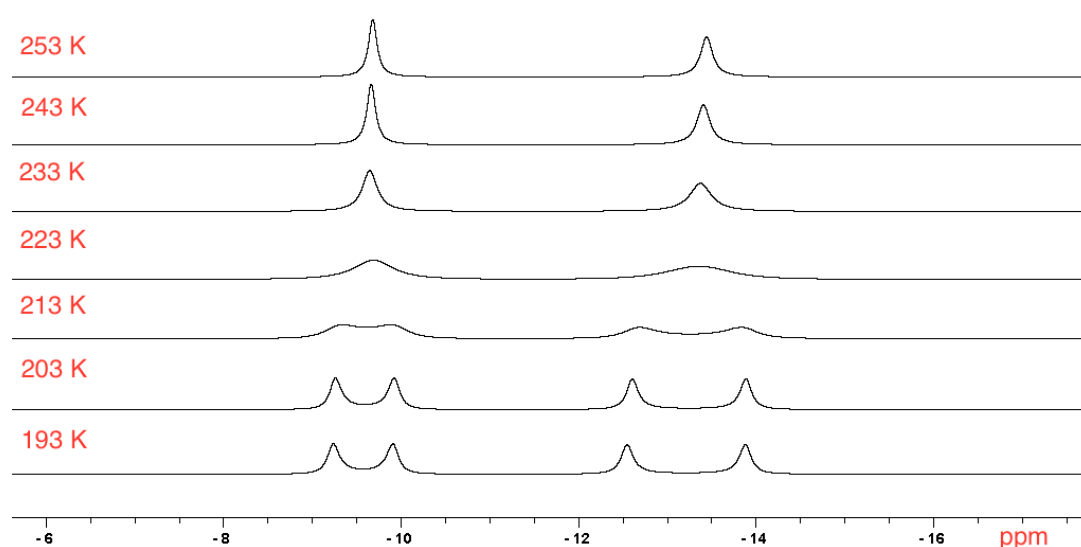


Figure S 5.61. Modelled VT ^1H NMR on a sample of $^{\text{Mes}}\text{Al}\cdot\text{Ru}$ generated from the reaction of $^{\text{Mes}}\text{BDIAL}(\text{H})_2$ with **1**

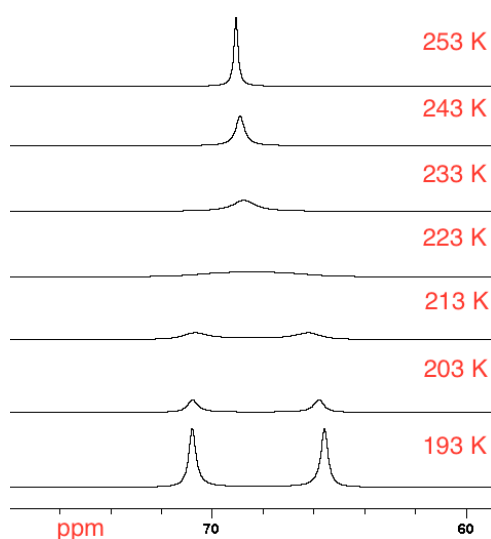


Figure S 5.62. Modelled VT $^{31}\text{P} \{^1\text{H}\}$ NMR on a sample of $^{\text{Mes}}\text{Al}\cdot\text{Ru}$ generated from the reaction of $^{\text{Mes}}\text{BDIAL}(\text{H})_2$ with **1**

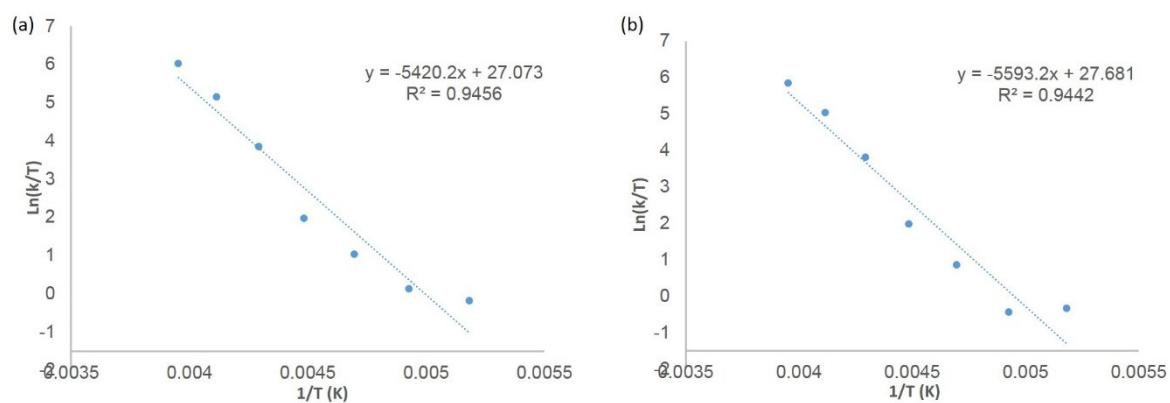
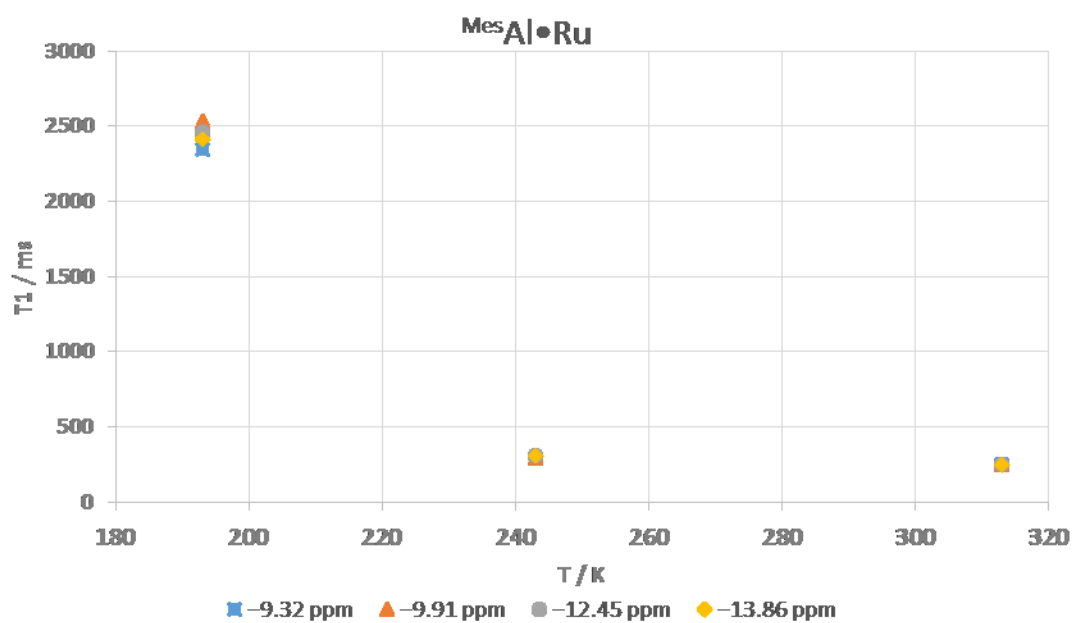
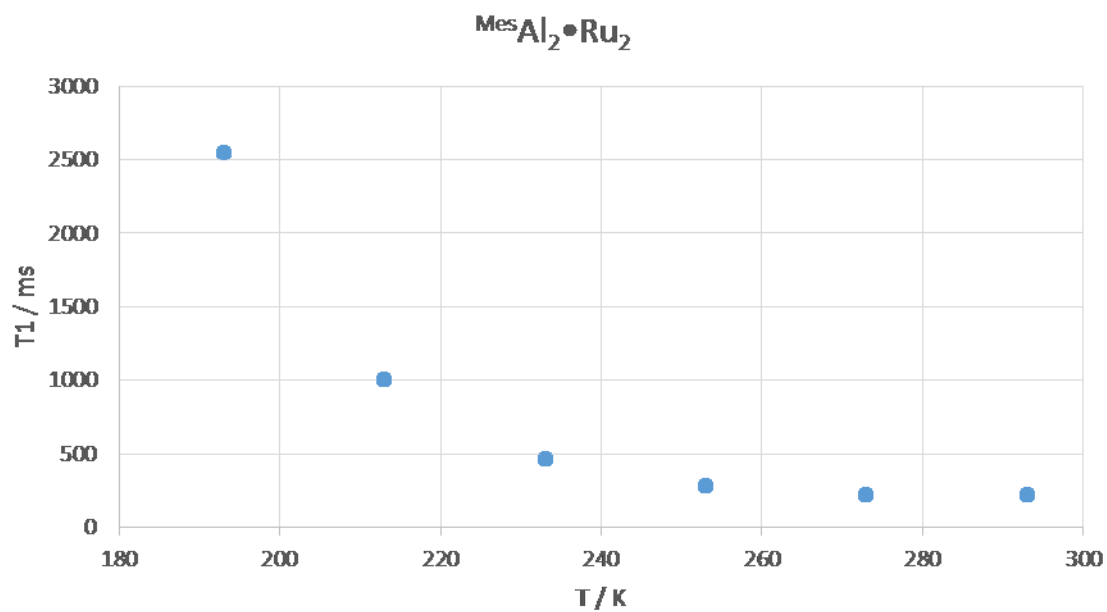


Figure S 5.63 Eyring analysis: (a) Modelled VT $^{31}\text{P}\{^1\text{H}\}$ NMR data, (b) Modelled VT ^1H NMR data.

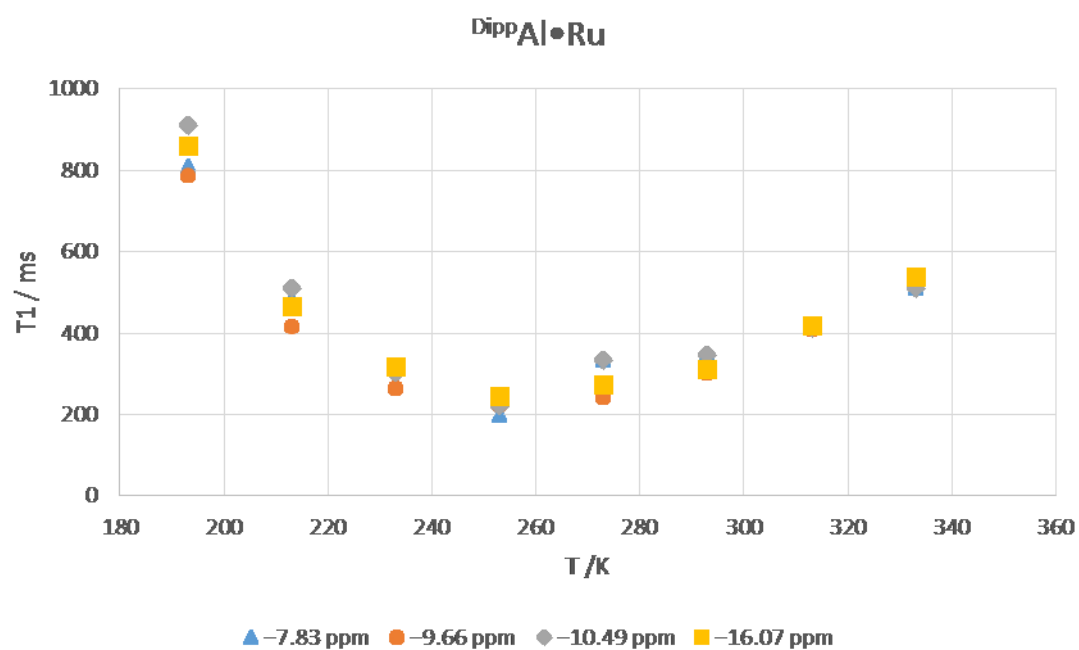
5.5.4 T_1 Data



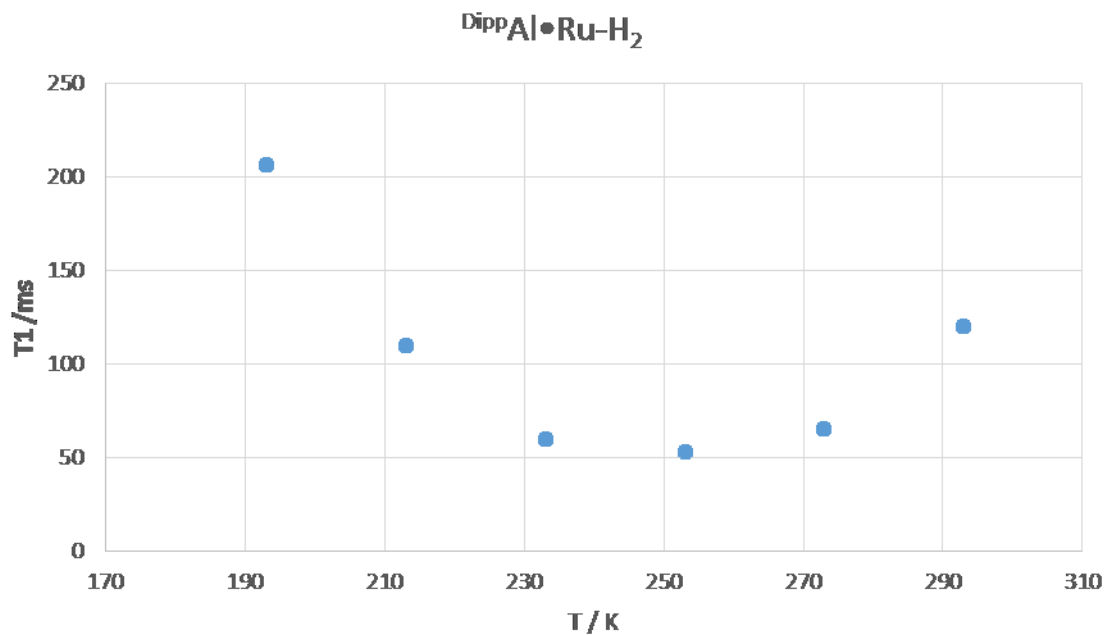
Graph S 5.1. T_1 measurements of $\text{MesAl}\cdot\text{Ru}$ taken across 193 – 313 K temperature range



Graph S 5.2 T₁ measurements of $^{\text{Mes}}\text{Al}_2\bullet\text{Ru}_2$ taken across 193 – 293 K temperature range



Graph S 5.3. T₁ measurements of $^{\text{Dipp}}\text{Al}\bullet\text{Ru}$ taken across 193 – 333 K temperature range



Graph S 5.4. T₁ measurements of ^{Dipp}Al•Ru-H₂ taken across 193 – 293 K temperature range

- 1 P. Pertici, G. Vitulli, M. Paci and L. Porri, *J. Chem. Soc. Dalton Trans.*, 1980, 1961–1964.
- 2 M. L. Christ, S. Sabo-Etienne, G. Chung and B. Chaudret, *Inorg. Chem.*, 1994, **33**, 5316–5319.
- 3 T. Arliguie, B. Chaudret, R. H. Morris and A. Sella, *Inorg. Chem.*, 1988, **27**, 598–599.
- 4 B. Chaudret and R. Poilblanc, *Organometallics*, 1985, **4**, 1722–1726.
- 5 S. K. Karmee, *Synth. Commun.*, 2013, **43**, 450–455.
- 6 C. Battilocchio, J. M. Hawkins and S. V. Ley, *Org. Lett.*, 2013, **15**, 2278–2281.
- 7 S. Sabo-Etienne and B. Chaudret, *Coord. Chem. Rev.*, 1998, **178–180**, 381–407.
- 8 A. F. Borowski, S. Sabo-Etienne, M. L. Christ, B. Donnadieu and B. Chaudret, *Organometallics*, 1996, **15**, 1427–1434.
- 9 S. Bontemps, L. Vendier and S. Sabo-Etienne, *Angew. Chem., Int. Ed.*, 2012, **51**, 1671–1674.
- 10 Y. Guari, A. Castellanos, S. Sabo-Etienne and B. Chaudret, *J. Mol. Catal. A Chem.*, 2004, **212**, 77–82.
- 11 A. F. Borowski, S. Sabo-Etienne and B. Chaudret, *J. Mol. Catal. A Chem.*, 2001, **174**, 69–79.
- 12 J. Feldman, S. J. McLain, A. Parthasarathy, W. J. Marshall, J. C. Calabrese and S. D. Arthur, *Organometallics*, 1997, **16**, 1514–1516.

- 13 S. Yow, S. J. Gates, A. J. P. White and M. R. Crimmin, *Angew. Chem., Int. Ed.*, 2012, **51**, 12559–12563.
- 14 S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards and G. J. McIntyre, *Chem. Eur. J.*, 2010, **16**, 938–955.
- 15 J. Spielmann, D. Piesik, B. Wittkamp, G. Jansen and S. Harder, *Chem. Commun.*, 2009, 3455.
- 16 S. Harder and J. Brettar, *Angew. Chem., Int. Ed.*, 2006, **45**, 3474–3478.
- 17 M. L. Christ, S. Sabo-Etienne and B. Chaudret, *Organometallics*, 1994, **13**, 3800–3804.
- 18 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. H. P., A. F. Izmaylov, J. Bloino, G. Zheng, D. J. Sonnenb, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V Ortiz, J. Cioslowski, D. J. Fox, R. D. 0. Gaussian 09, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. H. P., A. F. Izmaylov, J. Bloino, G. Zheng, D. J. Sonnenb, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V Ortiz, J. Cioslowski, D. J. Fox and 2009. Gaussian, Inc., Wallingford CT, *Gaussian Inc.*, 2009.
- 19 A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899–926.
- 20 E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales and F. Weinhold, 2001.
- 21 P. Pykkö and M. Atsumi, *Chem. Eur. J.*, 2009, **15**, 186–197.

- 22 J. M. L. Martin and A. Sundermann, *J. Chem. Phys.*, 2001, **114**, 3408–3420.
- 23 D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123–141.
- 24 A. Bergner, M. Dolg, W. Küchle, H. Stoll and H. Preuß, *Mol. Phys.*, 1993, **80**, 1431–1441.
- 25 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213–222.
- 26 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261.
- 27 T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294–301.
- 28 Richard F. W. Bader, *Atoms in Molecules A Quantum Theory*, Clarendon Press, 1994.
- 29 R. F. W. Bader, *Chem. Rev.*, 1991, **91**, 893–928.
- 30 T. A. Keith, 2017.
- 31 L.-M. Tang, Y.-Q. Duan, X.-F. Li and Y.-S. Li, *J. Organomet. Chem.*, 2006, **691**, 2023–2030.
- 32 C. Cui, H. W. Roesky, H. Hao, H. G. Schmidt and M. Noltemeyer, *Angew. Chem., Int. Ed.*, 2000, **39**, 1815–1817.
- 33 C. Cui, H. W. Roesky, H. G. Schmidt, M. Noltemeyer, H. Hao and F. Cimpoesu, *Angew. Chem., Int. Ed.*, 2000, **39**, 4274–4276.

6 APPENDIX

6.1 MULTINUCLEAR NMR SPECTRA

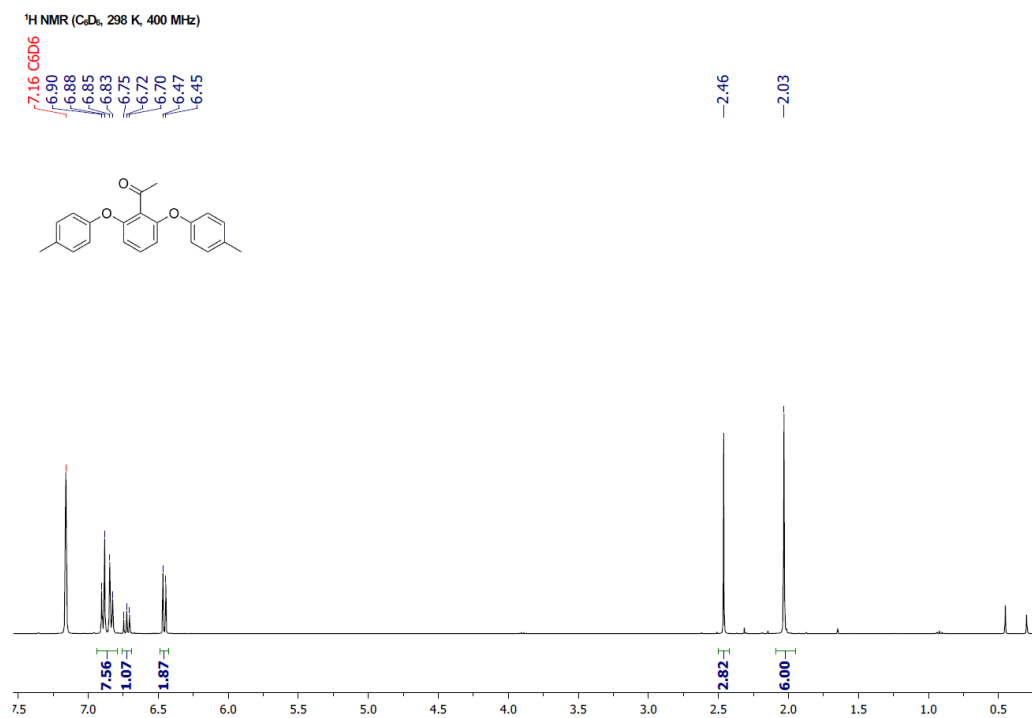


Figure A 1. ¹H NMR spectrum of 3b

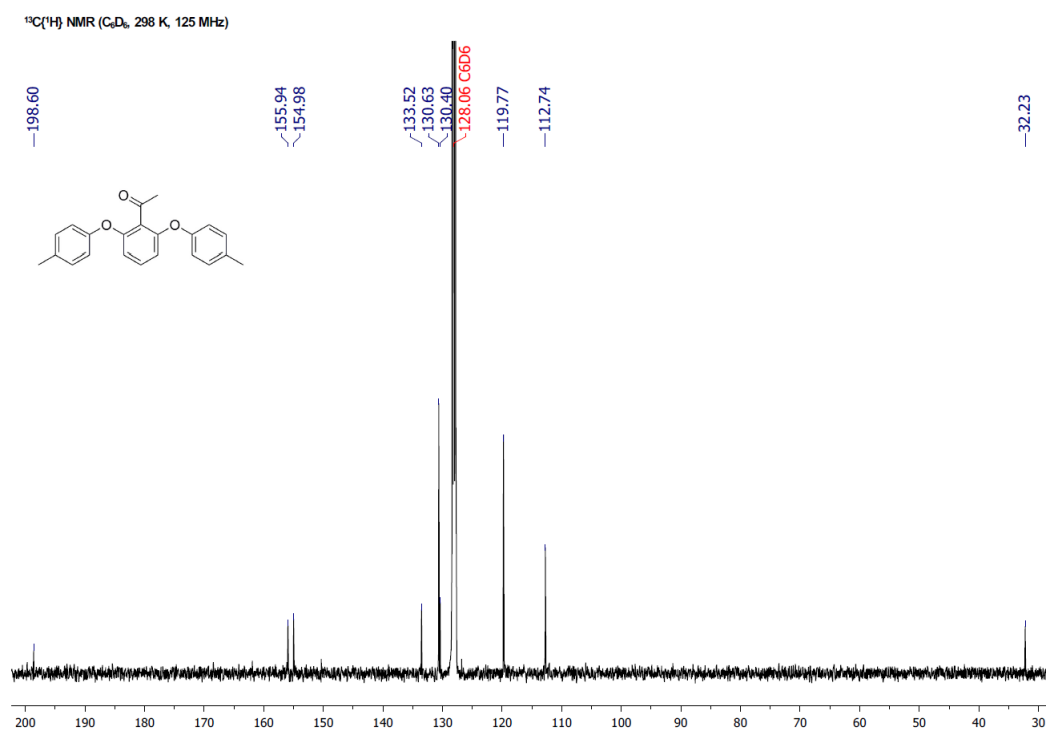


Figure A 2. ¹³C{¹H} NMR spectrum of 3b

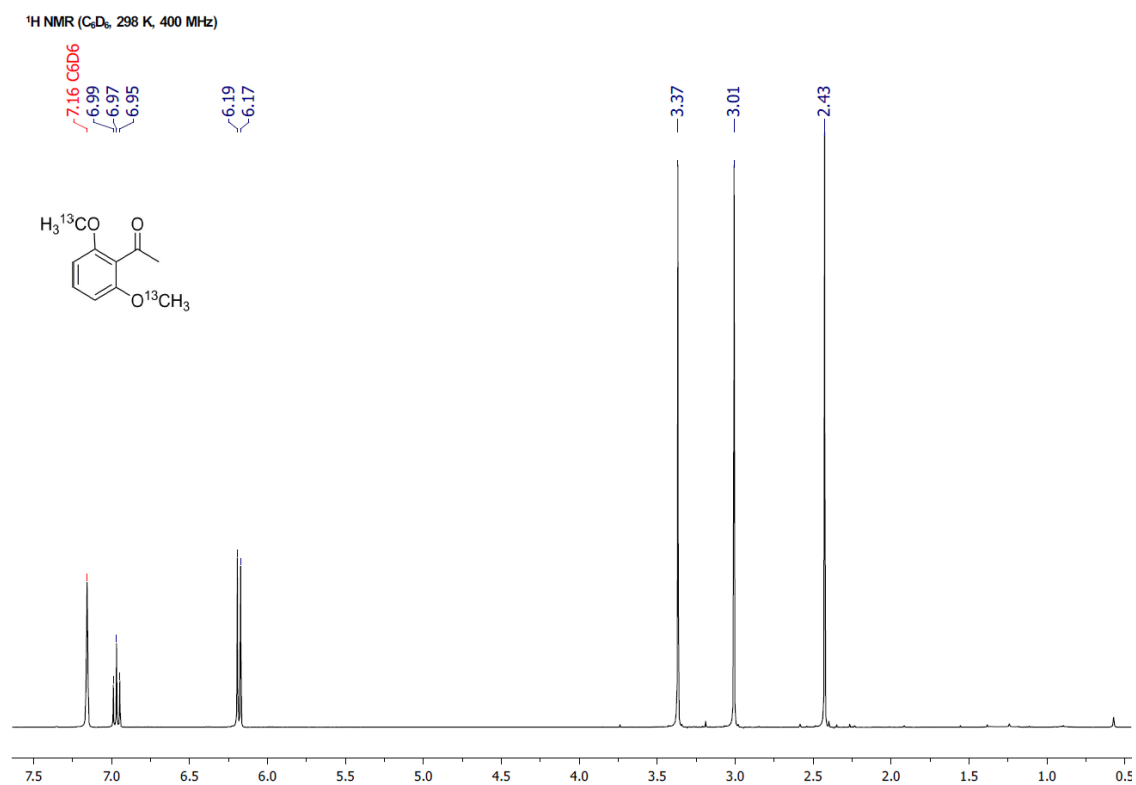


Figure A 3. ¹H NMR spectrum of ¹³C₂-3a

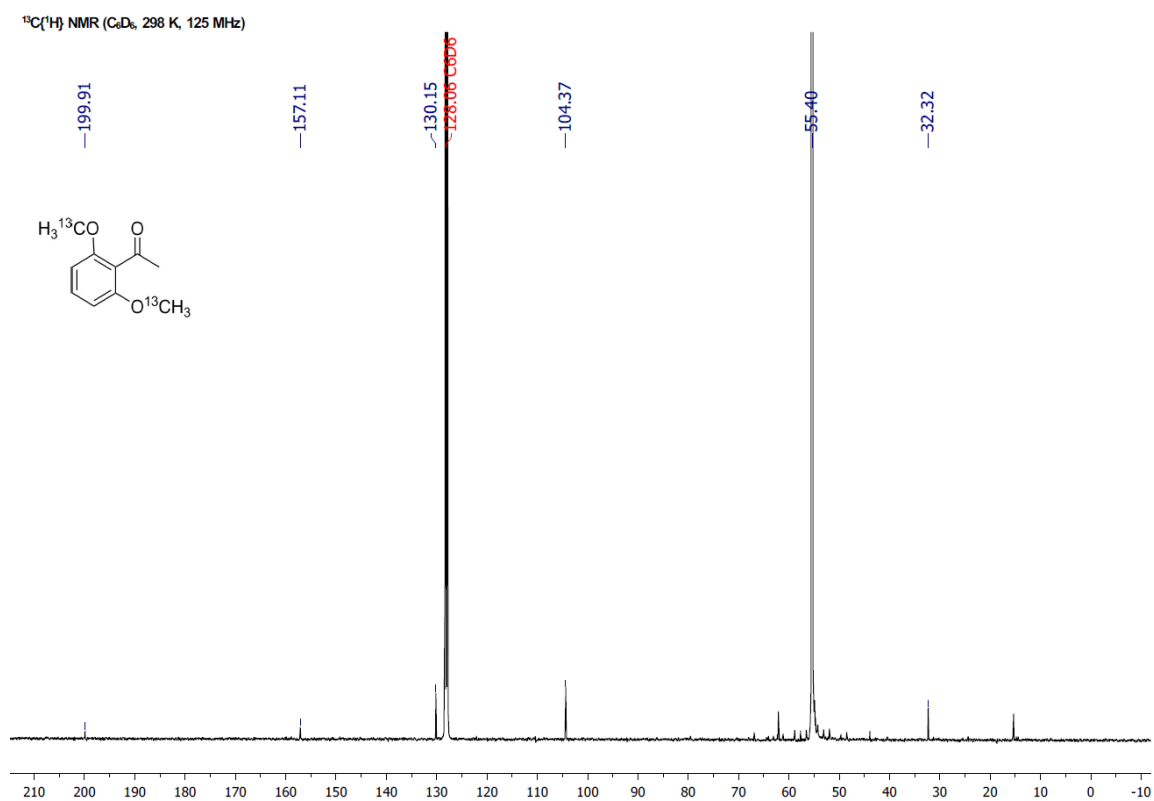


Figure A 4. ¹³C{¹H} NMR spectrum of ¹³C₂-3b

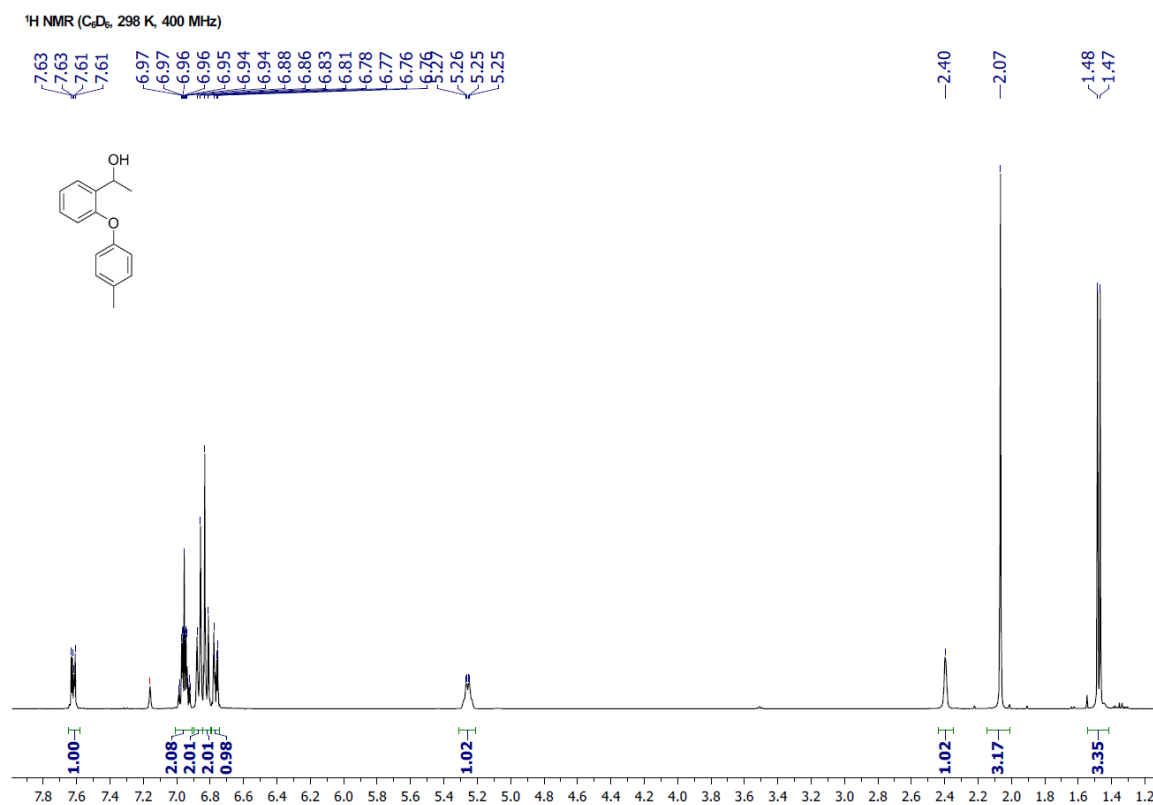


Figure A 5. ¹H NMR spectrum of transfer hydrogenation product of **2b**

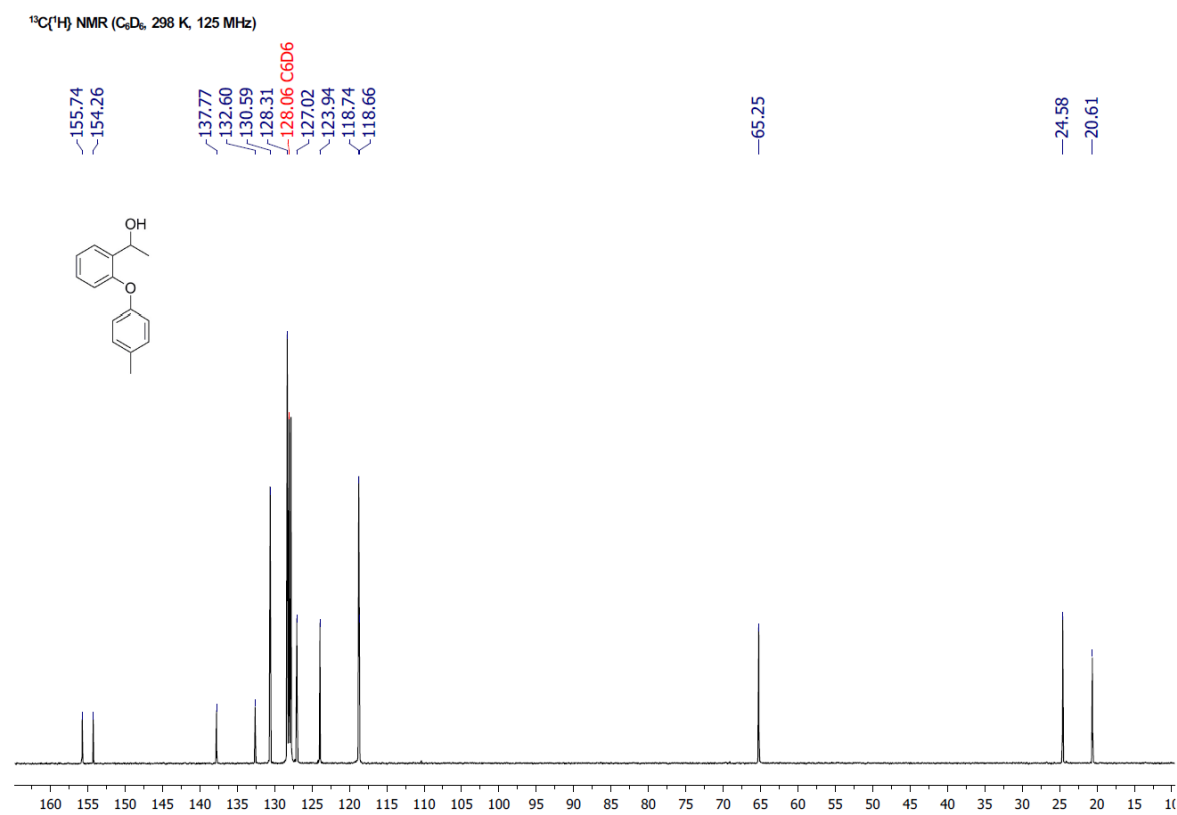


Figure A 6. ¹³C{¹H} NMR spectrum of transfer hydrogenation product of **2b**

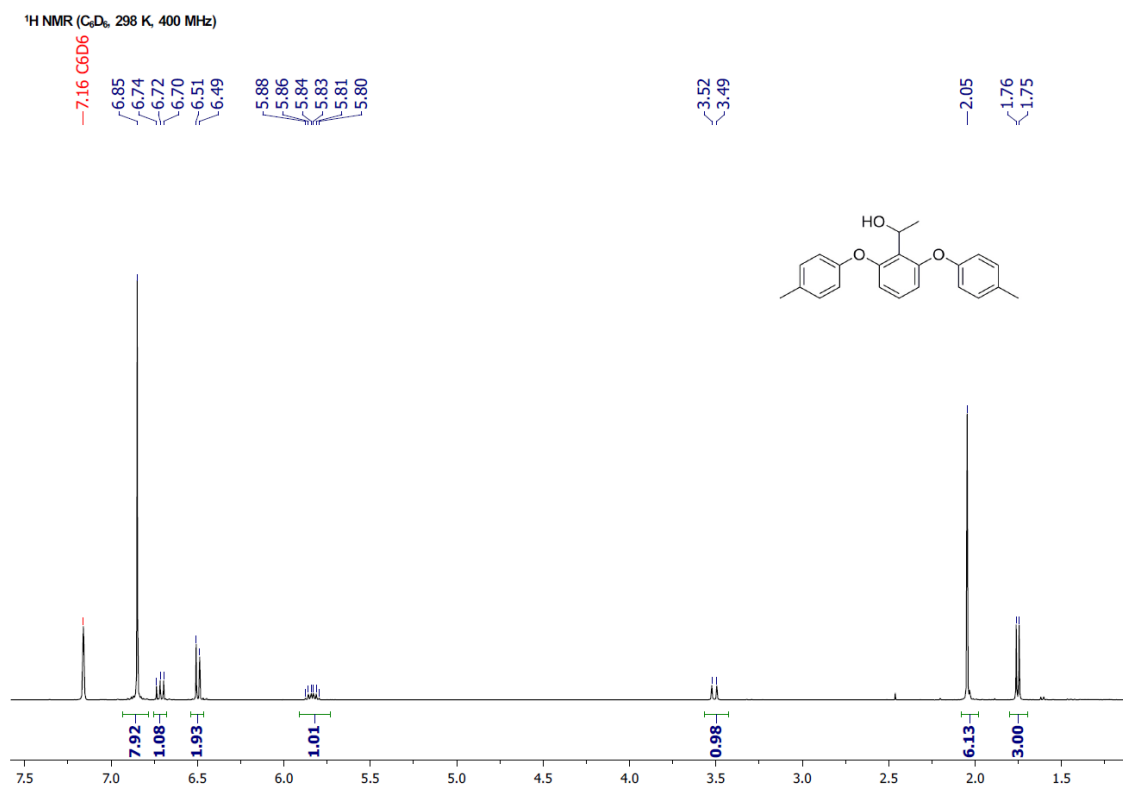


Figure A 7. ^1H NMR spectrum of transfer hydrogenation product of **3b**

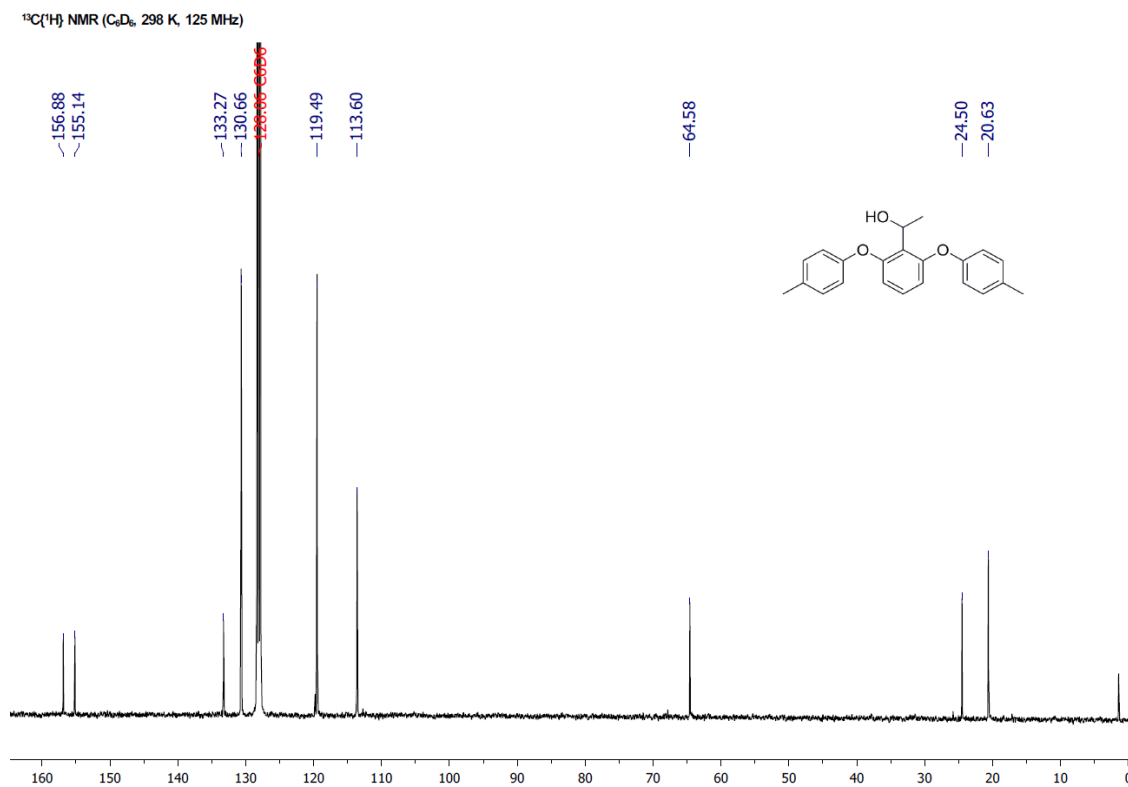


Figure A 8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of transfer hydrogenation product of **3b**

Jul31-2017.120.fid
sl397 (after distillation)

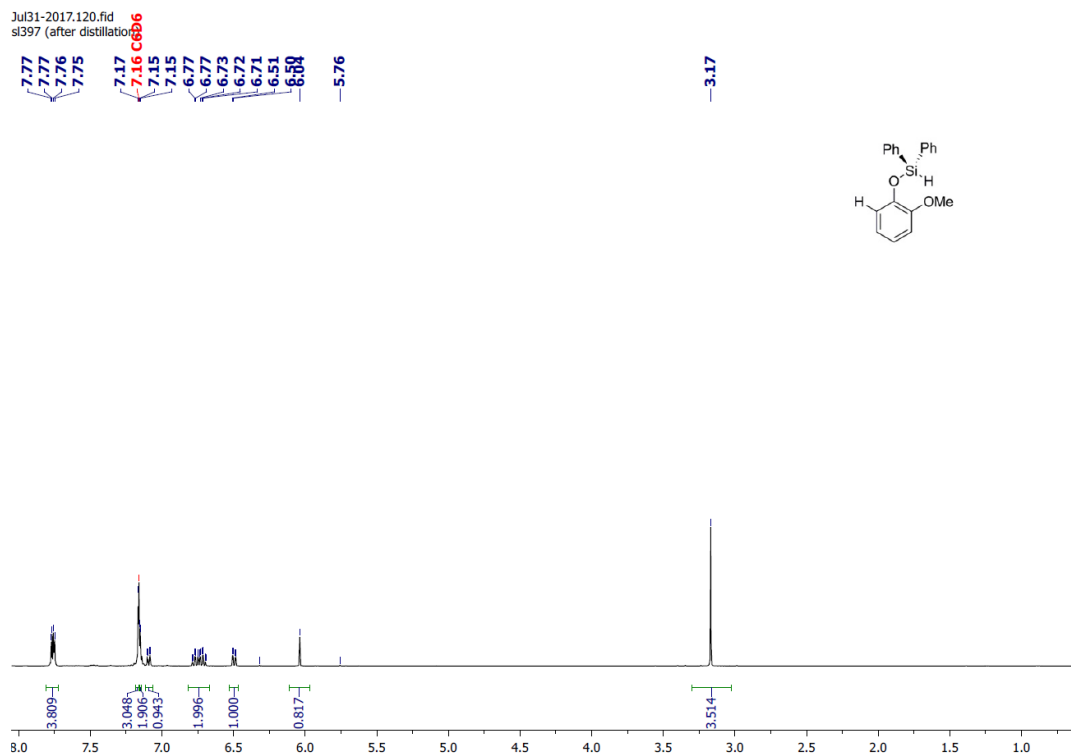


Figure A 9. ^1H NMR spectrum of 9a

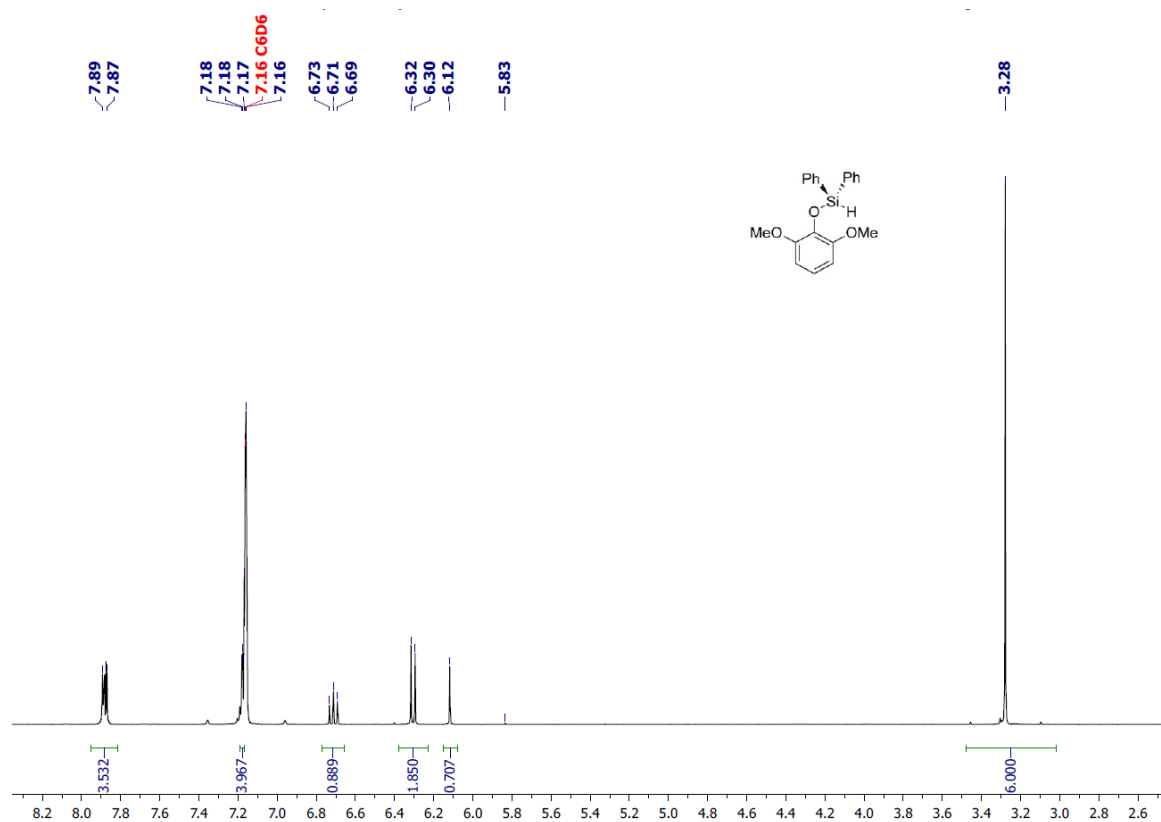


Figure A 10. ^1H NMR spectrum of 9b

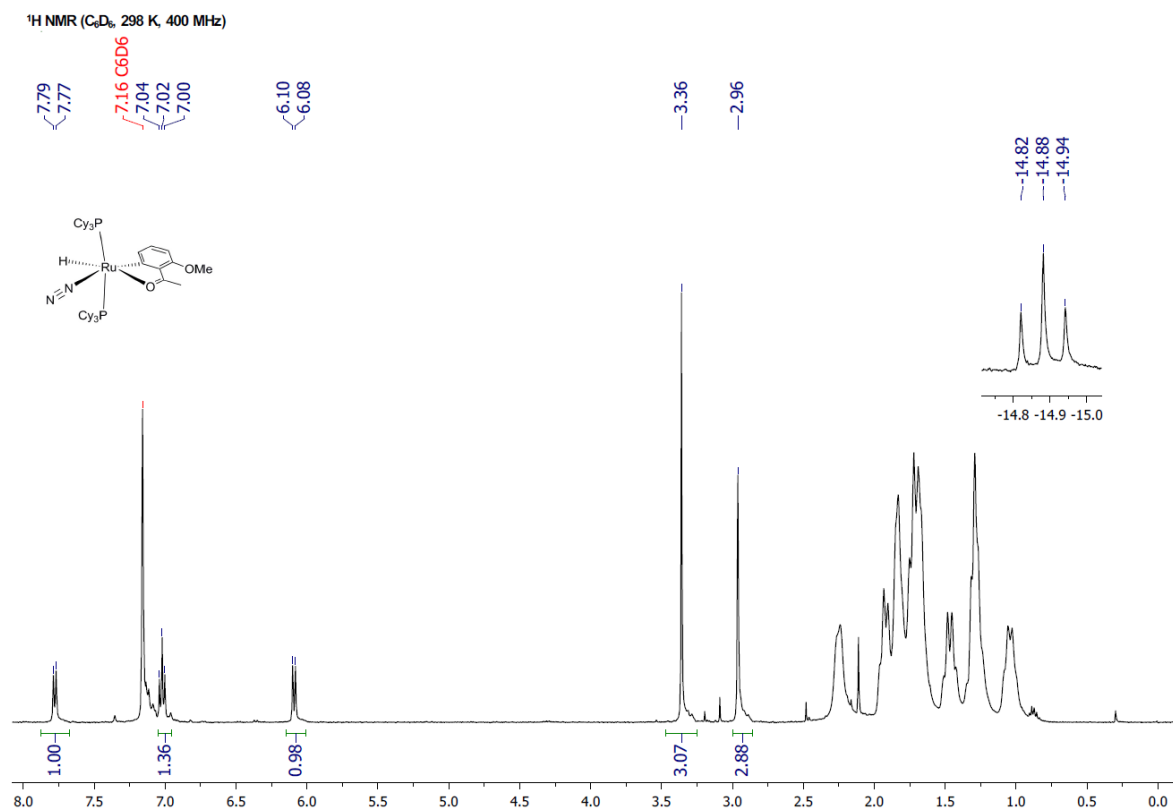


Figure A 11. ^1H NMR spectrum of **4a**

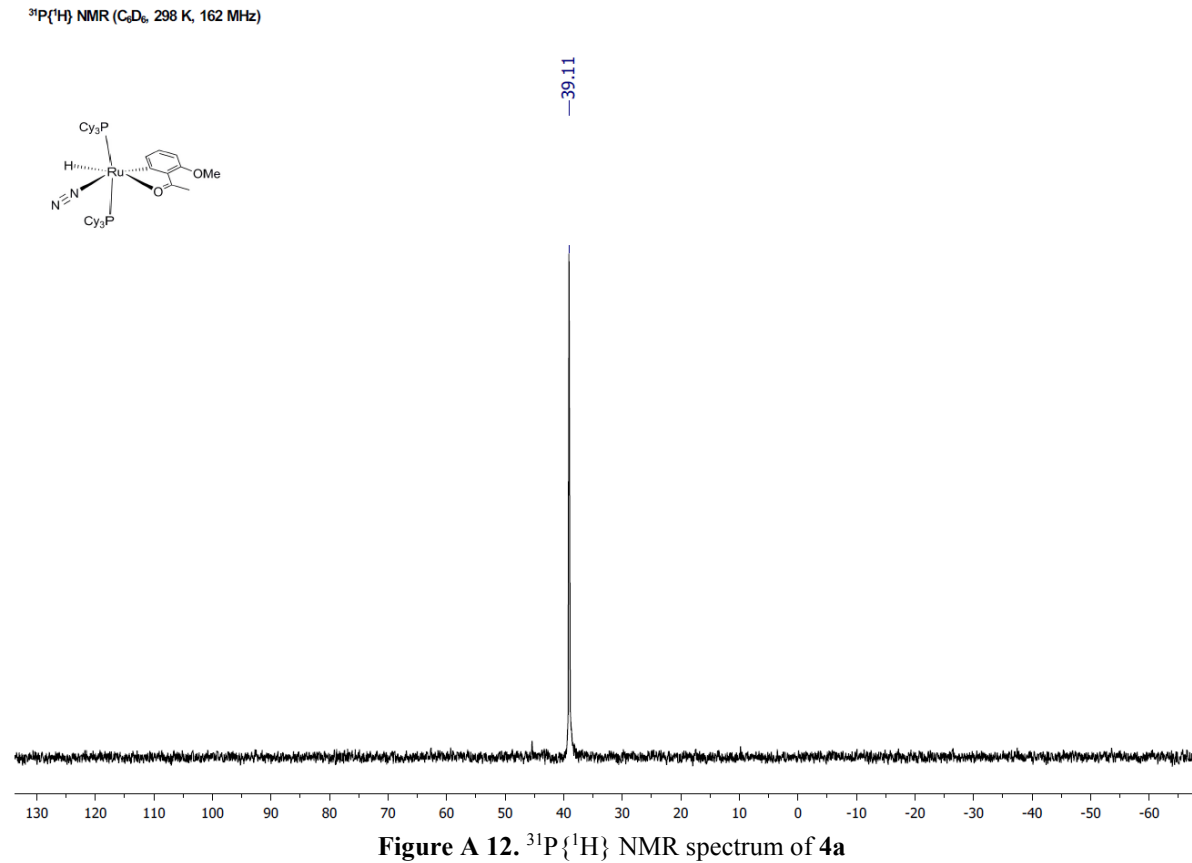


Figure A 12. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4a**

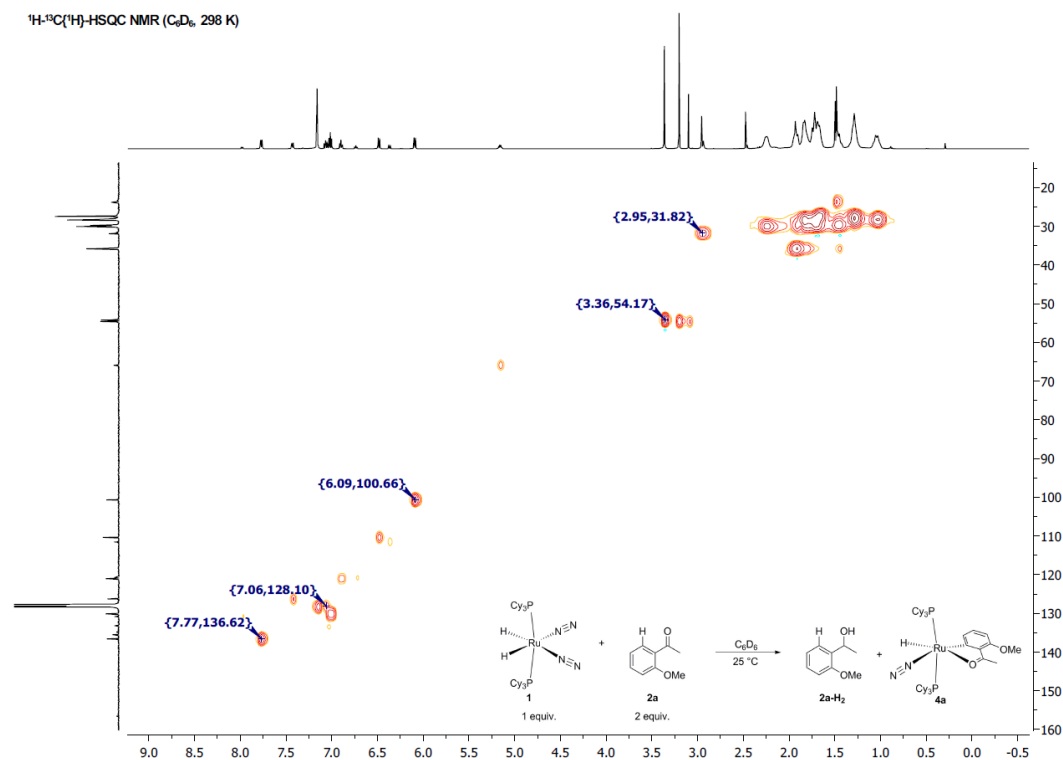


Figure A 13. HSQC NMR spectrum of the reaction of **1** with **2a**

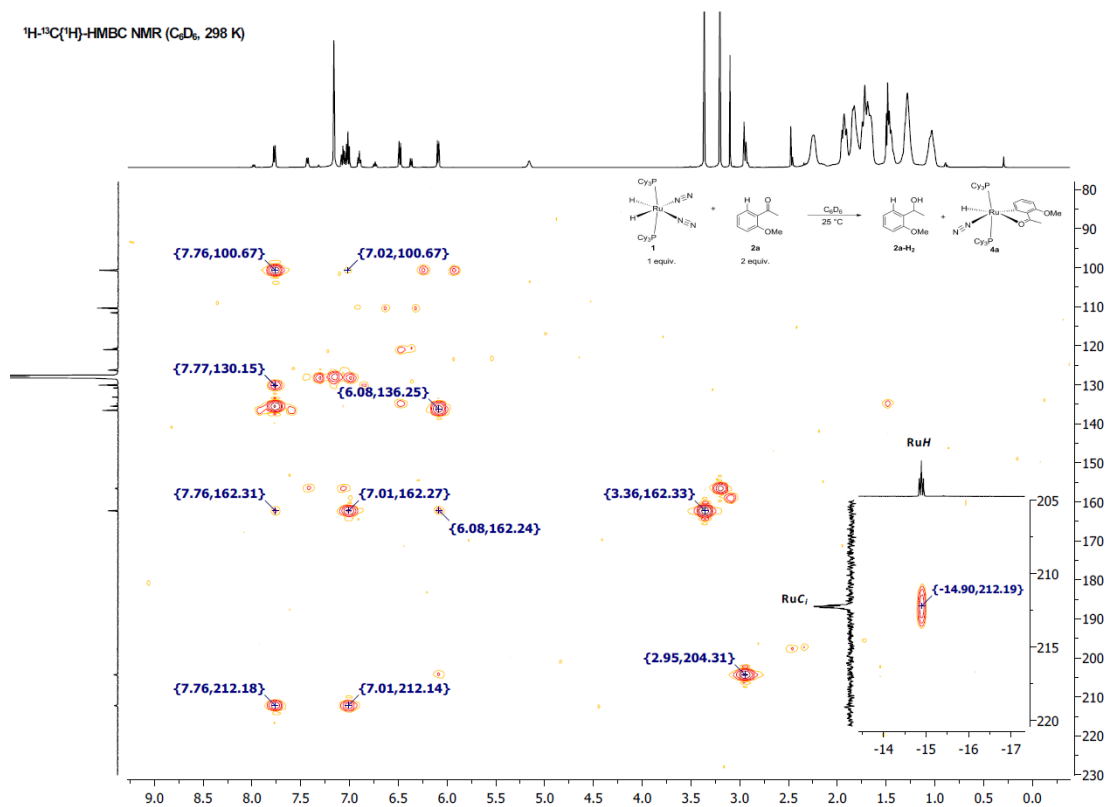
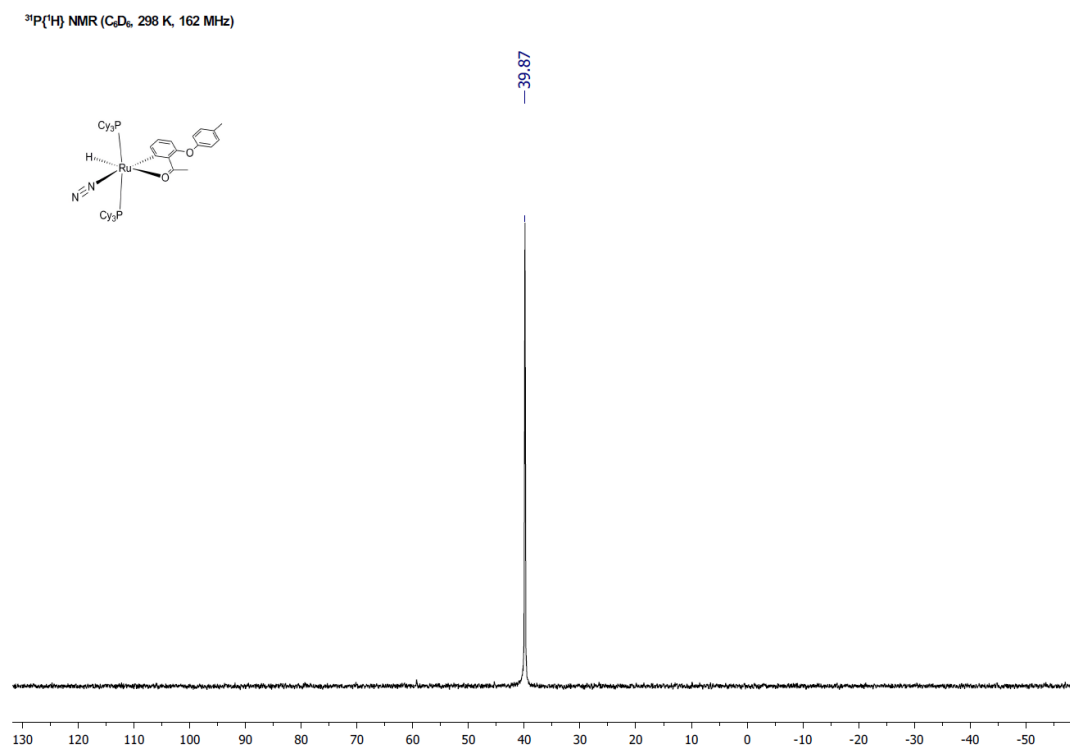
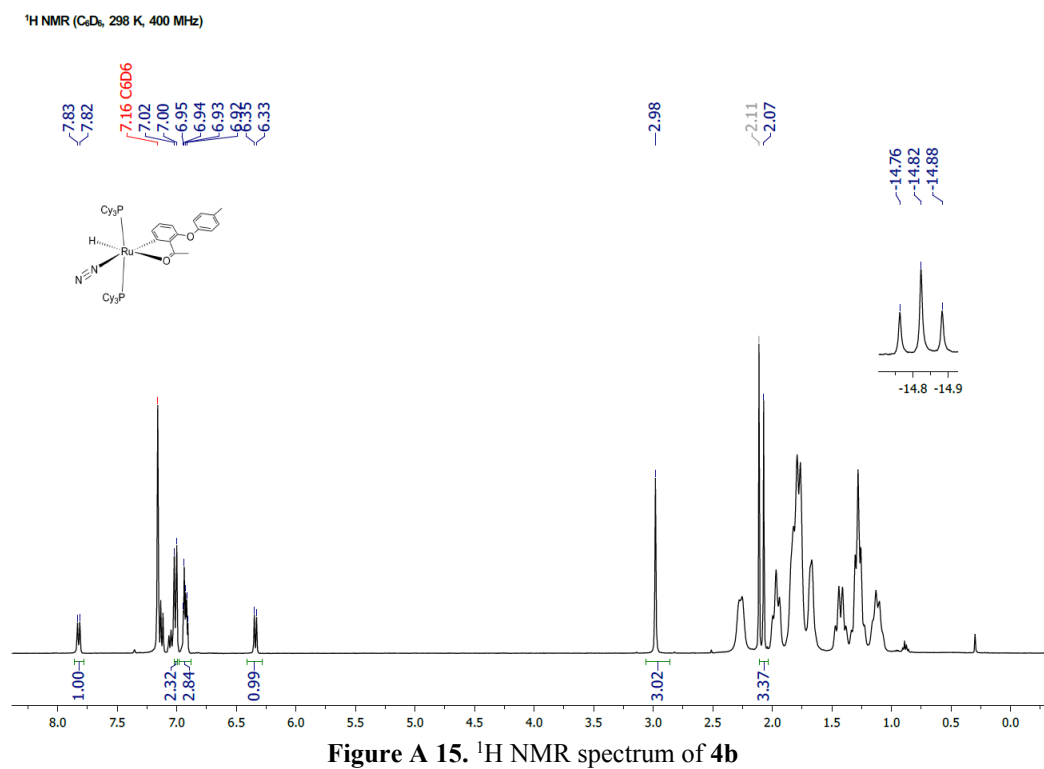


Figure A 14. HMBC NMR spectrum of the reaction of **1** with **2a**



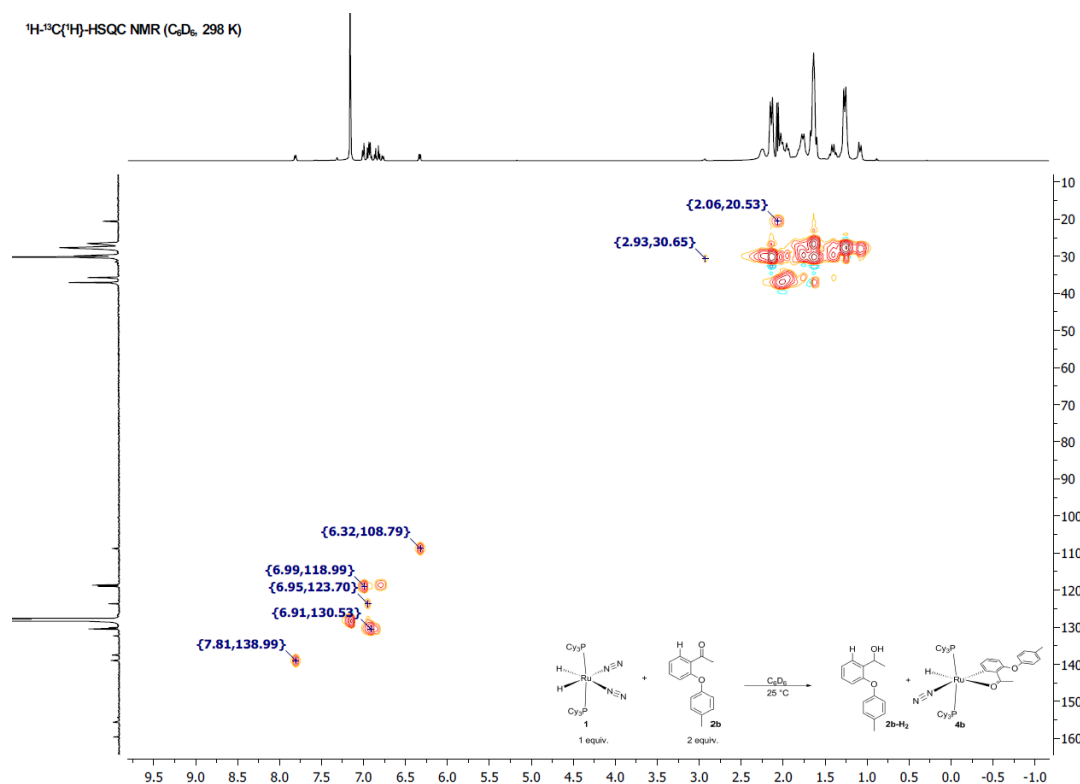


Figure A 17. HSQC NMR spectrum of the reaction of **1** with **3a**

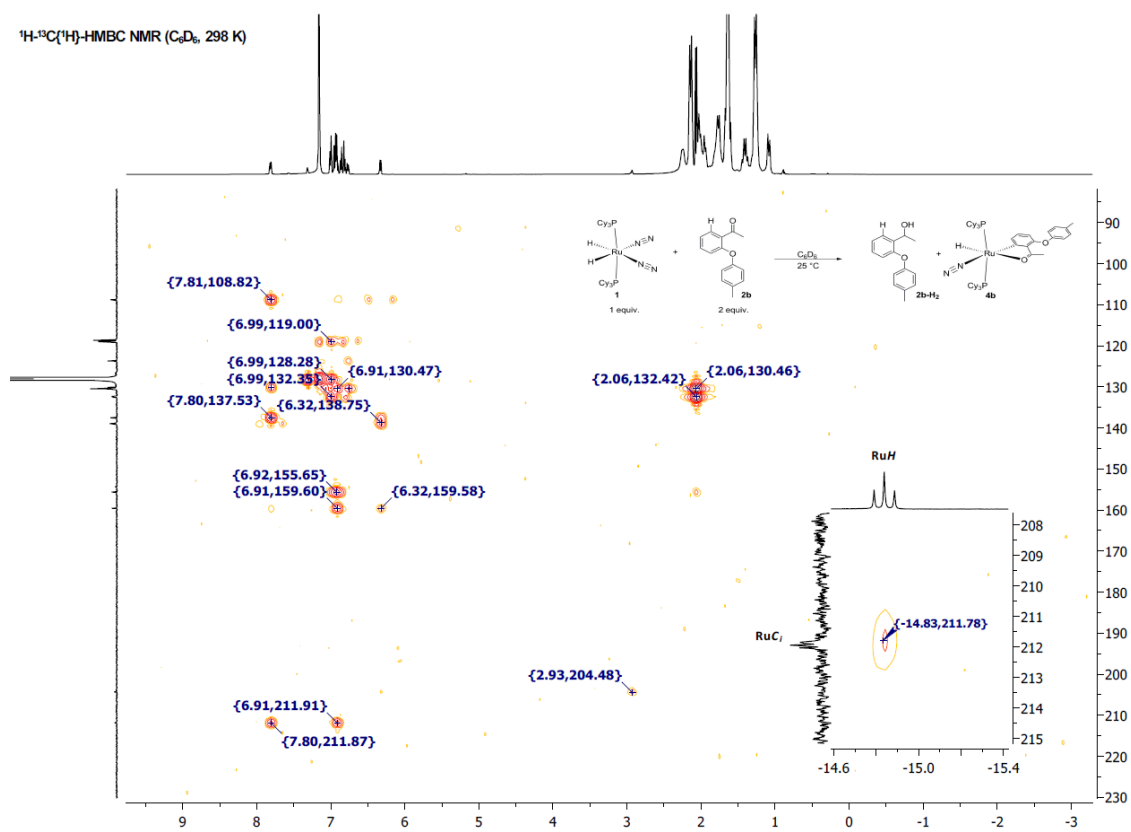


Figure A 18. HMBC NMR spectrum of the reaction of **1** with **3a**

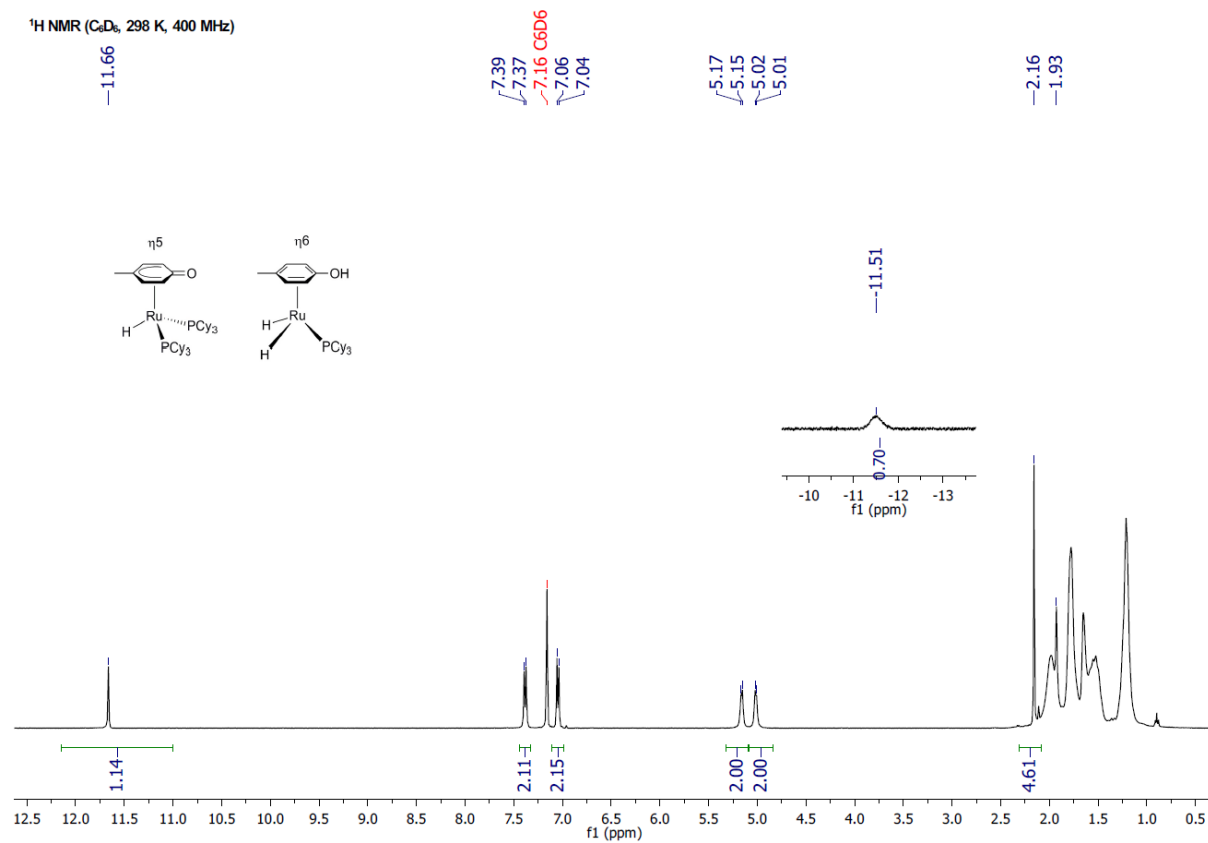


Figure A 19. ^1H NMR spectrum of **7a/8a**

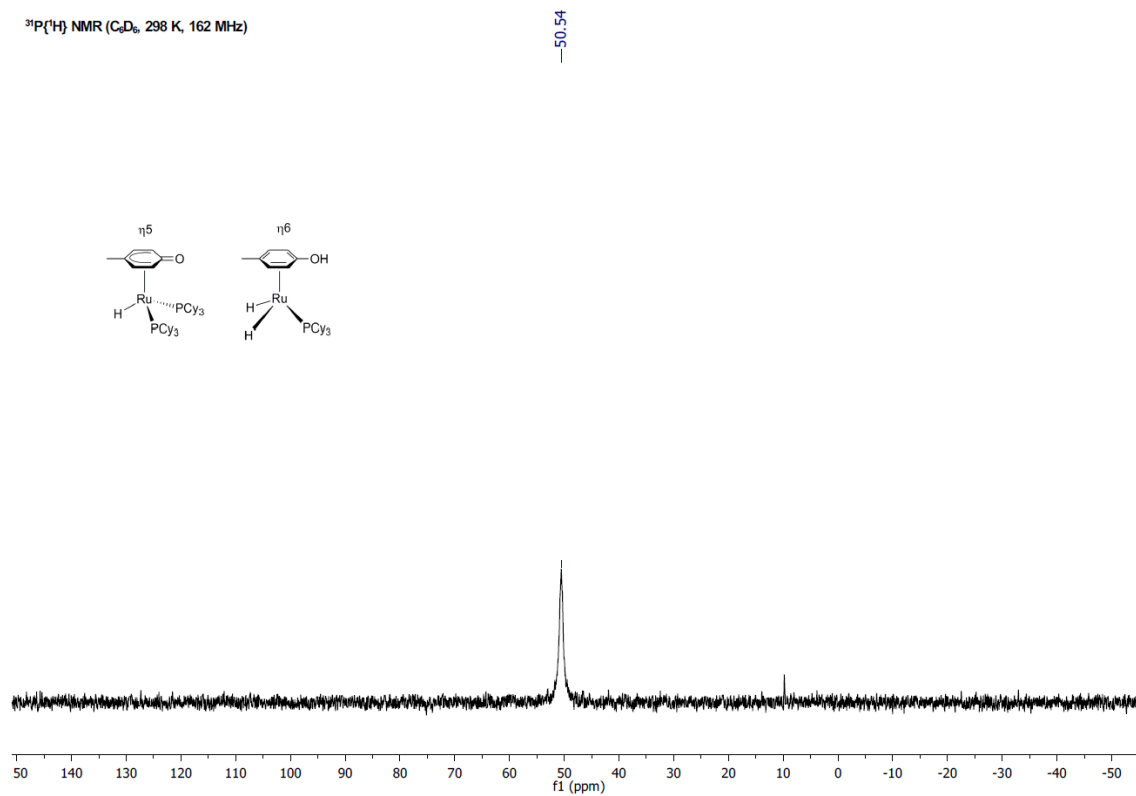


Figure A 20. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7a/8a**

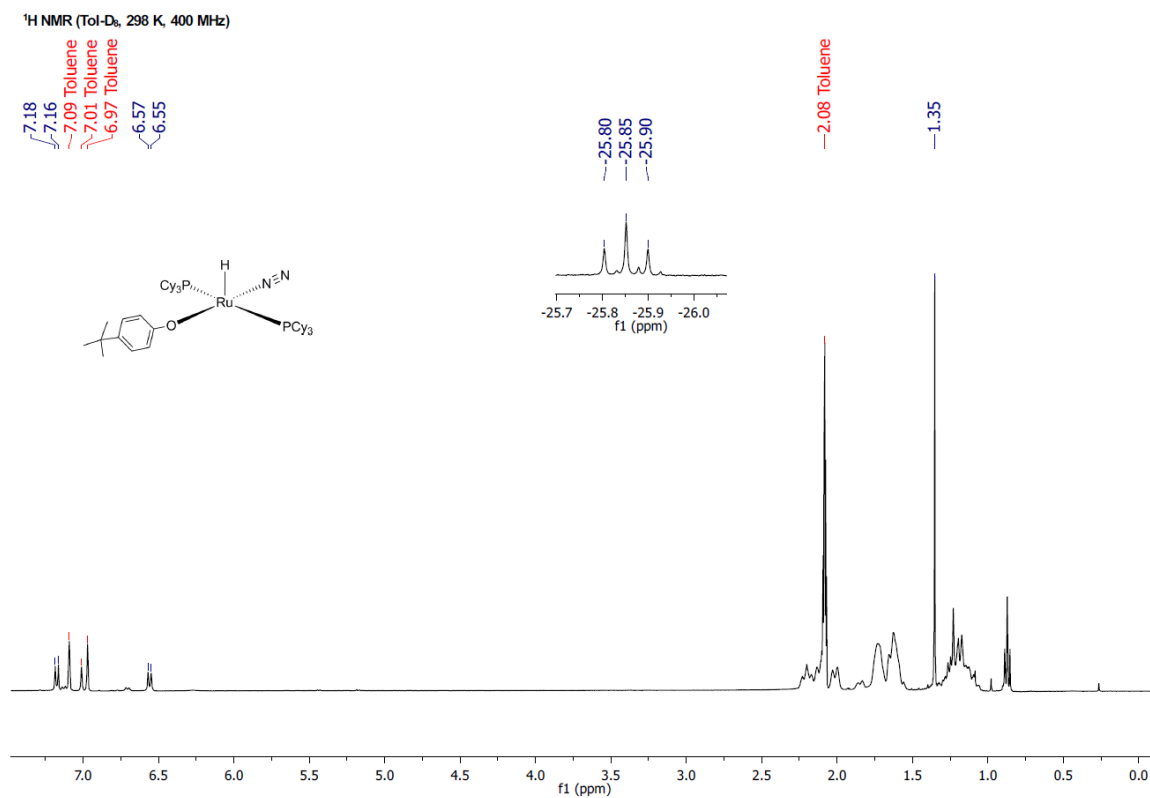


Figure A 21. ¹H NMR spectrum of **6b**

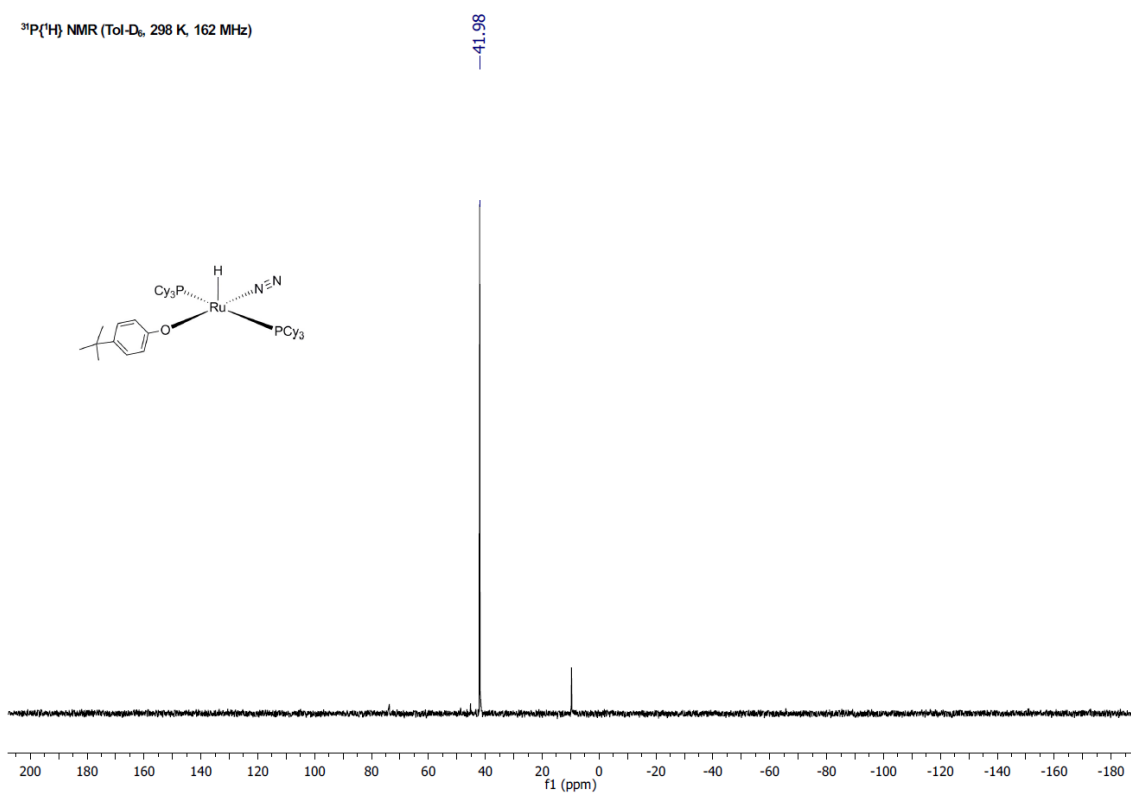


Figure A 22. ³¹P{¹H} NMR spectrum of **6b**

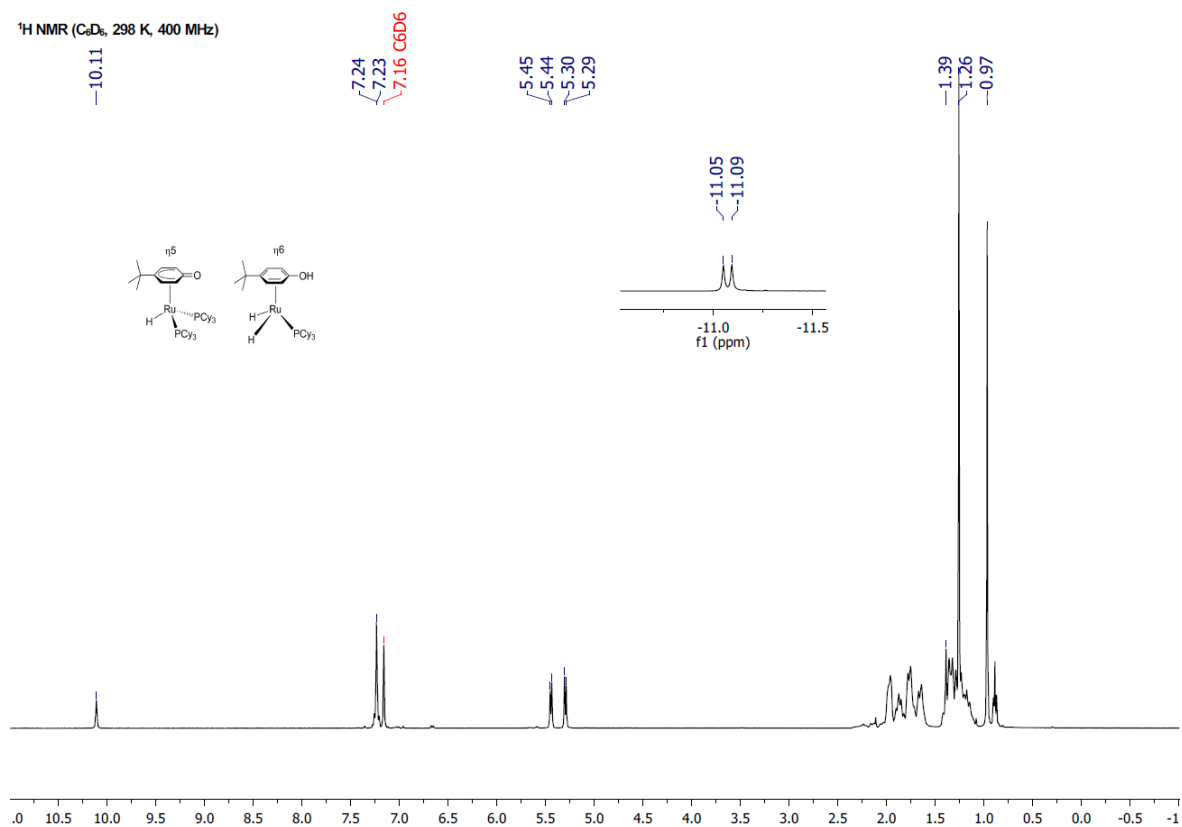


Figure A 23. ^1H NMR spectrum of **7b/8b**

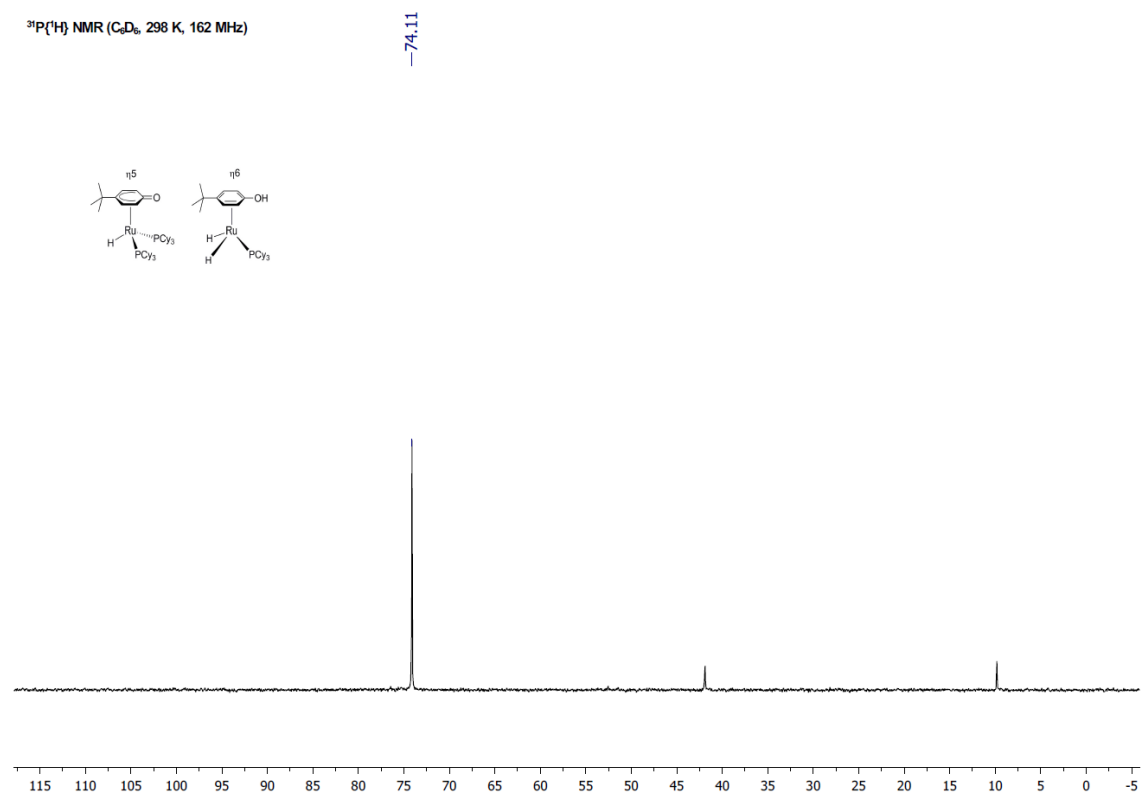


Figure A 24. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7b/8b**

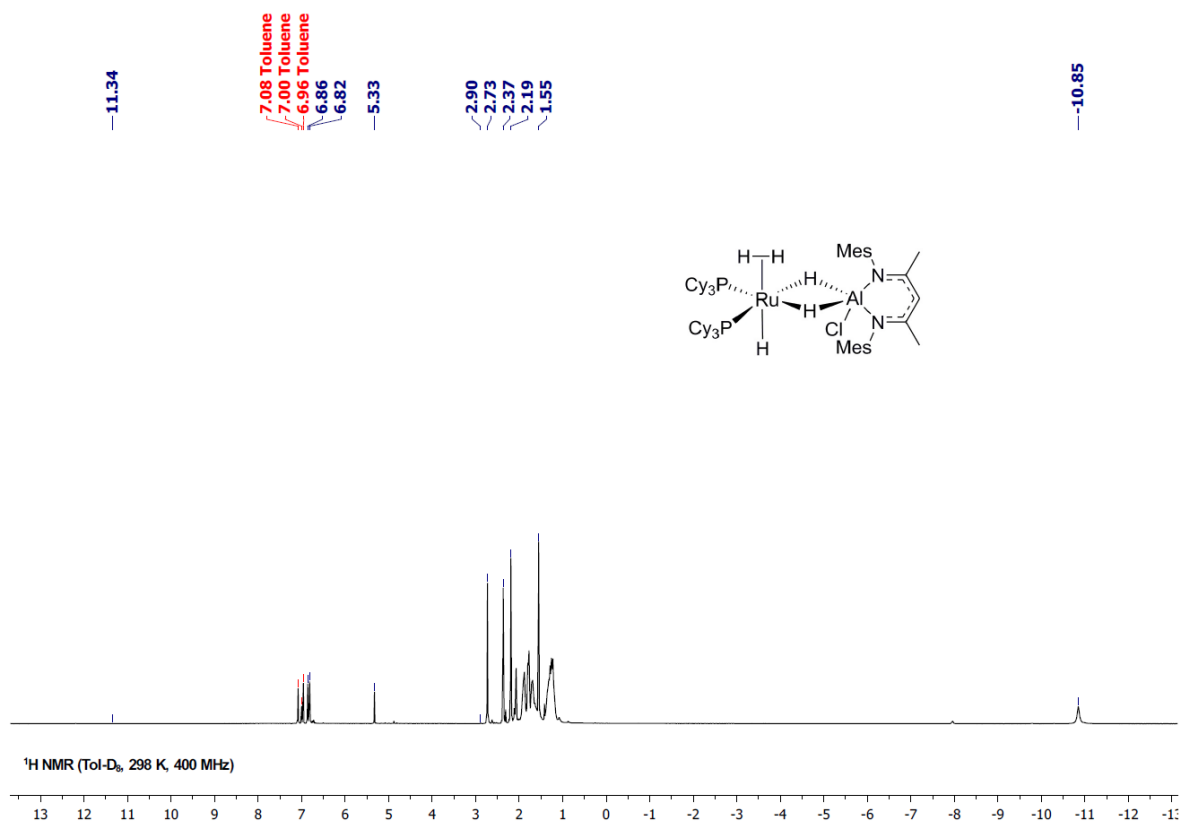


Figure A 25. ¹H NMR spectrum of Al•Ru-H₂

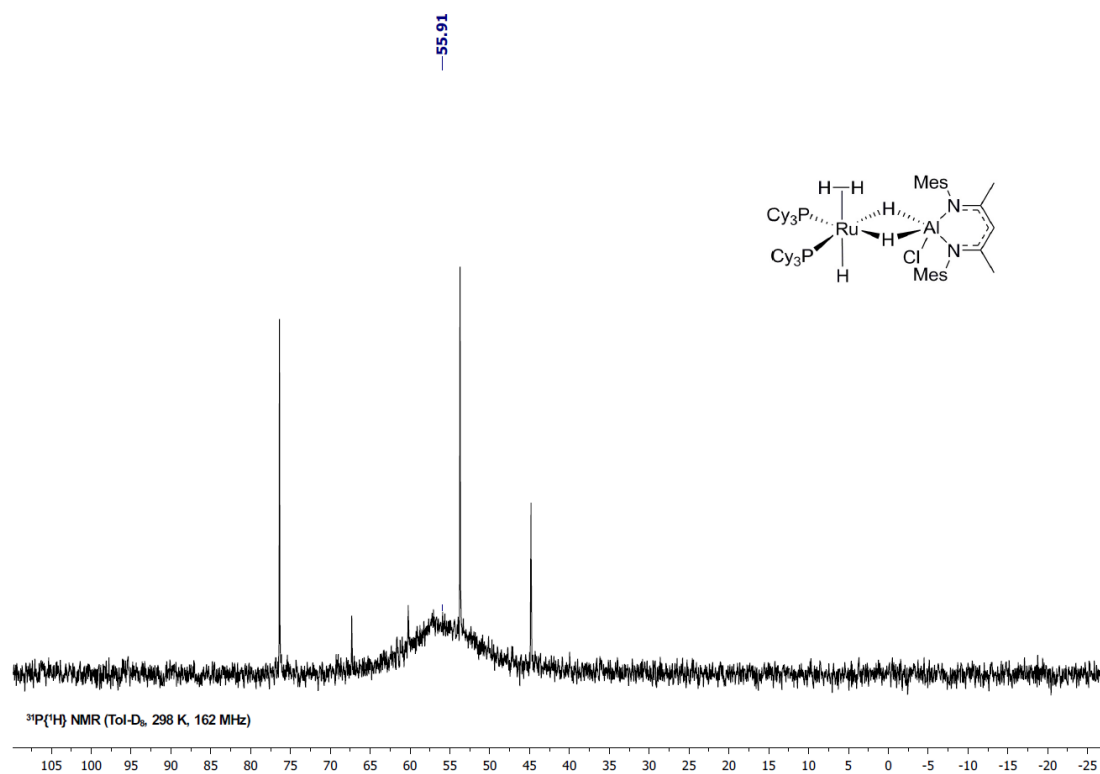


Figure A 26. ³¹P{¹H} NMR spectrum of Al•Ru-H₂

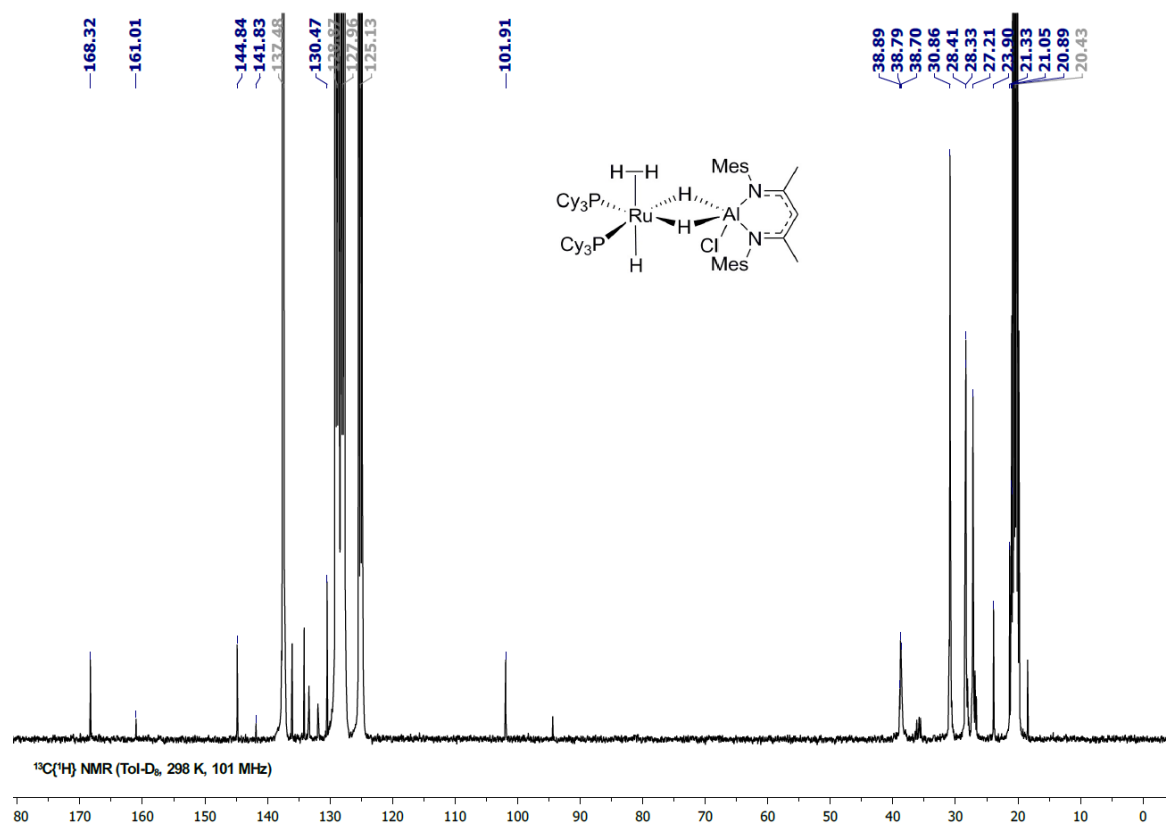


Figure A 27. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Al}\cdot\text{Ru}-\text{H}_2$

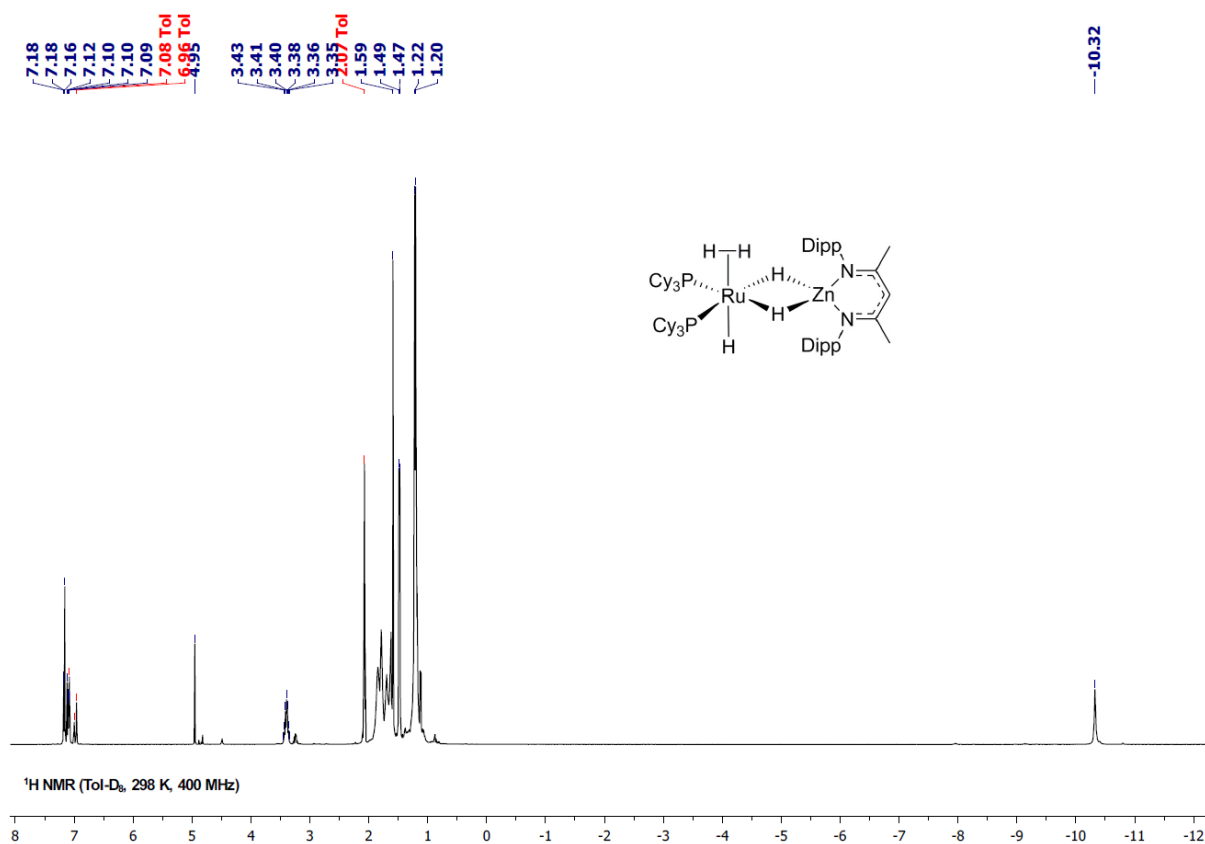


Figure A 28. ^1H NMR spectrum of $\text{Zn}\cdot\text{Ru}-\text{H}_2$

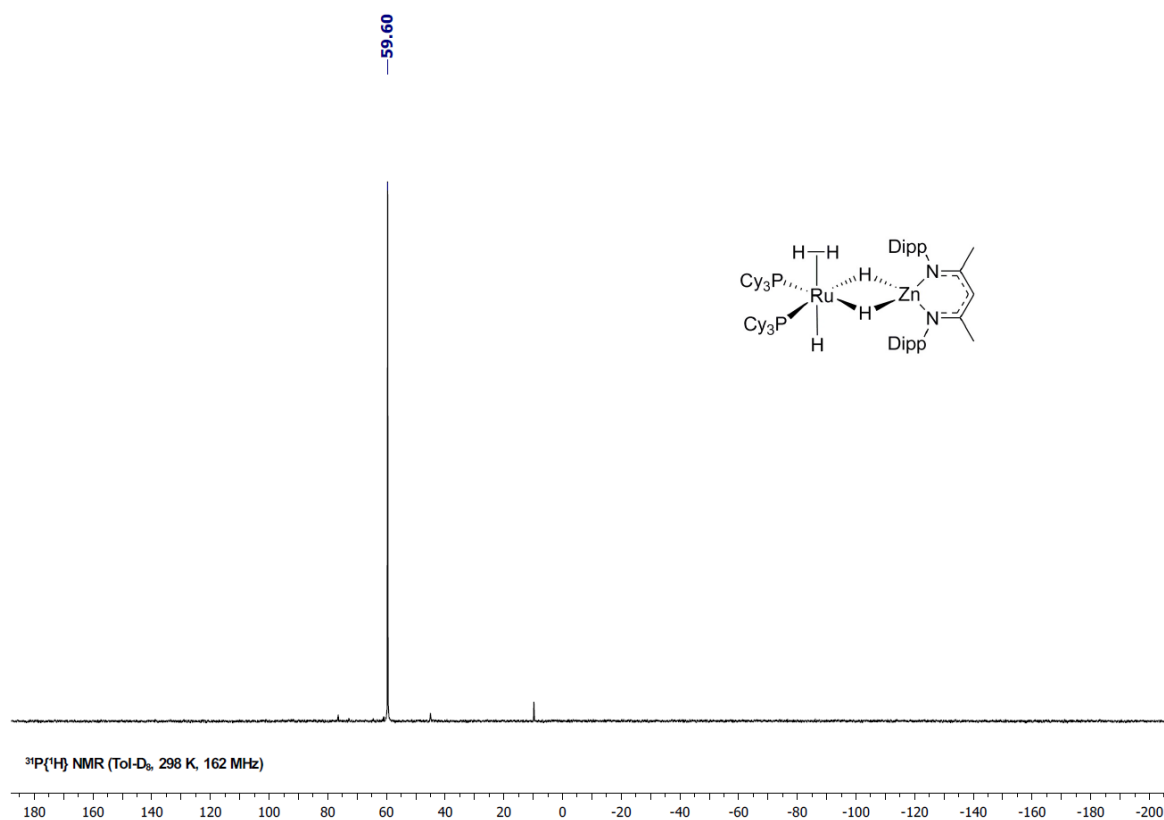


Figure A 29. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Zn}\cdot\text{Ru-H}_2$

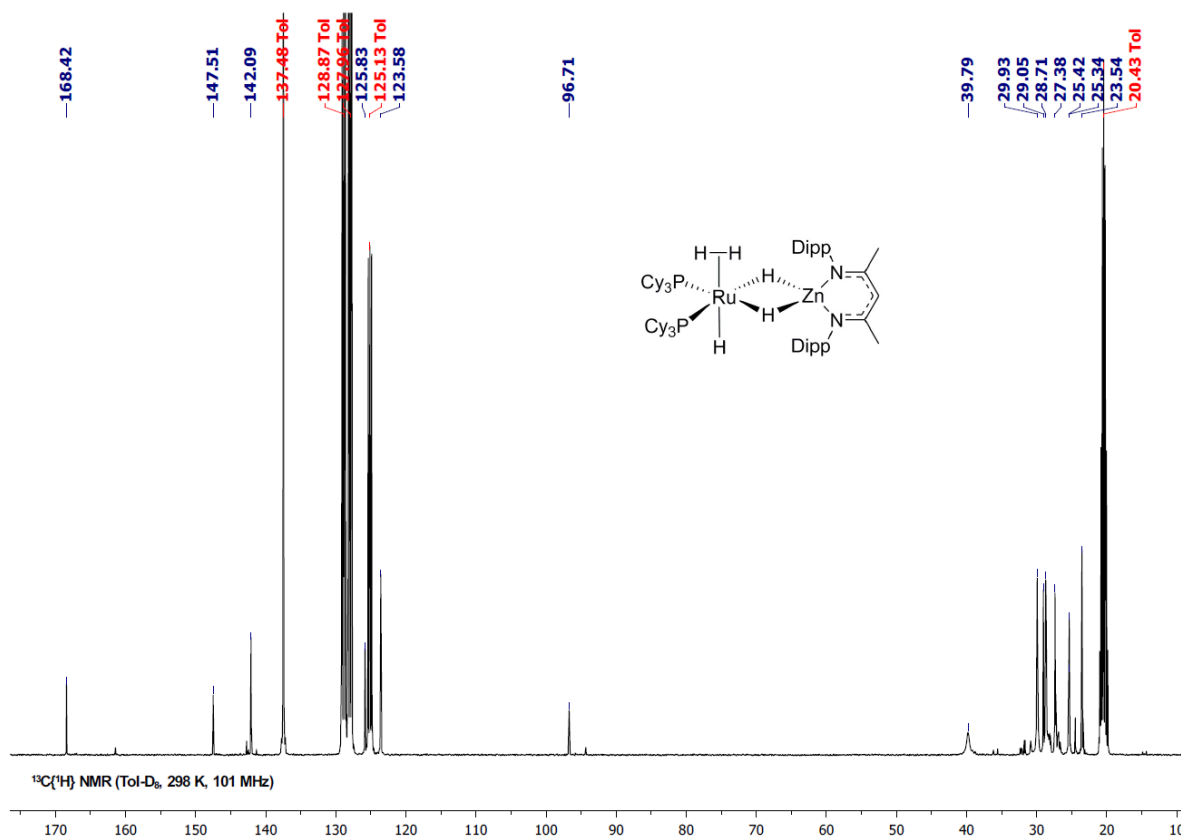


Figure A 30. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Zn}\cdot\text{Ru-H}_2$

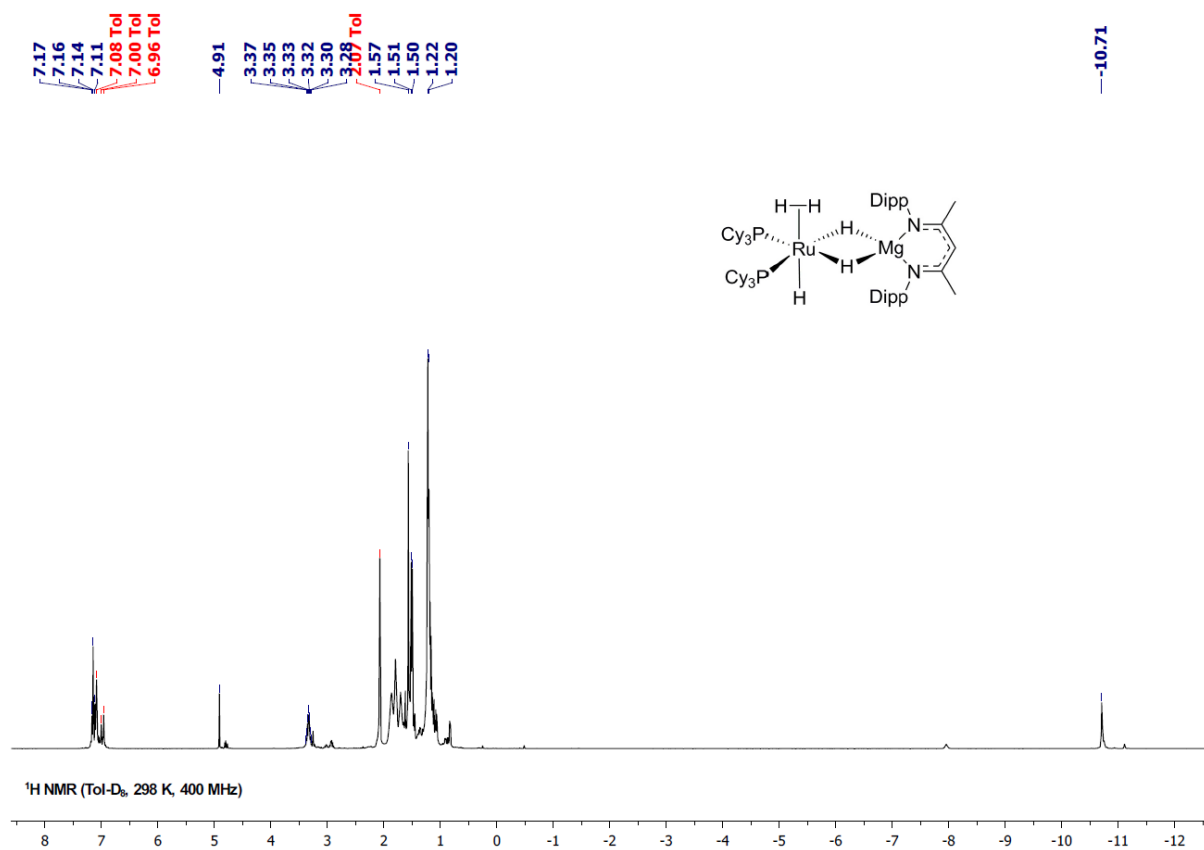


Figure A 31. ¹H NMR spectrum of **Mg•Ru-H₂**

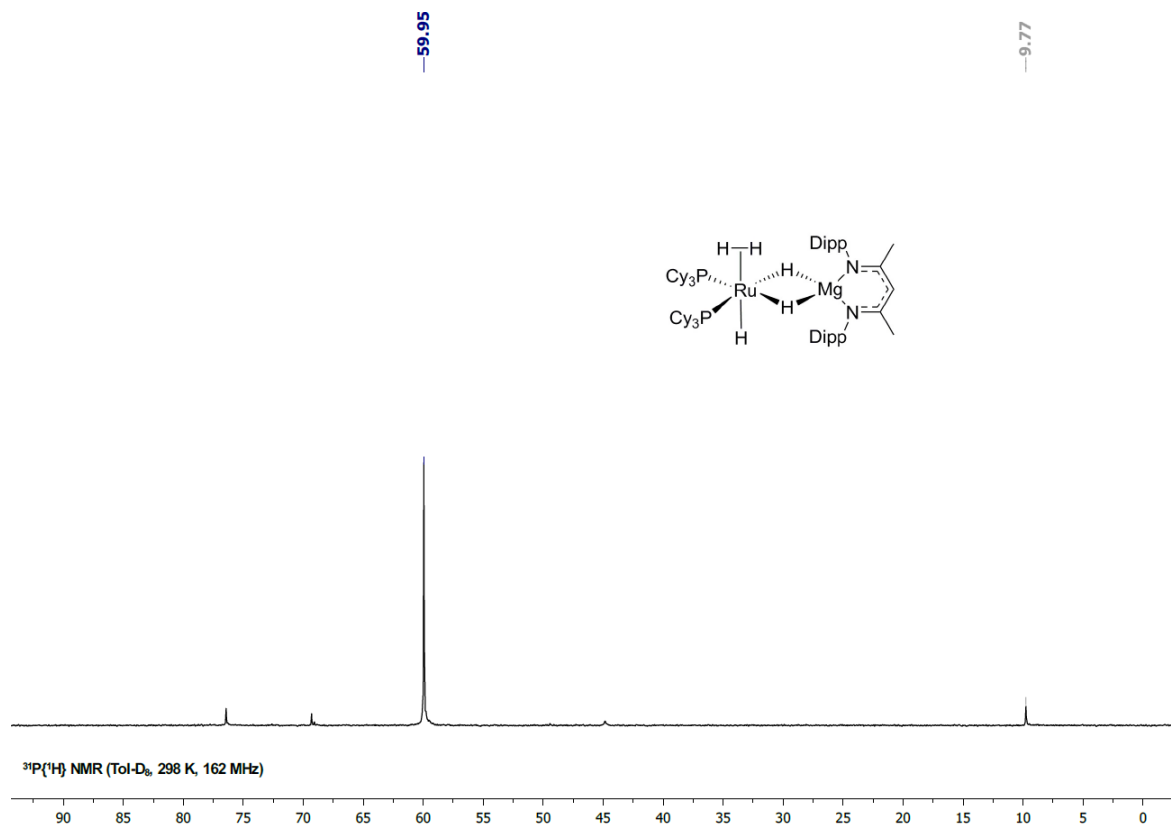
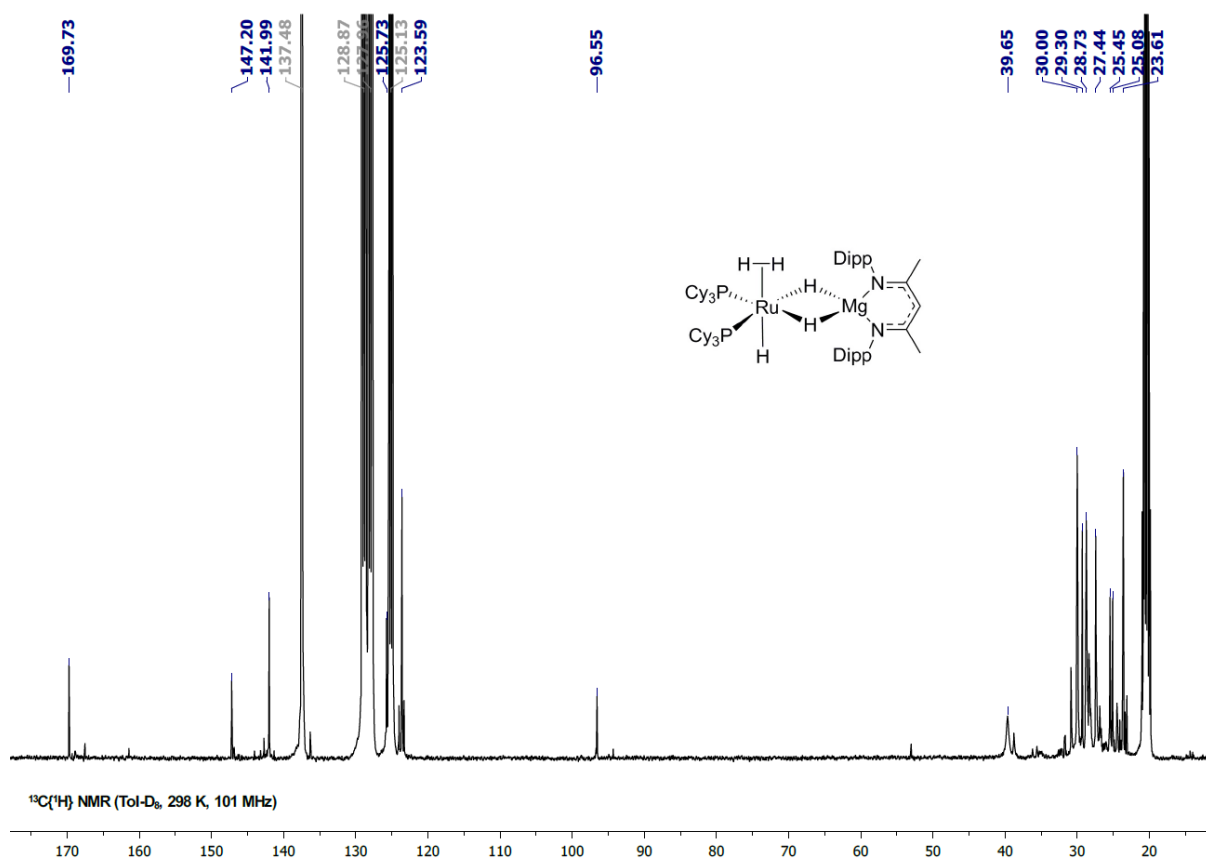


Figure A 32. ³¹P{¹H} NMR spectrum of **Mg•Ru-H₂**



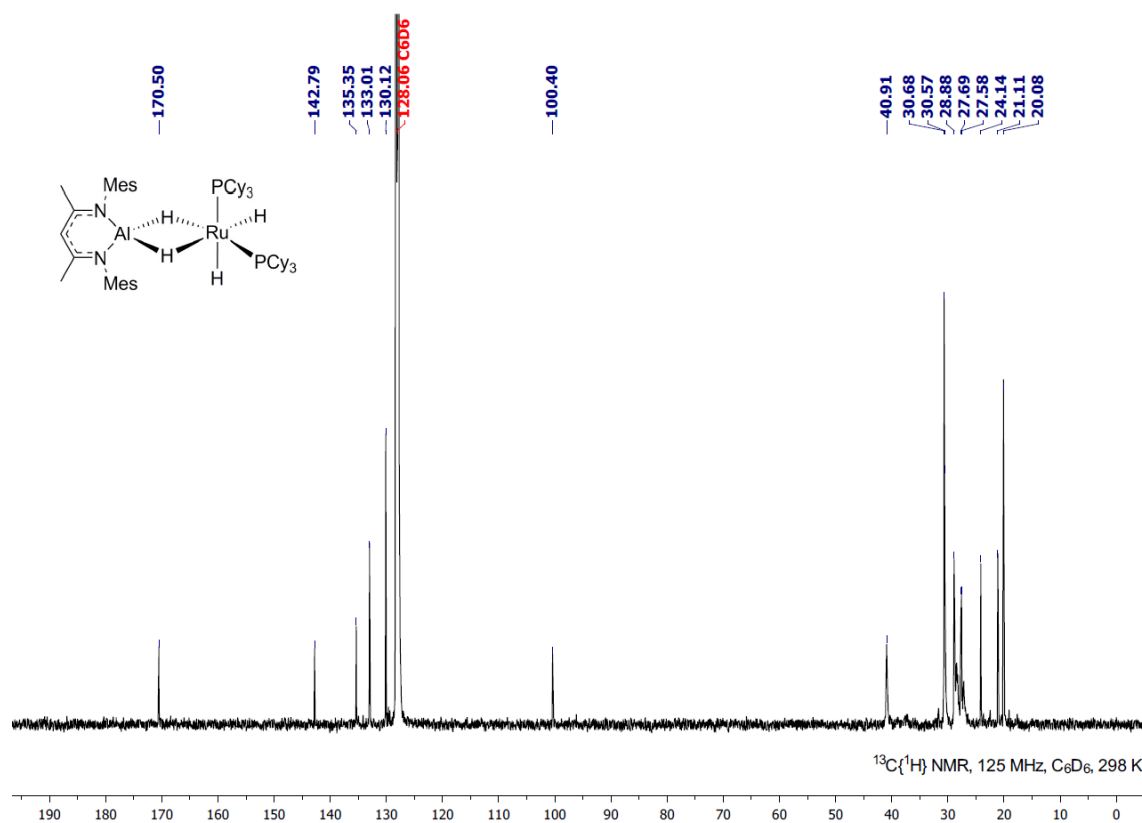


Figure A 35. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{MesAl} \cdot \text{Ru}$

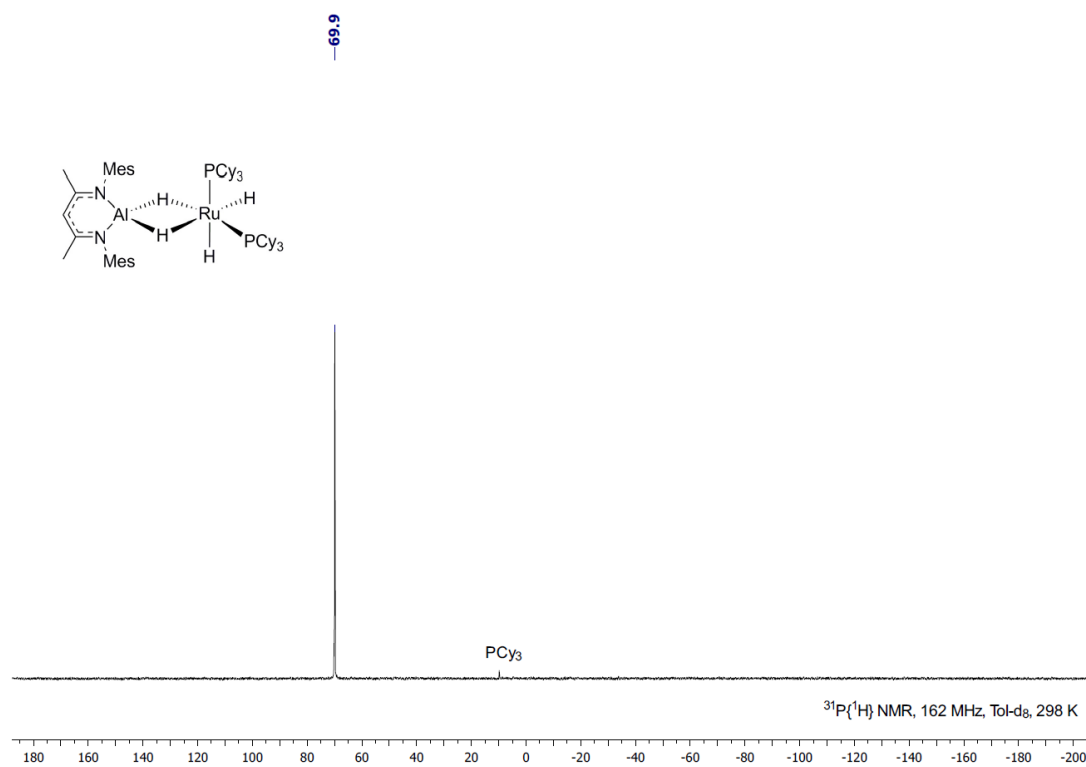


Figure A 36. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{MesAl} \cdot \text{Ru}$

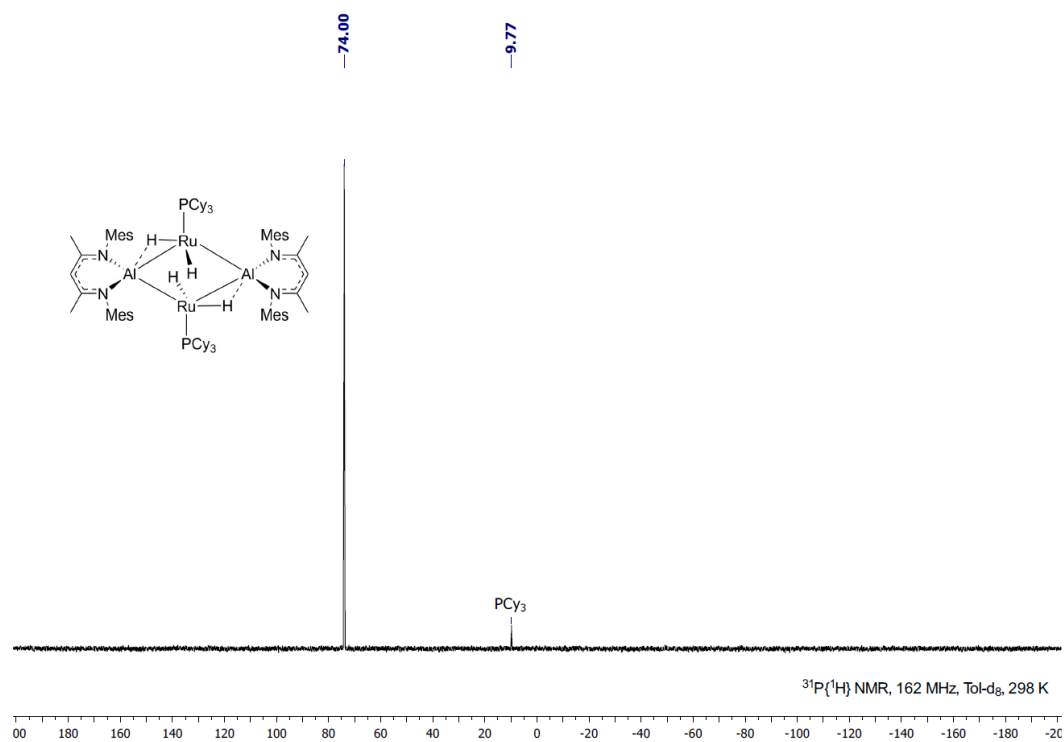


Figure A 39. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $^{\text{Mes}}\text{Al}_2\text{Ru}_2$

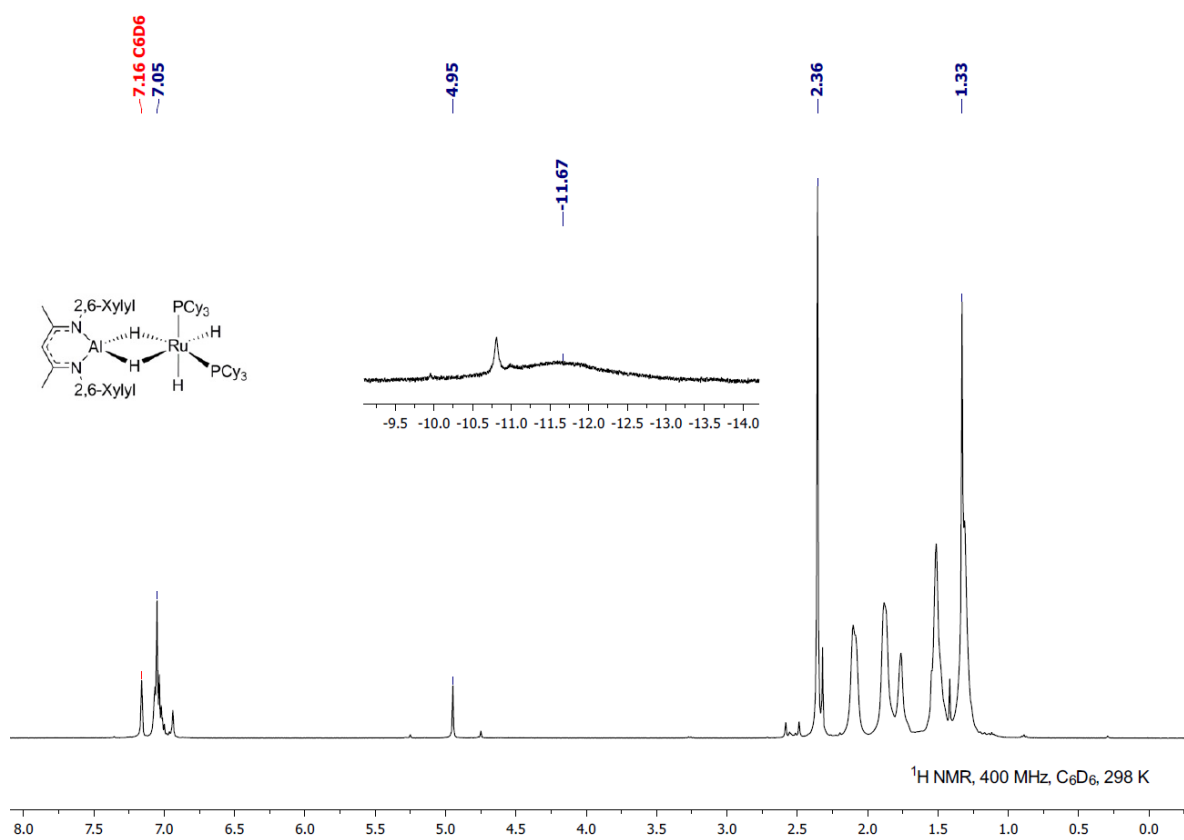


Figure A 40. ^1H NMR spectrum of $2,6\text{-XylylAl}\cdot\text{Ru}$

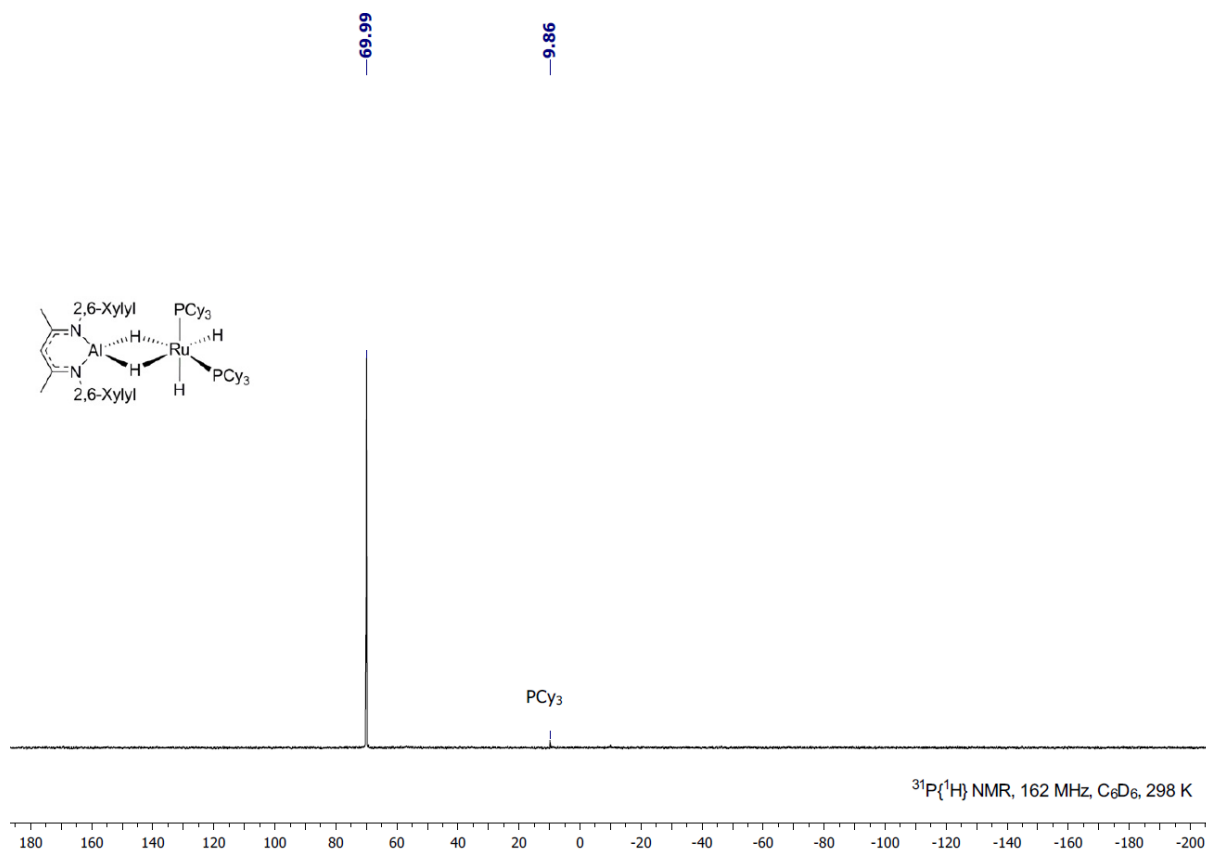


Figure A 41. ³¹P{¹H} NMR spectrum of ^{2,6-Xylyl}Al•Ru

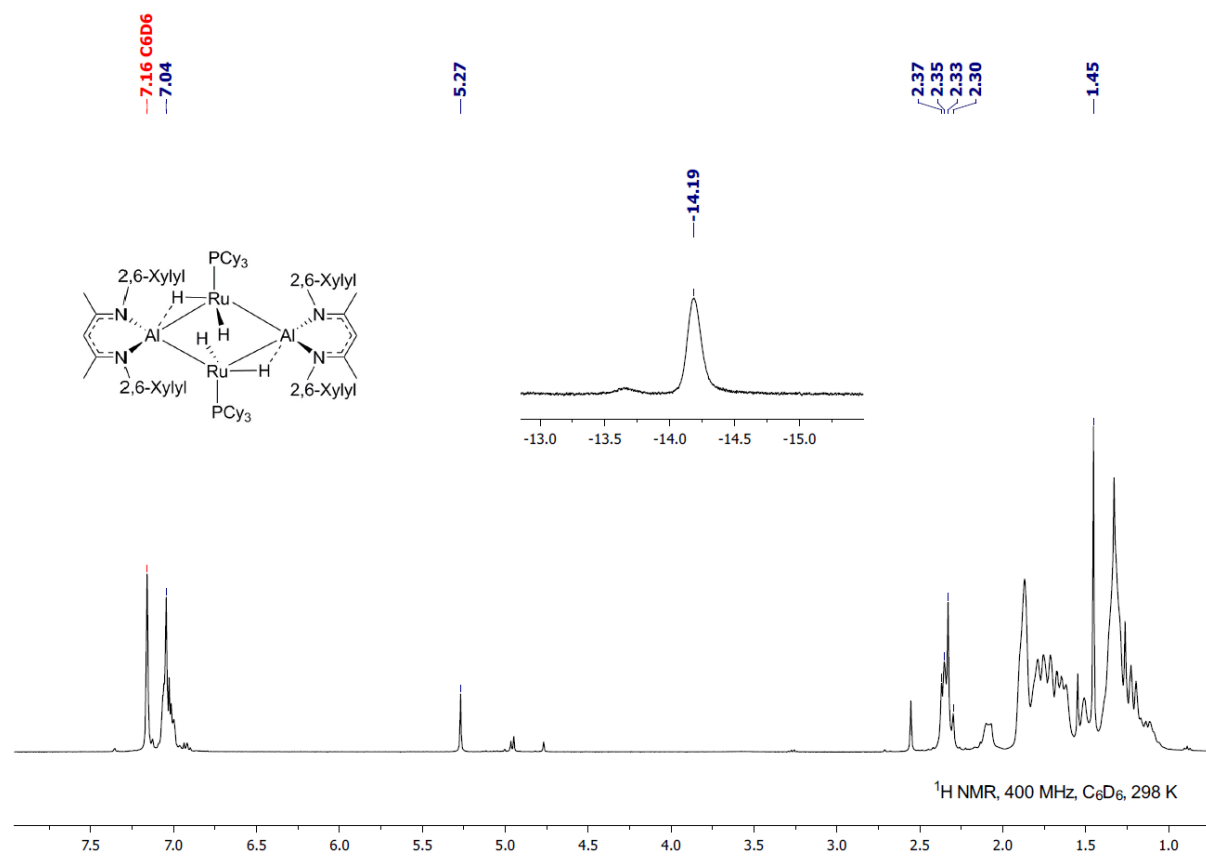


Figure A 42. ¹H NMR spectrum of ^{2,6-Xylyl}Al₂•Ru₂

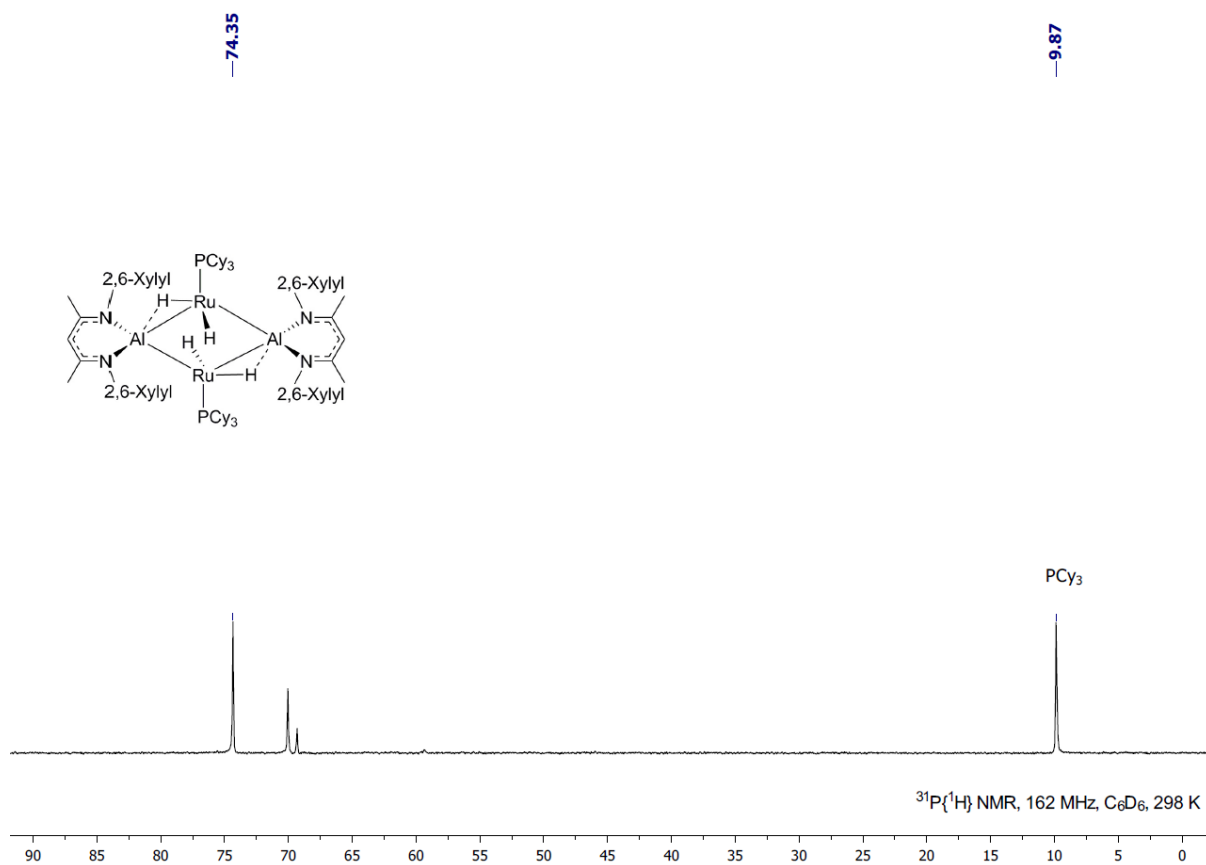


Figure A 43. ³¹P{¹H} NMR spectrum of 2,6-XylylAl₂Ru₂

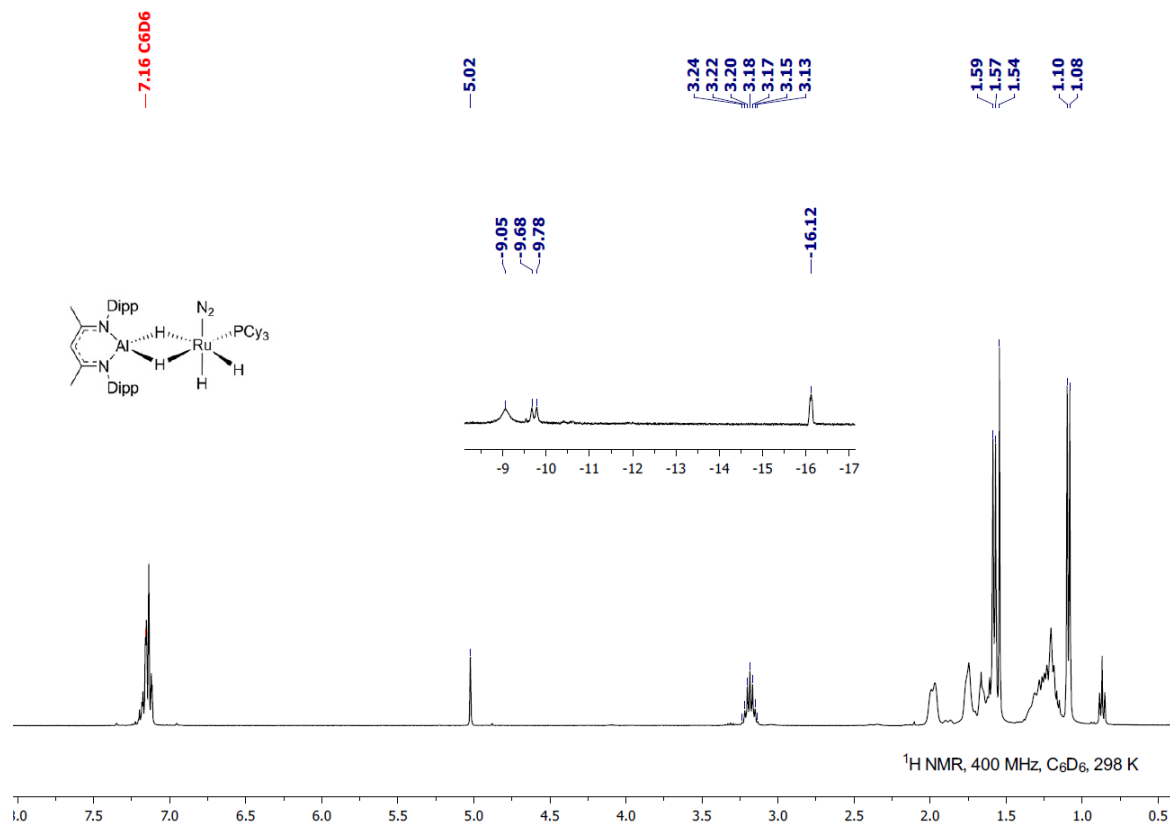


Figure A 44. ¹H NMR spectrum of ^{Dipp}Al•Ru

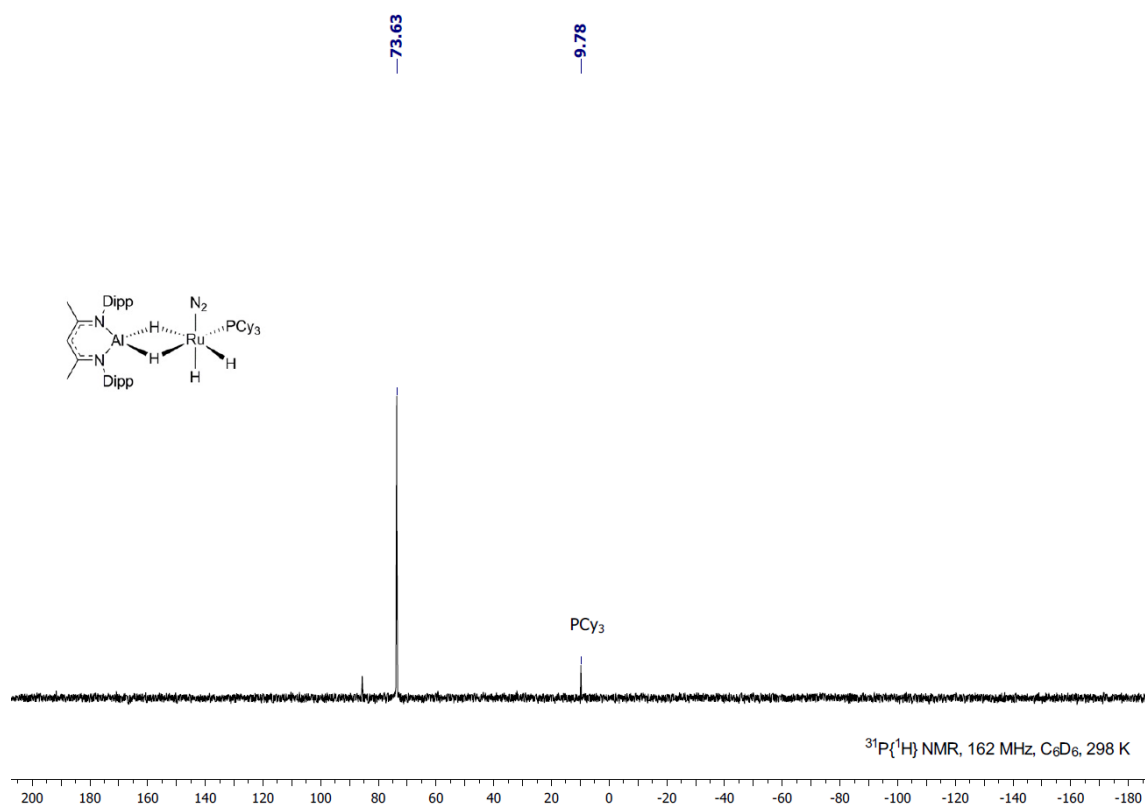


Figure A 45. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{DippAl}\cdot\text{Ru}$

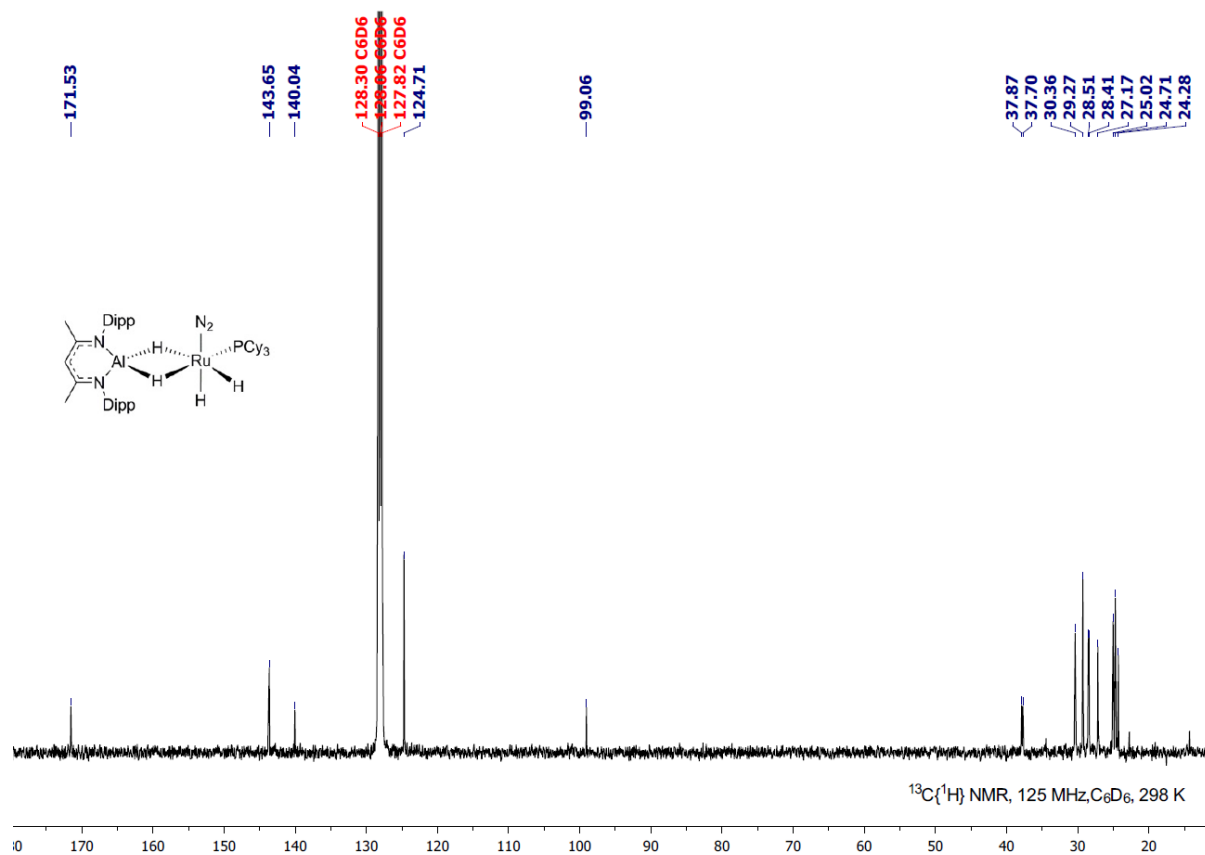


Figure A 46. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{DippAl}\cdot\text{Ru}$

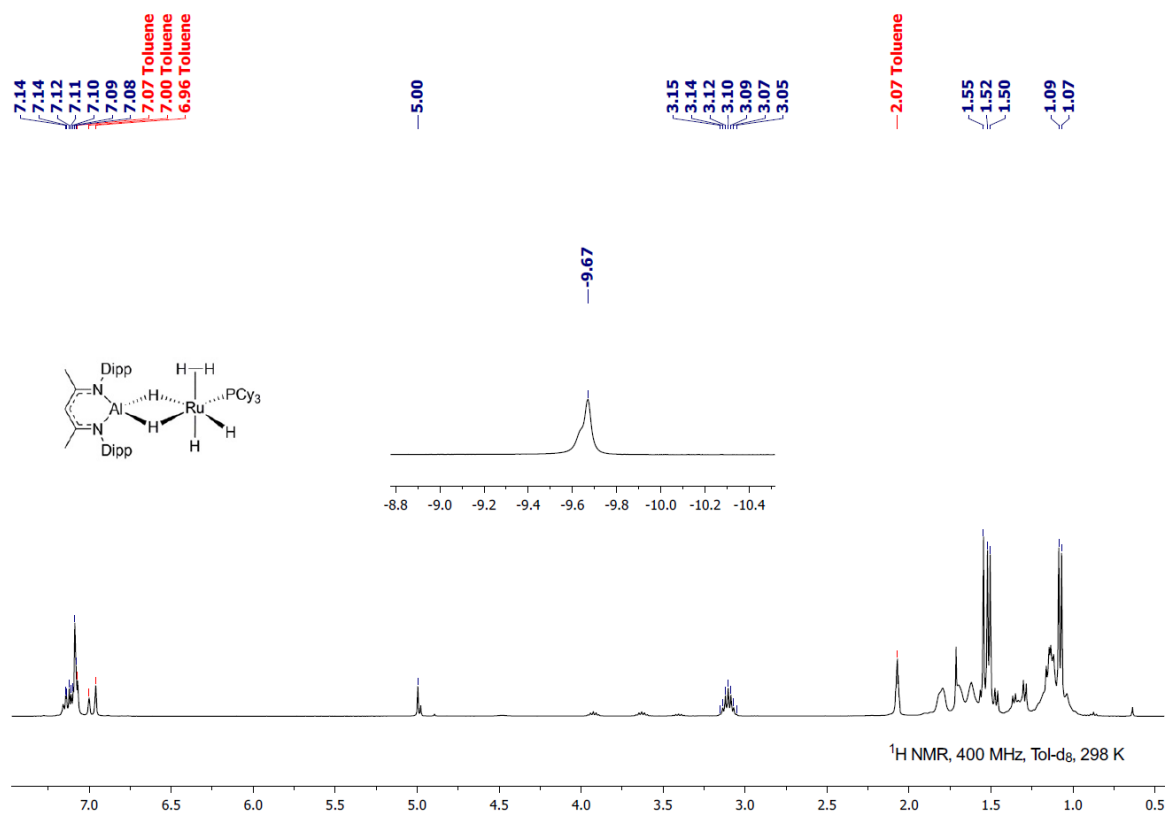


Figure A 47. ^1H NMR spectrum of $\text{DippAl}\cdot\text{Ru-N}_2$

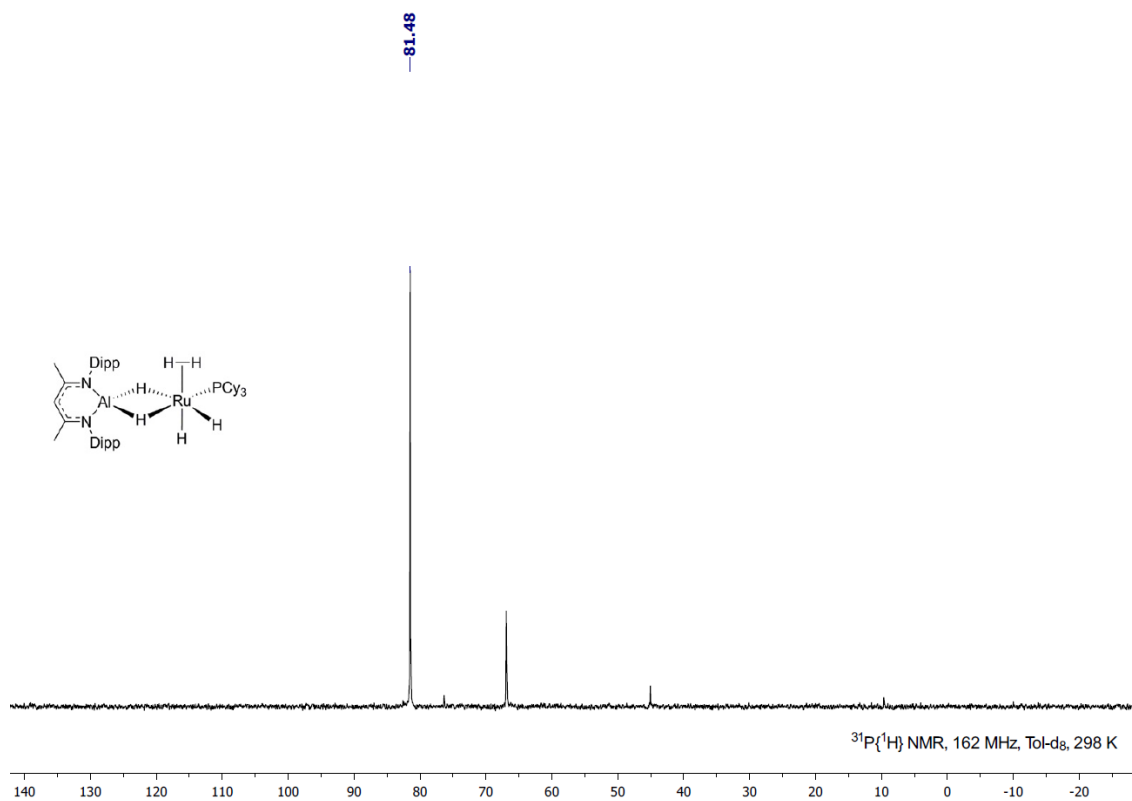


Figure A 48. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{DippAl}\cdot\text{Ru-N}_2$

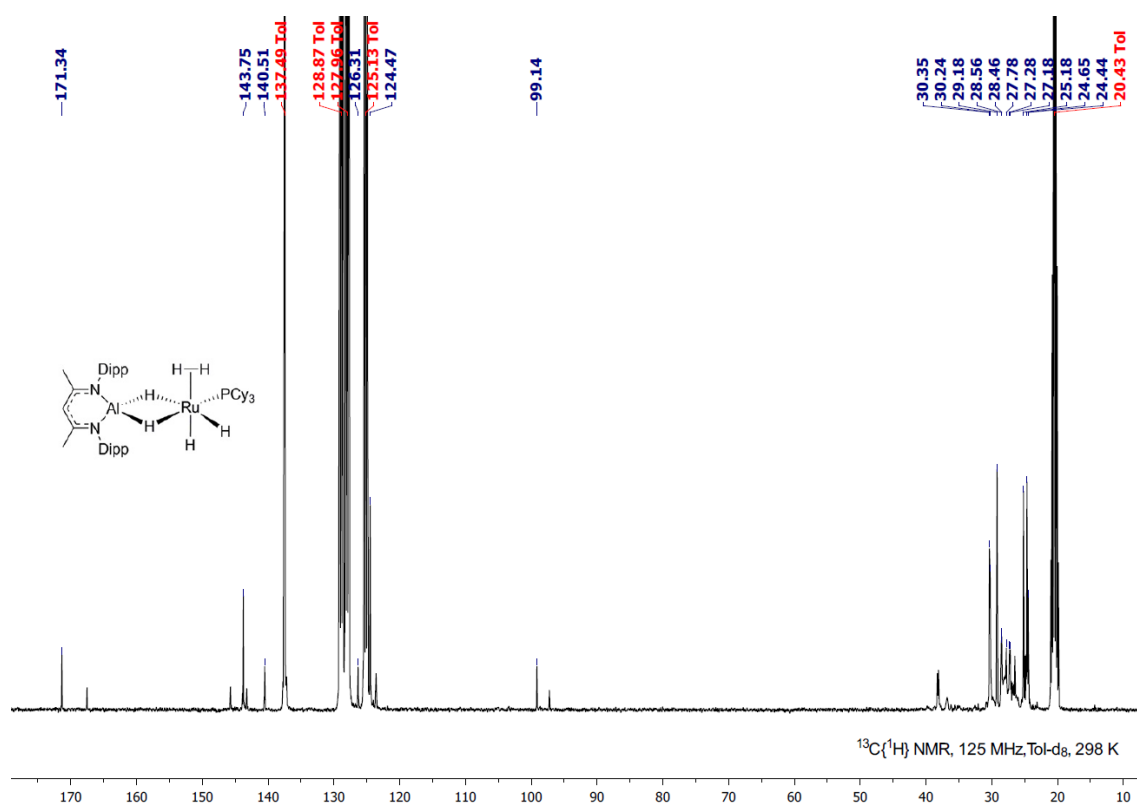


Figure A 49. ¹³C{¹H} NMR spectrum of ^{Dipp}Al•Ru-N₂

6.2 X-RAY DATA

data	1	Ru•Ru
formula	C ₃₆ H ₆₈ N ₄ P ₂ Ru	C ₇₂ H ₁₃₆ N ₂ P ₄ Ru ₂
solvent	—	2(C ₇ H ₁₆)
formula weight	719.95	1556.23
colour, habit	colourless blocks	red plates
temperature / K	173	173
crystal system	triclinic	triclinic
space group	<i>P</i> -1 (no. 2)	<i>P</i> -1 (no. 2)
<i>a</i> / Å	10.5596(4)	14.1128(5)
<i>b</i> / Å	12.4028(3)	14.8186(4)
<i>c</i> / Å	15.6498(7)	21.5303(6)
α / deg	88.329(3)	81.546(2)
β / deg	75.575(4)	78.635(3)
γ / deg	69.144(3)	81.221(3)
<i>V</i> / Å ³	1850.92(13)	4330.7(2)
<i>Z</i>	2	2
<i>D_c</i> / g cm ⁻³	1.292	1.193
radiation used	Mo-K α	Cu-K α
μ / mm ⁻¹	0.540	3.820
2 θ max / deg	57	148
no. of unique reflns		
measured (<i>R</i> _{int})	7287 (0.0168)	16572 (0.0430)
obs, <i>F</i> _o > 4 σ (<i>F</i> _o)	6552	12614
no. of variables	397	721
<i>R</i> ₁ (obs), <i>wR</i> ₂ (all) [a]	0.0273, 0.0637	0.0430, 0.1121

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

data	4a	4b	4c
formula	C ₄₅ H ₇₆ N ₂ O ₂ P ₂ Ru	C ₅₁ H ₈₀ N ₂ O ₂ P ₂ Ru	C ₄₇ H ₈₀ N ₂ OP ₂ Ru
solvent	0.5(C ₇ H ₈)	—	C ₆ H ₆
formula weight	886.15	916.18	930.24
colour, habit	orange blocks	orange/red plates	orange/red blocks
temperature / K	173	173	173
crystal system	triclinic	monoclinic	monoclinic
space group	<i>P</i> -1 (no. 2)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>P</i> 2 ₁ / <i>m</i> (no. 11)
<i>a</i> / Å	11.8536(4)	23.1291(6)	9.5014(3)
<i>b</i> / Å	14.4237(5)	9.99749(19)	19.4797(6)
<i>c</i> / Å	15.6682(6)	24.1334(7)	14.2610(5)
α / deg	75.180(3)	90	90
β / deg	70.083(3)	118.120(4)	107.376(4)
γ / deg	74.522(3)	90	90
<i>V</i> / Å³	2386.76(16)	4921.8(3)	2519.04(14)
<i>Z</i>	2	4	2 [b]
<i>D_c</i> / g cm⁻³	1.233	1.236	1.226
radiation used	Mo-K α	Mo-K α	Mo-K α
μ / mm⁻¹	0.433	0.423	0.412
2θ max / deg	57	57	56
no. of unique reflns			
measured (<i>R</i>_{int})	9409 (0.0250)	9886 (0.0250)	5159 (0.0256)
obs, $F_o > 4\sigma(F_o)$	8061	7856	4627
no. of variables	508	529	305
<i>R</i>₁(obs), <i>wR</i>₂(all) [a]	0.0366, 0.0823	0.0341, 0.0733	0.0311, 0.0725

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$. [b] The molecule has crystallographic *C_s* symmetry.

data	6b	8a	12
formula	C ₄₆ H ₈₀ N ₂ OP ₂ Ru	C ₄₃ H ₇₄ OP ₂ Ru	C ₄₄ H ₇₂ N ₄ OP ₂ Ru
solvent	0.85(C ₅ H ₁₂)	2(C ₇ H ₈ O)·C ₇ H ₁₆	—
formula weight	901.45	1086.49	836.06
colour, habit	orange/red blocky needles	yellow tablets	orange blocks
temperature / K	173	173	173
crystal system	triclinic	triclinic	monoclinic
space group	<i>P</i> -1 (no. 2)	<i>P</i> -1 (no. 2)	<i>P</i> 2 ₁ /c
<i>a</i> / Å	9.7664(4)	12.2080(5)	12.7413(6)
<i>b</i> / Å	12.8007(5)	14.6654(6)	13.1737(5)
<i>c</i> / Å	21.1604(9)	17.5782(7)	26.6964(11)
α / deg	84.095(3)	96.721(3)	90
β / deg	80.949(4)	97.490(3)	101.183(4)
γ / deg	72.184(4)	99.217(3)	90
<i>V</i> / Å³	2482.98(19)	3049.2(2)	4395.9(3)
<i>Z</i>	2	2	4
<i>D</i>_c / g cm⁻³	1.206	1.183	1.263
radiation used	Mo-K α	Cu-K α	Mo-K α
μ / mm⁻¹	0.416	2.886	0.466
2θ max / deg	56	148	56
no. of unique reflns			
measured (<i>R</i>_{int})	9818 (0.0201)	11628 (0.0312)	10457 (0.0621)
obs, $F_o > 4\sigma(F_o)$	8192	9853	8733
no. of variables	476	705	511
<i>R</i>₁(obs), <i>wR</i>₂(all) [a]	0.0402, 0.921	0.0454, 0.1185	0.0624, 0.1512

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

data	Al•Ru-N ₂	Zn•Ru-N ₂	Mg•Ru-N ₂
formula	C ₅₉ H ₉₈ AlClN ₄ P ₂ Ru	C ₆₅ H ₁₁₀ N ₄ P ₂ RuZn	C ₆₅ H ₁₁₀ MgN ₄ P ₂ Ru
solvent	3.5(C ₆ H ₁₄)	0.5(C ₇ H ₈)·0.5(C ₆ H ₁₄)	C ₅ H ₁₂
formula weight	1390.45	1265.10	1207.03
colour, habit	colourless blocks	yellow tablets	yellow plates
temperature / K	173	173	173
crystal system	trigonal	monoclinic	monoclinic
space group	<i>R</i> -3 (no. 148)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>P</i> 2 ₁ (no. 4)
<i>a</i> / Å	33.4244(14)	14.14983(17)	13.90589(14)
<i>b</i> / Å	33.4244(14)	18.9381(2)	18.8961(2)
<i>c</i> / Å	38.8822(8)	26.2063(3)	27.0146(3)
α / deg	90	90	90
β / deg	90	101.4337(11)	101.4715(10)
γ / deg	120	90	90
<i>V</i> / Å³	37619(3)	6883.16(13)	6956.74(12)
<i>Z</i>	18	4	4 [c]
<i>D_c</i> / g cm⁻³	1.105	1.221	1.152
radiation used	Mo-K α	Cu-K α	Cu-K α
μ / mm⁻¹	0.309	2.949	2.641
2θ max / deg	56	148	148
no. of unique reflns			
measured (<i>R</i>_{int})	16262 (0.0268)	13285 (0.0299)	17480 (0.0429)
obs, $F_o > 4\sigma(F_o)$	8407	10839	15216
no. of variables	621	691	1994
<i>R</i>₁(obs), <i>wR</i>₂(all) [a]	0.0846, 0.2417	0.0330, 0.0854	0.0514, 0.1332

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$. [c] There are two crystallographically independent molecules. [d] The complex has crystallographic *C_i* symmetry.

data	S1	S2
formula	C ₃₆ H ₆₇ ClN ₂ P ₂ Ru	C ₅₉ H ₉₇ AlN ₄ OP ₂ Ru, C ₃₆ H ₆₈ N ₄ P ₂ Ru
solvent	—	0.5(C ₅ H ₁₂)
formula weight	726.37	1824.41
colour, habit	dark orange blocks	colourless blocks
temperature / K	173	173
crystal system	triclinic	triclinic
space group	<i>P</i> -1 (no. 2)	<i>P</i> -1 (no. 2)
<i>a</i> / Å	9.8115(4)	14.0924(3)
<i>b</i> / Å	10.1972(6)	18.4804(5)
<i>c</i> / Å	10.8309(7)	19.7456(5)
α / deg	114.344(6)	76.299(2)
β / deg	108.393(5)	87.9291(19)
γ / deg	91.102(4)	78.993(2)
<i>V</i> / Å³	922.76(10)	4904.0(2)
<i>Z</i>	1 [d]	2
<i>D</i>_c / g cm⁻³	1.307	1.236
radiation used	Mo-K α	Mo-K α
μ / mm⁻¹	0.610	0.431
2θ max / deg	57	56
no. of unique reflns		
measured (<i>R</i>_{int})	3628 (0.0181)	19208 (0.0234)
obs, $F_o > 4\sigma(F_o)$	3379	14499
no. of variables	210	1065
<i>R</i>₁(obs), <i>wR</i>₂(all) [a]	0.0266, 0.0673	0.0459, 0.1294

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.
[d] The complex has crystallographic *C*_i symmetry.

data	MesAl ₂ •Ru ₂	DippAl•Ru	1•NacNac
formula	C ₈₂ H ₁₂₈ Al ₂ N ₄ P ₂ Ru ₂	C ₄₇ H ₇₈ AlN ₄ PRu	C ₅₇ H ₉₂ N ₄ P ₂ Ru
formula weight	1488.00	858.15	996.35
colour, habit	yellow plates	pale yellow blocks	yellow needles
temperature / K	173	173	173
crystal system	triclinic	triclinic	Monoclinic
space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ /c
<i>a</i> / Å	14.7022(13)	10.7298(5)	10.1743(3)
<i>b</i> / Å	18.7987(15)	11.8650(5)	45.0719(9)
<i>c</i> / Å	20.300(2)	19.6541(7)	12.0441(2)
α / deg	72.990(8)	83.163(3)	90
β / deg	73.914(9)	86.568(3)	102.760(2)
γ / deg	86.539(7)	70.525(4)	90
<i>V</i> / Å ³	5153.8(9)	2341.67(17)	5386.7(2)
<i>Z</i>	2	2	4
<i>D</i> _c / g cm ⁻³	0.956	1.217	1.229
radiation used	Mo-K α	Mo-K α	Cu-K α
μ / mm ⁻¹	0.375	0.422	3.203
2 θ max / deg	57	56	147
no. of unique reflns			
measured (<i>R</i> _{int})	20269 (0.0680)	9230 (0.0170)	10377 (0.0412)
obs, $ F_o > 4\sigma(F_o)$	11246	7932	10377
no. of variables	846	513	587
<i>R</i> ₁ (obs), <i>wR</i> ₂ (all) [a]	0.1494, 0.4304	0.0445, 0.1116	0.0429, 0.1135

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Summary of the crystallographic data for the structures listed above. The structures were refined using the SHELXTL and SHELX-2013 program systems.^{11,12} The absolute structure of **Mg•Ru-N₂** was determined by use of the Flack parameter [$x = 0.032(9)$].

CCDC 1530724 to 1530730

CCDC 1843865 to 1843869.

¹¹ SHELXTL v5.1, Bruker AXS, Madison, WI, 1998.

¹² SHELX-2013, G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

The X-ray crystal structure of 1

The two Ru–H hydrogen atoms in the structure of **1** were located from ΔF maps and refined freely.

The X-ray crystal structure of 4a

The Ru–H hydrogen atom in the structure of **4a** was located from a ΔF map and refined freely. The included toluene solvent molecule was found to be disordered across a centre of symmetry, and two unique orientations of *ca.* 29 and 21% occupancy were identified (with the action of the inversion centre generating two further orientations of the same occupancies). The geometries of both orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and all of the atoms were refined isotropically.

The X-ray crystal structure of 4b

The Ru–H hydrogen atom in the structure of **4b** was located from a ΔF map and refined freely.

The X-ray crystal structure of 4c

The Ru–H hydrogen atom in the structure of **4c** was located from a ΔF map and refined freely. The complex lists across a mirror plane that passes through Ru1, H1, C1 to C7, O7, C8, C10, N11 and N12. When refined using AFIX 137, the methyl hydrogen atoms on C10 would not settle, and so the AFIX 33 command was used instead. The included benzene solvent molecule was found to be disordered across a mirror plane, and this was modelled using one complete 50% occupancy molecule (with the action of the mirror plane generating a second 50% occupancy orientation). The geometry of the unique orientation was optimised, and all of the non-hydrogen atoms were refined anisotropically.

The X-ray crystal structure of 6b

The Ru–H hydrogen atom in the structure of **6b** was located from a ΔF map and refined freely. The included solvent was found to be highly disordered, and the best approach to handling this diffuse electron density was found to be the SQUEEZE routine of PLATON.³ This suggested a total of 73 electrons per unit cell, equivalent to 36.5 electrons per asymmetric unit. Before the use of SQUEEZE the solvent clearly resembled a straight chain disordered across a centre of symmetry, but the length of the chain was uncertain. Pentane (C₅H₁₂, 42 electrons) was chosen as it was the most recently used crystallisation solvent. 0.85 pentane molecules corresponds to 35.7 electrons, so this was used as the

solvent present. As a result, the atom list for the asymmetric unit is low by $0.85(\text{C}_5\text{H}_{12}) = \text{C}_{4.25}\text{H}_{10.2}$ (and that for the unit cell low by $\text{C}_{8.5}\text{H}_{20.4}$) compared to what is actually presumed to be present.

The X-ray crystal structure of **8a**

The Ru–H hydrogen atom in the structure of **8a** was located from a ΔF map and refined freely. The O–H hydrogen atoms of the O50- and O60-based included 4-methylphenol moieties were also located from ΔF maps, and were refined freely subject to an O–H distance constraint of 0.90 Å. The included heptane solvent molecule was found to be disordered. Three orientations were identified of *ca.* 51, 28 and 21% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientations were refined isotropically).

The X-ray crystal structure of **Al•Ru-N₂**

The presumed three metal-hydride atoms in the structure of **Al•Ru-N₂** could not be located, so the contents of the asymmetric unit are low by 3H.

The included solvent was found to be highly disordered, and the best approach to handling this diffuse electron density was found to be the SQUEEZE routine of PLATON.¹³ This suggested a total of 3290 electrons per unit cell, equivalent to 182.8 electrons per asymmetric unit. Before the use of SQUEEZE the solvent could not be identified, and so the most recently used solvent (hexane, C_6H_{14} , 50 electrons) was chosen, and since 3.5 hexane molecules corresponds to 175 electrons this was used as the solvent present. As a result, and combined with the three “missing” metal-hydride atoms, the atom list for the asymmetric unit is low by $3.5(\text{C}_6\text{H}_{14}) + 3\text{H} = \text{C}_{21}\text{H}_{52}$ (and that for the unit cell low by $\text{C}_{378}\text{H}_{936}$) compared to what is actually presumed to be present.

The X-ray crystal structure of **Zn•Ru-N₂**

The three metal-hydride atoms in the structure of **Zn•Ru-N₂** (two Zn–H–Ru bridging and one Ru–H terminal) were all located from ΔF maps and refined freely. The C27-based isopropyl group was found to be disordered. Two orientations were identified of *ca.* 58 and 42% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-

¹³ A.L. Spek (2003, 2009) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. See also A.L. Spek, *Acta. Cryst.*, 2015, **C71**, 9-18.

hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

The included solvent was found to be highly disordered, and the best approach to handling this diffuse electron density was found to be the SQUEEZE routine of PLATON.³ This suggested a total of 168 electrons per unit cell, equivalent to 42 electrons per asymmetric unit. Before the use of SQUEEZE the solvent most resembled an approximately 50:50 mixture of toluene (C₇H₈, 50 electrons) and hexane (C₆H₁₄, 50 electrons), and a mixture of 0.5 toluene molecules and 0.5 hexane molecules corresponds to 50 electrons, so this was used as the solvent present. As a result, the atom list for the asymmetric unit is low by $0.5(\text{C}_7\text{H}_8) + 0.5(\text{C}_6\text{H}_{14}) = \text{C}_{6.5}\text{H}_{11}$ (and that for the unit cell low by C₂₆H₄₄) compared to what is actually presumed to be present.

The X-ray crystal structure of **Mg•Ru-N₂**

The structure of Mg•Ru-N₂ was found to contain two independent molecules, **Mg•Ru-N₂-A** and **Mg•Ru-N₂-B**, in the asymmetric unit. Complex **Mg•Ru-N₂-B** was found to be completely disordered with a second overlapping orientation of the whole complex being identified in a *ca.* 51:49 ratio. The geometries of the two orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and all of the non-hydrogen atoms of both orientations were refined anisotropically. Complex **Mg•Ru-N₂-A** appears to be disordered in a similar fashion, but to a much lesser extent (with a *ca.* 96:4 ratio) such that only the ruthenium atom of the second orientation could be reliably located. Separately, the C12-, C15-, and C24-based isopropyl groups in **Mg•Ru-N₂-A** were found to be disordered, and in each case two orientations were identified, of *ca.* 64:36, 57:43 and 67:33% occupancy respectively. The geometries of each pair of orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically (those of the minor occupancy orientations were refined isotropically). The presumed three metal-hydride atoms could not be located for either independent molecule, so the contents of the asymmetric unit are low by 6H.

The included solvent was found to be highly disordered, and the best approach to handling this diffuse electron density was found to be the SQUEEZE routine of PLATON.³ This suggested a total of 169 electrons per unit cell, equivalent to 42.3 electrons per asymmetric unit. Before the use of SQUEEZE the solvent most resembled pentane (C₅H₁₂, 42 electrons), and 1 pentane molecule corresponds to 42 electrons, so this was used as the solvent present. As a result, and combined with the six “missing” metal-hydride atoms, the atom list for the asymmetric unit is low by $2(\text{C}_5\text{H}_{12}) + 6\text{H} = \text{C}_{10}\text{H}_{30}$ (and that for the unit cell low by C₂₀H₆₀) compared to what is actually presumed to be present.

The X-ray crystal structure of S1

The ruthenium centre in the structure of **S1** was found to sit on a centre of symmetry, and as a consequence the chloride, dinitrogen and hydride ligands are inherently disordered. This was modelled by refining each ligand at 50% occupancy. The Ru–H hydride atom was located from a ΔF map and refined freely, though at 50% occupancy as mentioned above.

The X-ray crystal structure of S2

The three metal-hydride atoms in the structure of **S2** (one Al–H–Ru bridging and two Ru–H terminal) were all located from ΔF maps and refined freely. The O–H hydrogen atom on O24 was located from a ΔF map and refined freely subject to an O–H distance constraint of 0.90 Å. The C111-based included pentane solvent molecule was found to be disordered across a centre of symmetry, and two unique orientations were identified of *ca.* 27 and 23% occupancy (with two further orientations of the same occupancies being generated by operation of the inversion centre). The geometries of both unique orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and all of the atoms of both orientations were refined isotropically.

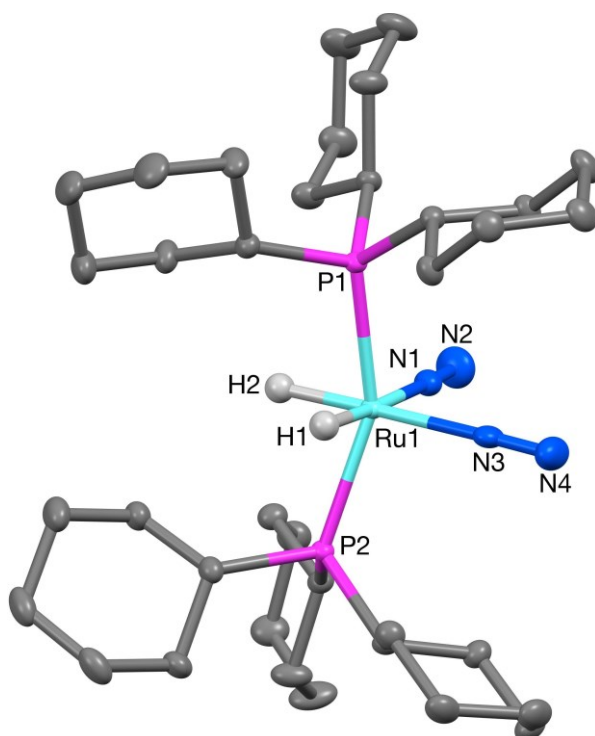


Figure A 50. The crystal structure of **1** (50% probability ellipsoids).

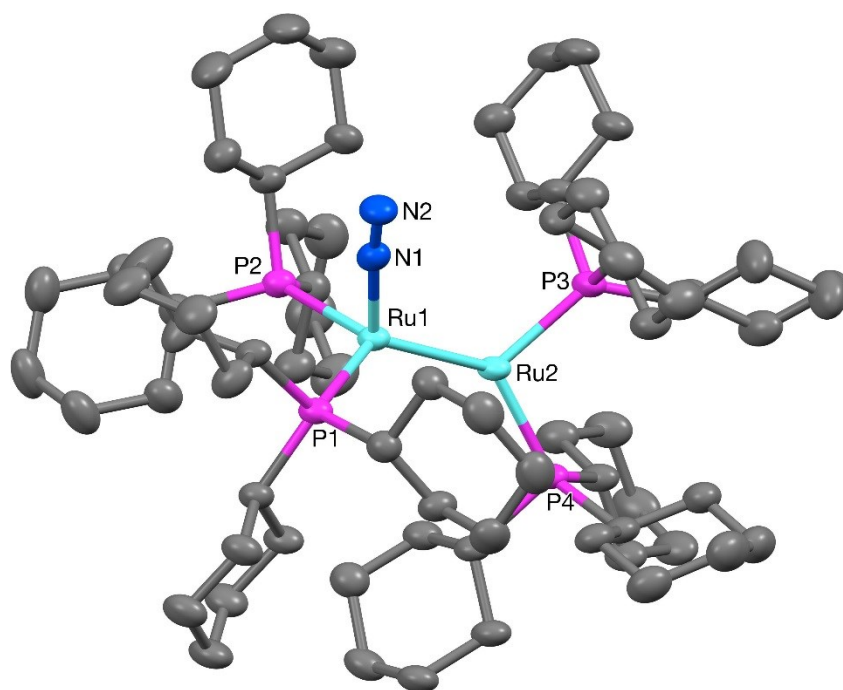


Figure A 51. The crystal structure of Ru•Ru (50% probability ellipsoids).

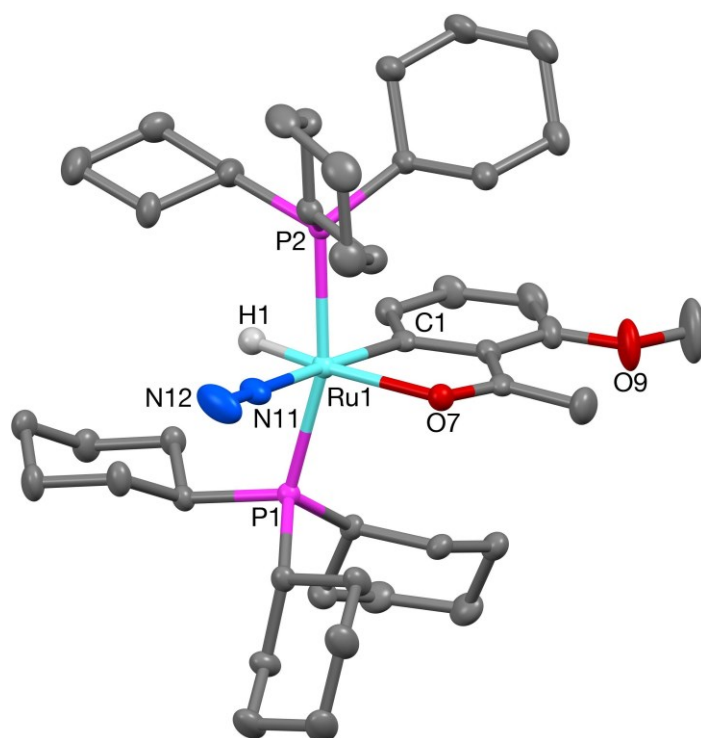


Figure A 52. The crystal structure of 4a (50% probability ellipsoids).

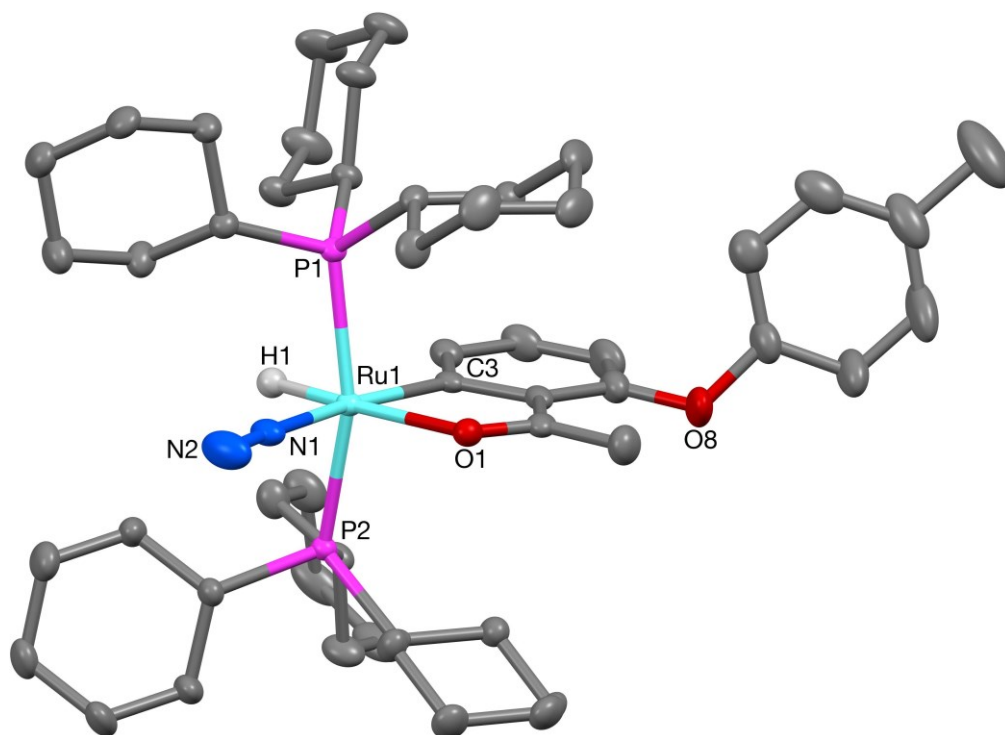


Figure A 53. The crystal structure of **4b** (50% probability ellipsoids).

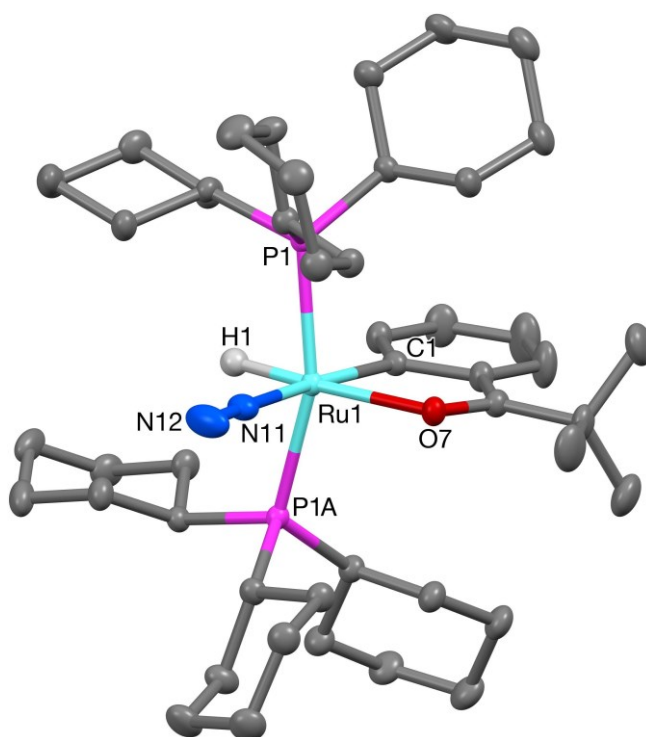


Figure A 54. The crystal structure of the C_5 -symmetric complex **4c** (50% probability ellipsoids). The mirror plane passes through Ru1, H1, the N_2 unit, and all of the phenyl-*tert*-butyl ketone ligand with the exception of two of the *t*-Bu methyl groups.

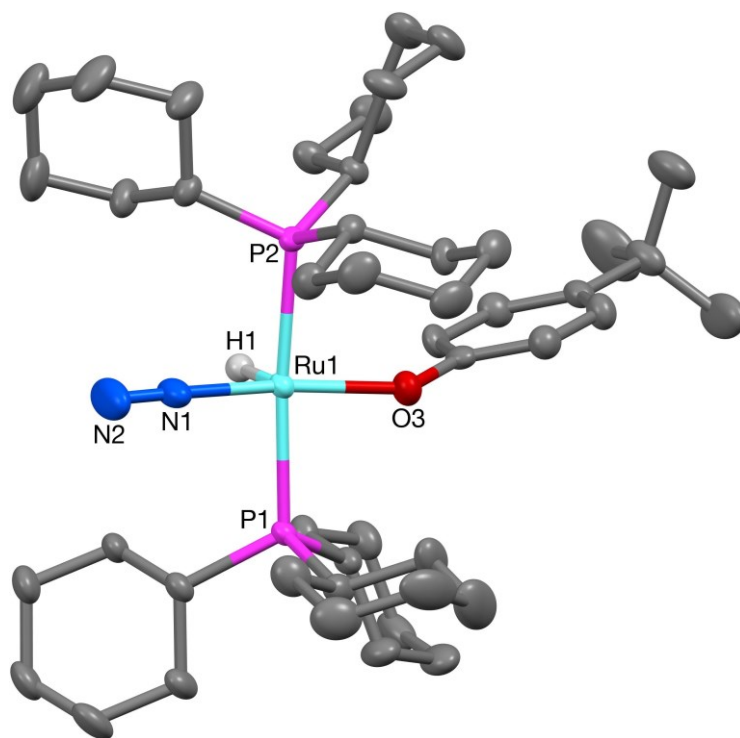


Figure A 55. The crystal structure of **6b** (50% probability ellipsoids).

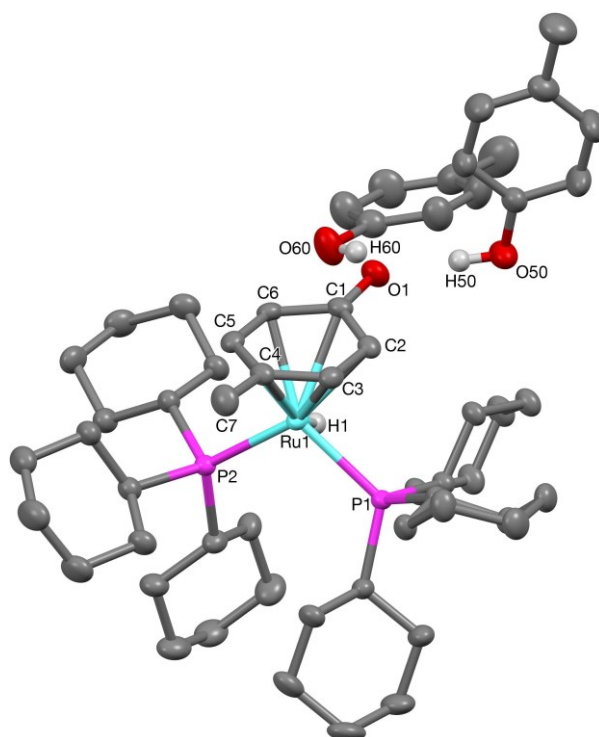


Figure A 56. The crystal structure of **8a** (50% probability ellipsoids).

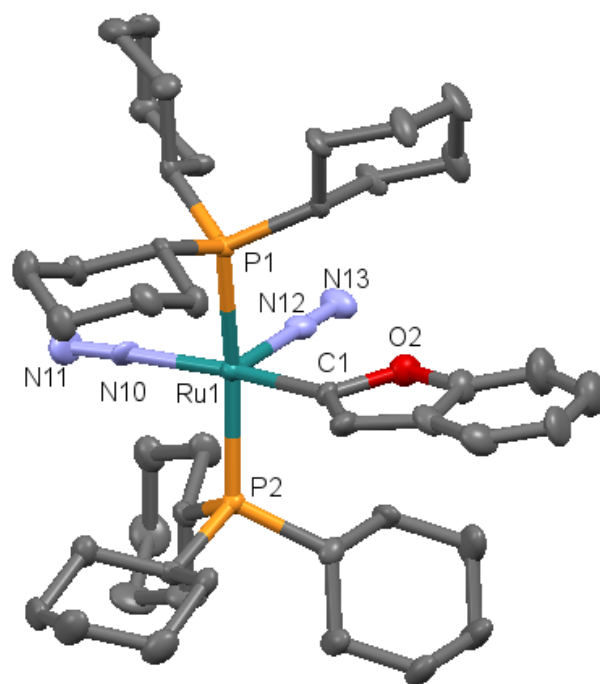


Figure A 57. The crystal structure of **12** (50% probability ellipsoids).

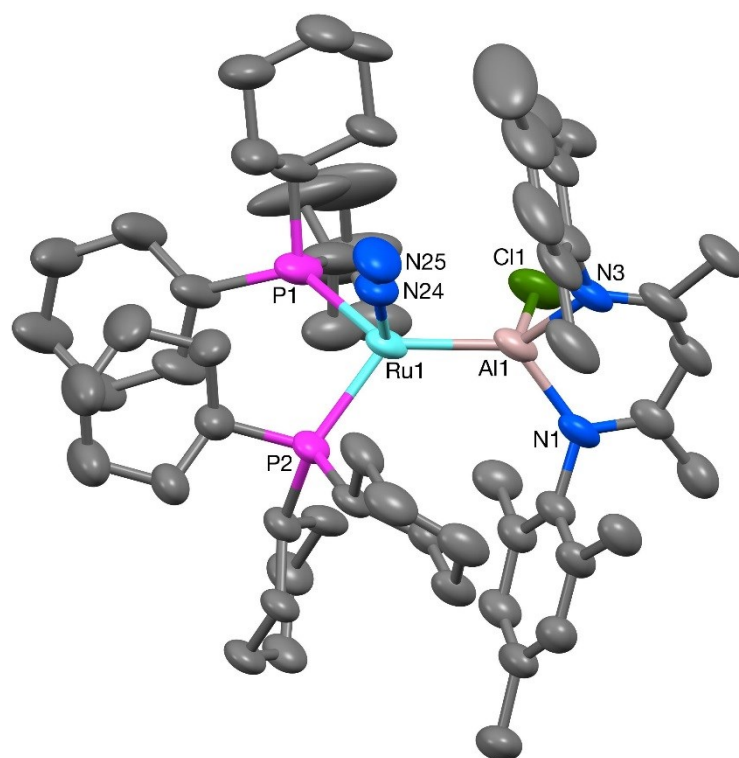


Figure A 58. The crystal structure of **Al•Ru-N₂** (50% probability ellipsoids).

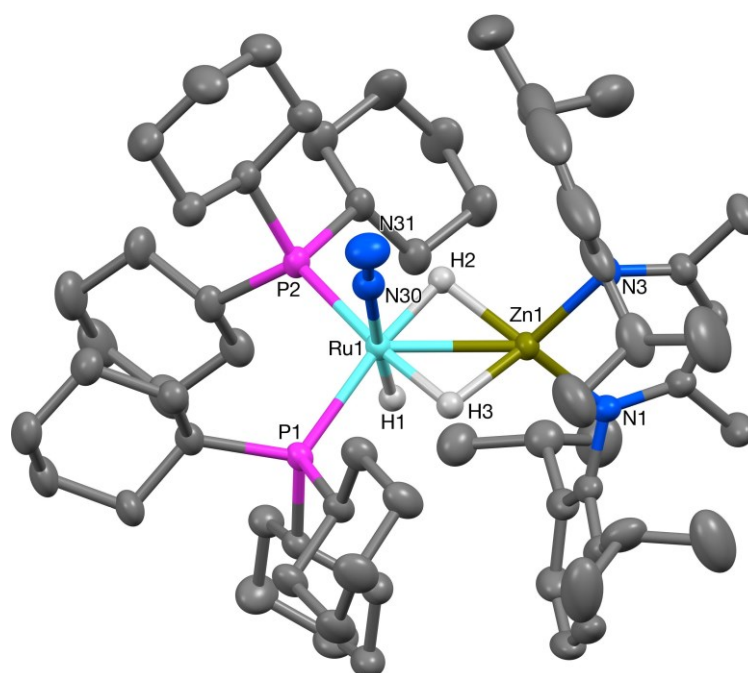


Figure A 59. The crystal structure of **Zn•Ru-N₂** (50% probability ellipsoids).

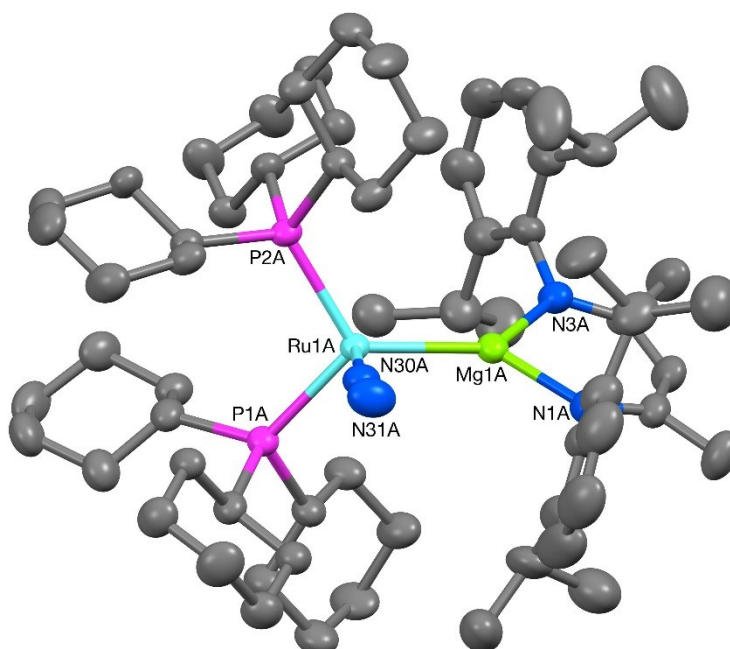


Figure A 60. The structure of one (**Mg•Ru-N₂-A**) of the two independent complexes present in the crystal of **Mg•Ru-N₂** (50% probability ellipsoids).

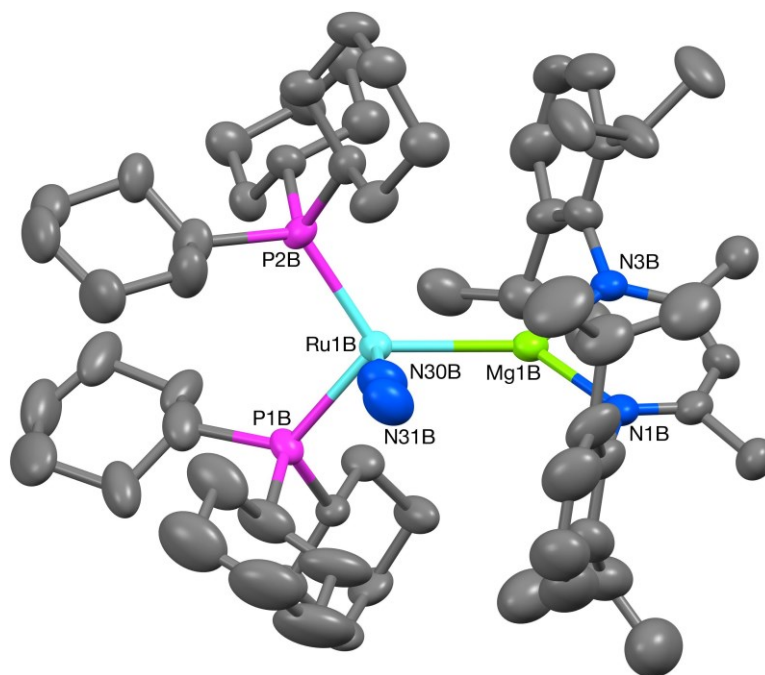


Figure A 61. The structure of one ($\text{Mg}\cdot\text{Ru}-\text{N}_2\cdot\text{B}$) of the two independent complexes present in the crystal of $\text{Mg}\cdot\text{Ru}-\text{N}_2$ (50% probability ellipsoids).

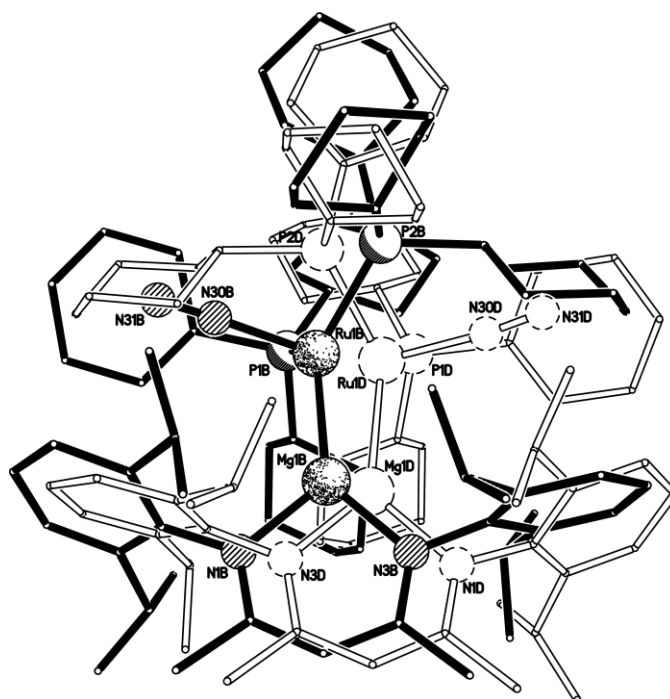


Figure A 62. The structure of $\text{Mg}\cdot\text{Ru}-\text{N}_2\cdot\text{B}$ showing the disorder of the complete complex with the major orientation (ca. 51% occupancy) drawn with dark bonds, and the minor orientation (ca. 49% occupancy) drawn with open bonds.

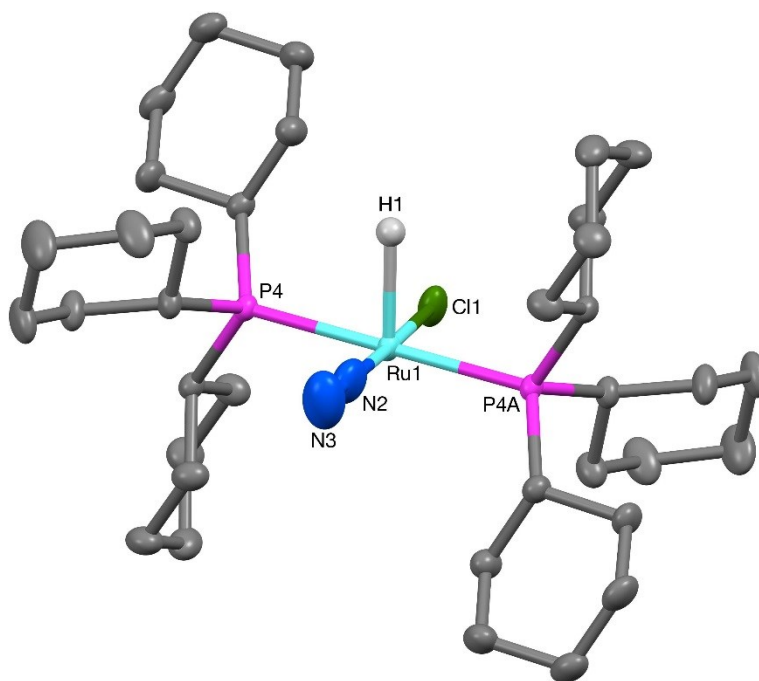


Figure A 63. The crystal structure of the Ci-symmetric complex **S1** (50% probability ellipsoids).

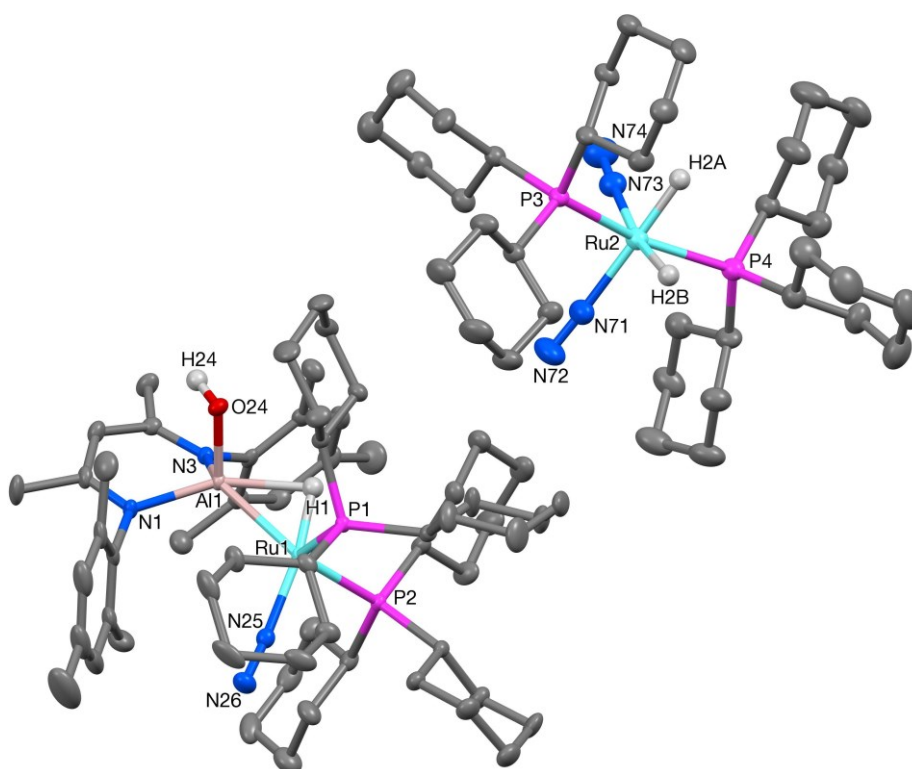


Figure A 64. The crystal structure of **S2** (50% probability ellipsoids).

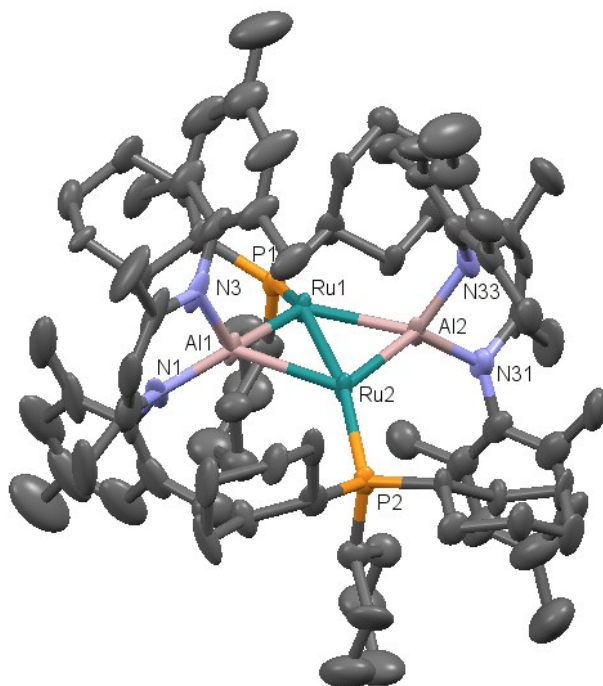


Figure A 65. The crystal structure of $\text{Mes}_2\text{Al}_2\text{Ru}_2$. Hydrogens omitted for clarity. (50% probability ellipsoids)

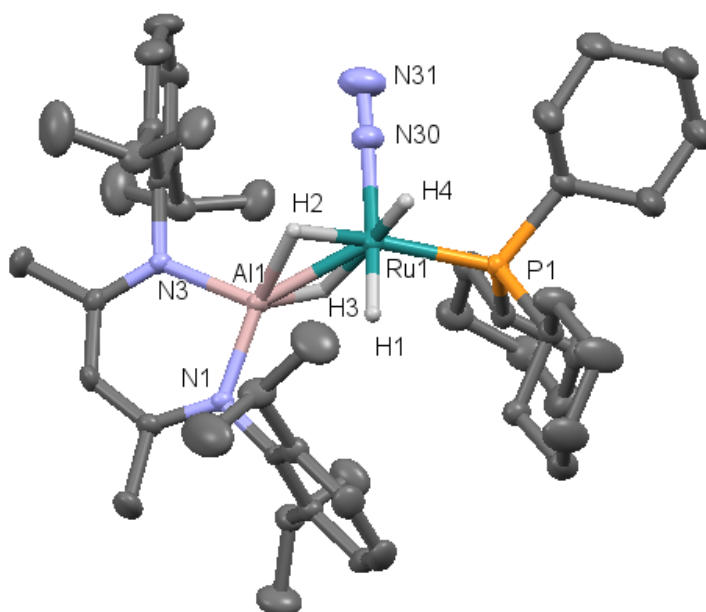


Figure A 66. The crystal structure of DippAlRu . (50% probability ellipsoids)

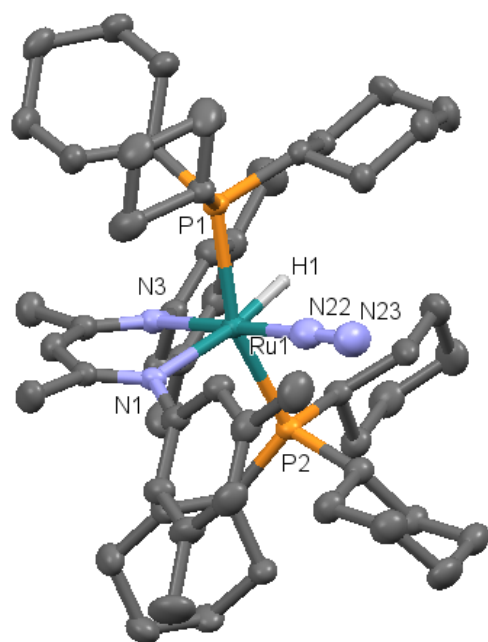


Figure A 67. The crystal structure of **1•NacNac**. (50% probability ellipsoids)

