

**MIGRATION AND DECARBONYLATION REACTIONS
OF GROUP 6 ORGANOMETALLIC COMPLEXES
USING SOLVENT-FREE PROCEDURES**

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USING SOLVENT-FREE PROCEDURES**

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DECLARATION

I declare that this thesis is my own, unaided work, performed under the supervision of Professor N. J. Coville. It is submitted for the Degree of Doctor of Philosophy in the University of Witwatersrand, Johannesburg, South Africa. It has not been submitted before for any degree or examination in any other university.

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ABSTRACT

The solvent-free migratory-insertion reactions between $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ and L ($\text{R} = \text{Me}$, $\text{L} = \text{PPh}_3$; $\text{R} = \text{COH}$, H , $\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$) were performed using NMR spectroscopy. Their rate constants for the reactions were found to be $2.75 \times 10^{-4} \text{ s}^{-1}$ ($42 - 43^\circ\text{C}$), $3.06 \times 10^{-4} \text{ s}^{-1}$ ($74 - 75^\circ\text{C}$) and $11.6 \times 10^{-4} \text{ s}^{-1}$ ($72 - 73^\circ\text{C}$), respectively. They introduced the various factors, like temperature, mole ratio, ligand effects and ring substituent effects that controlled the reaction.

The DRIFTS technique was implemented to investigate the factors that controlled the solvent-free migratory-insertion reaction between $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ and ($\text{R} = \text{H}$, Me , COH , COMe) and L ($\text{L} = \text{P}(p\text{-MeOC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, PPh_3) at $40 - 60^\circ\text{C}$ and 1:1, 1:5 and 1:10 mole ratios. The temperature study indicated complexities in the reaction at 40°C with variable mole ratios. The reaction rate increased as the temperature ($> 40^\circ\text{C}$) and as the mole ratio increased. The activation energy for the reaction at 50°C for 1:10 mole ratio was 52.0 kJmol^{-1} . The migratory-insertion reaction was observed under an optical microscope and digital photographs revealed that the reaction was facilitated by a eutectic melt $> 40^\circ\text{C}$ upon contact of the two reactants. The ligand effect study showed that electron-donating ligands have faster rates than electron withdrawing ligands. The ring substituent, R , also controlled the rate of the reaction, both sterically and electronically.

The subsequent reaction, also known as the reverse of migratory-insertion reaction, the decarbonylation reactions of $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{R} = \text{H}$, Me , COH , COMe) and L ($\text{L} = \text{P}(p\text{-MeOC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, PPh_3) were studied using the DRIFTS technique at $80 - 100^\circ\text{C}$. The rate of decarbonylation increased as the temperature increased. The activation energy for $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{R} = \text{H}$; $\text{L} = \text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$) were found to be 67 and 135 kJmol^{-1} respectively. The progression of the decarbonylation reaction under the optical microscope

revealed that it was a solid-state reaction. The ligand effect study showed that electron-withdrawing ligands have faster rates than electron donating ligands, which was opposite to that of migratory-insertion reactions. The steric and electronic effect of the R group also played a role in the rate of the decarbonylation reaction.

The similar W complex was used to investigate the migratory-insertion reaction between $\text{CpW(CO)}_3\text{Me}$ and L ($\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$) at 40 – 60 °C at varying mole ratios *via* DRIFTS. The activation energy for the reaction with $\text{P}(p\text{-FC}_6\text{H}_4)_3$ at 40 °C was 50.75 kJmol^{-1} . The study again showed complexities in the data. An optical microscopy study revealed that this was also a melt phase reaction (> 40 °C). The ligand effect study showed that electron-donating ligands have faster rates than electron withdrawing ligands, which was the same for the similar Mo complex. The decarbonylation reactions of $\text{CpW(CO)}_2(\text{L})\text{COMe}$ ($\text{L} = \text{P}(p\text{-MeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ and PPh_3) were done using DRIFTS at 100 – 120 °C. The rate of the decarbonylation increased as the temperature increased. The ligand effect study showed that no trend in the rate of the decarbonylation *versus* the electronic effect of the phosphine could be ascertained.

The final investigation involved the crystal structure analysis of some insertion Mo complexes, $(\text{CpR})\text{Mo(CO)}_2(\text{L})\text{COMe}$ ($\text{R} = \text{H}$, $\text{L} = \text{P}(p\text{-MeOC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ and $\text{R} = \text{Me}$, $\text{L} = \text{P}(p\text{-MeOC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ ($\text{L} = \text{P}(p\text{-MeC}_6\text{H}_4)_3$, PPh_3) and $(\text{CpR})\text{Mo(CO)}_3\text{Me}$ ($\text{R} = \text{COMe}$). This provided the necessary intermolecular information to make suggestions on the steric and electronic effect of the phosphine ligands and the ring substituent, R.

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Chapter 1: Introduction

The dawn of the new Millennium has brought with it an age of responsibility to find better ways of living that do not endanger the precious earth that we live upon. The mood calls for the safeguarding of our diminishing resources rather than ignorant destruction. Many have criticised the chemical industry as one of the biggest contributors to environmental destruction. This has led the chemical industries to re-evaluate reaction methodologies. Investigations in, among others, the following fields have been done: atom economy¹, the use of supercritical CO₂², ionic liquids³ and disposal problems associated with chemical reactions. Research into waste reduction by synthesising chemicals in the absence of solvents⁴ is also under investigation.

However, there are many problems that accompany the aforementioned research. The absence of solvent may not generate the same product as in the presence of solvent. It has been found that the solvent provides an encapsulating environment that is called the reaction cavity that may influence the generation of product/s⁵. Changes may also occur due to diffusion/interaction between reactants.

Recently, it was noted that organometallic complexes of the type CpML₄ undergo *cis-trans* isomerization reactions in the solid state⁵. This had stirred interest in our group in the reaction mechanisms of organometallic complexes in the solid state.⁶ As a

result other solvent-free systems have been investigated. The focus of this thesis investigation is the study of the well-known organometallic reactions – the migratory-insertion (also known as migration or CO insertion reactions) and decarbonylation reactions. The objective was to study these reactions in the absence of solvent. As the former name, “migratory-insertion,” suggests, one ligand already attached to the metal changes position or migrates and inserts itself into another metal attached ligand, thereby allowing the addition of the incoming ligand onto the metal. Decarbonylation is a reaction whereby a CO substituent is removed.

This thesis begins with a literature survey, Chapter two, which relates the history of the study of cyclopentadienyl-metal complexes and migratory-insertion reactions that have been historically performed in a solvent. Thereafter, green chemistry, and in particular solvent-free methodologies are introduced. The focal point discussed is the reaction between two solids; thus an in-depth description on solid-state reactions and, in particular, melt reactions is given.

Chapter three deals with the general experimental procedures used during the investigations carried out in this thesis. The experimental techniques used during the investigation have been given a brief explanation. Various metal complexes synthesized as starting materials have been previously prepared. Thus, only a description of both new insertion and decarbonylation products are highlighted.

Chapter four deals with the investigation of the kinetics of the migratory-insertion

reaction using NMR spectroscopy. The importance of reaction conditions such as temperature and ligand type is highlighted. The steric and electronic effects of the both the phosphine ligand and the substituent on the cyclopentadienyl ring on the rate of the migratory-insertion reaction was introduced.

Chapter five deals with the study of the kinetics of the migratory-insertion reaction, this time using DRIFTS. A more thorough investigation into reaction conditions, such as temperature, mole ratios, ligand effects, and cyclopentadienyl substituent effects was performed. The reaction was shown to occur in the melt. An in-depth look at the steric and electronic effects of the phosphine and the Cp substituent on the migratory-insertion reaction was done.

Chapter six deals with the subsequent reaction step after migratory-insertion, i.e. the decarbonylation reaction, which was also studied by DRIFTS. The reaction conditions, such as temperature, ligand and Cp substituent were also varied. The decarbonylation reaction in the absence of solvent was found to occur in the solid-state. An investigation into the steric and electronic effects of the phosphine ligand and the Cp substituent on the rate of the decarbonylation reaction was also investigated.

Chapter seven reports on the comparative migratory-insertion reaction and decarbonylation reaction of some tungsten complexes similar to the molybdenum complexes studied in the previous chapters. Temperature, mole ratio and type of

phosphine ligand were the reaction parameters that were varied for the migratory-insertion reactions involving the W complex. Temperature and type of ligand were also varied in the study of the decarbonylation reaction. Conclusions on the consequence of steric and electronic effects for both reactions were drawn from the respective studies.

Chapter eight entails an X-ray crystallographic study of products of the migratory-insertion reaction formed in the study. The six complexes formed in the migratory-insertion reaction, $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{R} = \text{H}$, $\text{L} = \text{P}(p\text{-MeOC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ and $\text{R} = \text{Me}$, $\text{L} = \text{P}(p\text{-MeOC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ ($\text{L} = \text{P}(p\text{-MeC}_6\text{H}_4)_3$, PPh_3) as well as one starting material, $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R} = \text{COMe}$) are reported. This study provided essential information on the intermolecular interactions and generated bond length and bond angle data allow for a comparative study of the complexes. The link between the structure of the insertion complexes and the rate of the decarbonylation was examined.

Chapter nine brings the thesis to an end with a summary of a listing of all conclusions obtained from this research project.

The body of the thesis consists of the figures, tables and reaction schemes, which are listed in a preliminary section of the thesis. More details and supplementary information can be found in the Appendix.

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CHAPTER 2: LITERATURE REVIEW

2.1 The origins of Organometallic chemistry

The story of organometallic chemistry began in 1951 with the synthesis of ferrocene, which was a serendipitous discovery by two independent groups, Pauson and Kealy at Duquesne University and Miller, Tebboth and Tremaine at the British Oxygen Company Ltd.^{1,2} The great organometallic chemist of his time, Geoffrey Wilkinson, had a profound interest in this sandwich compound and as a result he and his research group synthesised many novel organometallic compounds containing this ligand.³⁻¹⁸ The excitement in this research area was also fuelled by the competition between the Wilkinson group and other pioneers in this field such as the Fischer group in Germany.¹

This initiated an explosive production of novel compounds, unexpected reactions and rather interesting mechanisms and, thus organometallic chemistry was born.¹⁹⁻
²¹ Since then thousands of organometallic compounds have been synthesised and characterised.²⁰⁻²² Organometallic chemistry, which encompasses compounds that contain a metal-carbon bond, has followed a similar route to that of other sub-disciplines in chemistry in that the emphasis was initially on synthesis and structural studies and then on reaction mechanism studies.²³ Many of these new compounds were found to be homogenous catalysts and the industry-catalysis link has driven research in this area.¹⁹

Cyclopentadienyl-metal (Cp-M) compounds

The focus area of the research described in this thesis is cyclopentadienyl-metal chemistry, extending from the complexes first reported by the Wilkinson and Fischer groups around 1954.²²

Cyclopentadienyl-metal chemistry is constituted by the so-called sandwich compounds (having 2 Cp rings), and half sandwich or piano-stool complexes (having a single Cp ring). For example Piper, in the group of Wilkinson, concentrated on the synthesis and characterisation of compounds of the type $(\eta^5\text{-C}_5\text{H}_5)\text{MXYZ}$, where one Cp ($\eta^5\text{-C}_5\text{H}_5$) ring is attached to a metal (M), together with various ligands, X, Y, and Z. For example, X, Y, and Z can be CO, alkyl groups or halogen atoms etc.² This early work has provided the basis of most of the synthetic routes described in this thesis as will become apparent in the discussion that follows.

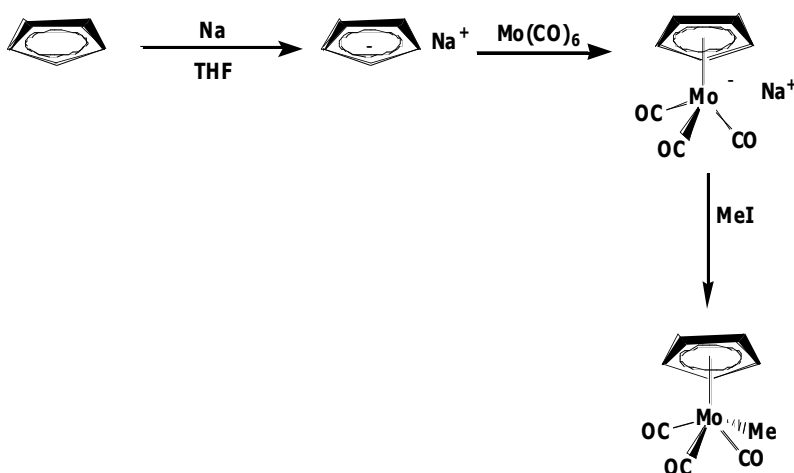
2.2. Syntheses of piano-stool complexes

2.2.1 The first synthetic routes to $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{X}$ (M = Cr, Mo, W)

Fischer and Hafner made $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{H}$ (M = Cr, Mo, and W) complexes in 1955.²⁴ This prompted Piper and Wilkinson to prepare the alkyl derivatives of these complexes, obtained according to the equation²⁴:



In the meanwhile Fischer had already reported a similar procedure to synthesise the related tungsten methyl and ethyl compounds.²⁴ Piper and Wilkinson abandoned the use of the diazomethane route, owing to the low yields obtained, in favour of a more general synthetic route that they had discovered for the preparation of the alkyl derivatives.²⁴



Scheme 2.1: Reaction scheme showing the preparation of CpMo(CO)₃Me

Their method entailed the synthesis of the sodium salt, i.e. CpM(CO)₃Na (M = Cr, Mo, and W) by adding the appropriate M(CO)₆ complex to a solution of Na[Cp] in THF and refluxing the mixture for approximately 12 hours. Thereafter, a sufficient amount of alkyl iodide was added and this mixture was allowed to react at about 40 °C for a few hours. The solvent was then removed and the product retrieved by sublimation in vacuum at about 50 °C.

Their IR spectra of the products, $\text{CpM}(\text{CO})_3\text{R}$, showed that two strong bands occurred in the $1900\text{-}2050\text{ cm}^{-1}$ region, owing to the three M-C-O groups, while one strong band occurred in the $1110\text{-}1190\text{ cm}^{-1}$ due to the M-C-O-R group.¹⁹

2.2.2 Functionalisation of the Cp ring

Once compounds of the general type, $\text{CpM}(\text{CO})_3\text{R}$ were successfully made, attempts to functionalise the cyclopentadienyl ring commenced. The problem in this endeavour, as pointed out by Hart and co-workers, was due either to the lack of aromatisation of the Cp ring or that a more accessible (and different) reaction was taking place in the reaction pathway.²⁵ The authors successfully showed how to add functional substituents to the Cp ring, where electrophilic aromatic substitution could not take place.²⁵

The key step in the Hart *et al.* reaction procedure was to add the substituent to the Cp ring prior to the addition of the metal carbonyl.²⁵ They allowed $\text{Na}[\text{Cp}]$ to react with the required functional group e.g. ethyl formate, methyl acetate, or dimethyl carbonate, in THF and refluxed the mixture for a few hours.²⁵ This resulted in a 60 - 90 % yield of very moisture sensitive formyl-, acetyl- or methoxycarbonylcyclopentadienylsodium.²⁵ This substituted ring, R^1Cp (with R^1 a functional group) was then reacted with an appropriate metal carbonyl and finally the alkyl iodide, R^2I , to produce $\text{R}^1\text{CpM}(\text{CO})_3\text{R}^2$ (R^2 being a functional group) a method similar to that used by Piper and Wilkinson.^{25,26} A summary of some of their research is shown in **Table 2.1**.

Table 2.1: Table of substituted Cp compounds of interest made by Rausch and co-workers with their yields

Cp compound	% Yield
(COH)CpMo(CO) ₃ Me	63
(COH)CpW(CO) ₃ Me	-
(COCH ₃)CpMo(CO) ₃ Me	91
(COCH ₃)CpW(CO) ₃ Me	57
(CH ₂ CH ₂)CpMo(CO) ₃ Me	11
(CH ₂ CH ₂)CpW(CO) ₃ Me	-
(CH ₂ CH ₃)CpMo(CO) ₃ Me	26
(CH ₂ CH ₃)CpW(CO) ₃ Me	38
(CO ₂ CH ₃)CpCr(CO) ₃ Me	26
(CO ₂ CH ₃)CpMo(CO) ₃ Me	36
(CO ₂ CH ₃)CpW(CO) ₃ Me	72
(COOH)CpW(CO) ₃ Me	82
(C ₂ H ₅ OH)CpMo(CO) ₃ Me	32

Thus Hart *et al.* provided a general route to the synthesis of ring-substituted cyclopentadienyl metal carbonyls.²⁵ Other work that followed in this area of chemistry was based on increasing the yield and creating a more facile reaction procedures.

For example Mouatassim *et al.*, added Li[^sBu] to CpMo(CO)₃Me in THF at -78 °C over 15 minutes.²⁶ Thereafter, solid CO₂ was added, and then the solution was acidified with 10 % concentrated HCl.²⁶ This yielded R¹CpMo(CO)₃Me (R¹ = COOH), a crystalline solid was extracted with dichloromethane in 61 % yield.²⁶

This reaction procedure afforded an easier way to substitute the cyclopentadienyl ring than that used in the of Hart *et al.* method.²⁶

2.3 Migratory-insertion reactions of $\text{CpM}(\text{CO})_3\text{R}$ complexes

While the work on the addition of substituents to Cp rings was underway. Bibler and Wojcicki found that $\text{CpFe}(\text{CO})_2\text{CH}_3$ reacted with either phosphines and phosphites (L) in refluxing THF to give a product of the type, $\text{CpFe}(\text{CO})(\text{COCH}_3)\text{L}$.²⁷ This, according to Butler and co-workers, had been the first reaction to give conclusive evidence of the production of the acetyl derivative from a reaction with a ligand other than carbon monoxide.²⁸ However, they do mention that the approach had been shown earlier by Coffield and colleagues in 1959.²⁸

Barnett and Treichel who had been working on substitution reactions²⁹, later pursued the reaction that Bibler and Wojcicki had done, and found that ultraviolet irradiation of a refluxing solution of $\text{CpFe}(\text{CO})_2\text{Me}$ and PPh_3 , gave a mixture of two products.³⁰ These two products were $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{CH}_3$ and $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COCH}_3$, and they proposed that the ‘methyl derivative is formed first with subsequent carbonylation to afford the acetyl derivative.’³⁰

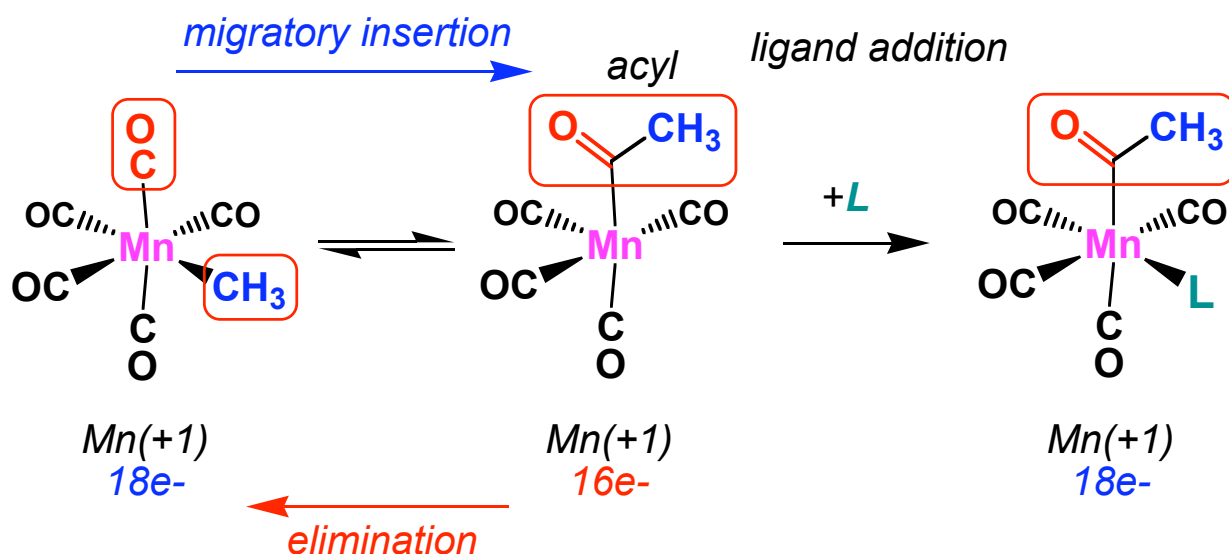
The authors noted that there might be two reaction pathways operating in the process owing to the intervention of a donor solvent.³⁰ They were able to decarbonylate $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{COCH}_3$ (as observed by the IR and NMR

spectroscopy) by refluxing the acetyl product in THF for two days.³⁰ The decarbonylation process was also solvent dependent indicated by different yields of decarbonylated products in reactions carried out in THF and hexane.³⁰

The kinetic data obtained led them to suggest that the molybdenum and the iron systems could not be compared as the systems were vastly different.³⁰ They also indicated that it was odd to find that the rates of molybdenum and tungsten systems were very different with the tungsten reaction giving extremely poor yields of product.³⁰

Barnett *et al.* also managed to successfully synthesise the first cyclopentadienylchromium alkyl complex. They added a ligand, L, (L = PPh₃, P(*p*-MeOC₆H₄)₃, P((Me)₂PPh)) to CpCr(CO)₃Me to produce CpCr(CO)₂L(COMe).³¹ Since the CpCr(CO)₃Me complex was thermally and oxidatively unstable, the ligand addition step was carried out *in situ* as soon as CpCr(CO)₃Me was made.³¹

Complexes can undergo a ligand substitution reaction whereby an acyl intermediate is produced. This type of reaction is called a CO insertion or migration (migratory-insertion) reaction (**Scheme 2.2**³²)



Scheme 2.2 The scheme showing CO insertion or migratory-insertion reaction³²

The pathways by which the organometallic complexes proceed can be easily studied. These studies have defined certain general features of migratory-insertion reactions, as summarised by Collman *et al.*¹⁹ :

- (i) The formal oxidation state does not change with the insertion of the ligand, except when the ligand is an alkylidene or alkylidyne ligand.
- (ii) The groups undergoing insertion must be in the *cis* geometry or insertion will not take place.
- (iii) If the ligand has a chiral carbon, then insertion will take place with the retention of the chirality.
- (iv) The position of the insertion equilibrium depends on the strength of the bonds to the metal.

Collman *et al.* differentiated two classes of migratory-insertion reactions depending on whether the inserted ligand is bound through a single atom, like CO, or two atoms, like alkenes.³

2.4 Use of Migratory-insertions reactions

Migratory-insertions allow chain-growth by inserting unsaturated substituents into a metal-carbon bond.²⁵ Migratory-insertions play a role in homogenous catalysis and hence contribute to industrial process e.g. : polyolefin chemistry, polyketone production, olefin oligomerisation, and the carbonylation / alkoxycarbonylation of alkenes and alkynes.²⁵

2.5 Fundamental questions in migratory-insertion chemistry

2.5.1 Insertion or migration

One of the fundamental questions in migratory-insertion chemistry has been whether the reaction takes place via CO insertion or substituent migration.³¹ Most, if not all, authors refer to the reaction as a migratory-insertion reaction, not wishing to choose one mechanism over the other.

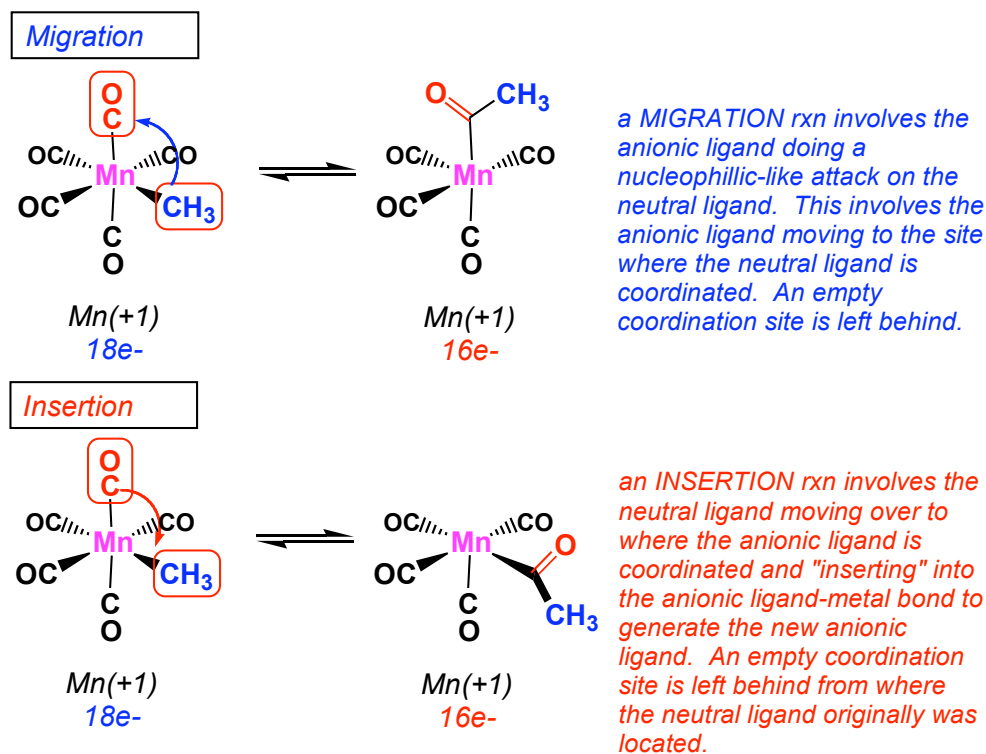
Example 1

Studies, by Mawby *et al.* and Calderazzo and Cotton, on methylmanganese carbonyl complexes indicate that the reaction occurs via alkyl migration.³¹

Calderazzo and Cotton indicated that although their results were ambiguous, this was the more reasonable reaction pathway and different from the previous proposal relating to “CO insertion”.²⁸ Calderazzo used ^{13}CO and infrared techniques which gave results that were open to criticism, but later studies by Flood using ^{13}C NMR spectroscopy, a more precise technique, verified Calderazzo’s results.¹⁹

Example 2

Recent work by van Leeuwen and colleagues involving alkylplatinum and palladium complexes containing a chelating phosphine ligands (P-P*), showed unambiguously through ^{31}P NMR spectroscopy, that the process occurred via ligand migration.³¹ Another, method to solve the dilemma was the use of chiral metal centres.¹⁹ **Scheme 2.3** shows the two pathways that can occur if either the alkyl migrates or the CO inserts.



Scheme 2.3. The various pathways followed if the first step towards migratory-insertion reaction is either alkyl migration or CO insertion³²

Example 3

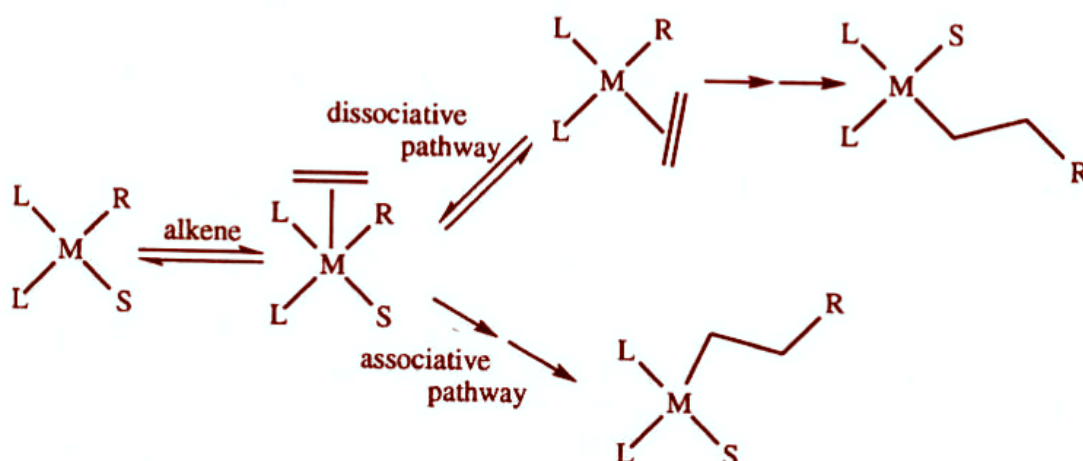
A study was done on the chiral, pseudotetrahedral complex, $\text{CpFe}(\text{CO})(\text{Et})(\text{PPh}_3)$. If it was carbonylated via an alkyl migration, an inversion of configuration at the Fe metal centre would occur, while if reaction occurred via CO insertion, there would be retention of the configuration at the Fe chain. However, both would proceed through a 16-electron intermediate that was assumed to retain its configuration. It was found that when nitroethane was used as the solvent, the reaction was stereospecific and alkyl migration occurred. However, when carried out in HMPA, the reaction was not stereospecific and CO insertion reaction seemed to dominate.

Similar studies were done on the complex, CpFe(CO)(L)Me (L = chiral phosphine) by Brunner *et al.* Unlike the reaction with $\text{CpFe(CO)(PPh}_3\text{)(Et)}$, this reaction took place stereospecifically and the resulting product confirmed that the reaction followed an alkyl migration.¹⁹

2.5.2 Associative or dissociative mechanism

Another puzzling question that has been studied is the question as to whether the insertion step occurs in an associatively or dissociatively process. It should be noted that both terms are difficult to define in relation to these piano-stool complexes, since both processes depend on the intermediate formed in the reaction.³³ The intermediate is that found at the pre-insertion step.³³ An associative pathway begins with a four co-ordinate intermediate, while a dissociative pathway begins with a five co-ordinate intermediate.³³ The problem, as pointed out by Cavell, is that a four co-ordinate complex can originate from a five co-ordinate complex.³³

Garrou and Heck showed that the complex, $\text{MR(L)}_2\text{X}$ ($\text{M} = \text{Ni}$, R = hydrocarbyl group, L = phosphine, X = halide), undergoes CO insertion dissociatively when insufficient ligand was used and associatively when an excess of ligand was used.³³ Cavell pointed out that the aforementioned study indicated that both mechanisms can take place simultaneously depending on the type of metal complex studied and the reaction conditions used.³³



Scheme 2.4. The dissociative and associative pathways of the migratory-insertion reaction

However, other researchers, like Vreize and colleagues and Boersma and co-workers (as stated in Cavell's review), have observed a five co-ordinate intermediate in their studies, indicating a dissociative process.³³ The above results are therefore ambiguous and have led authors to suggest that different pathways may be possible depending on the metal system and the reaction conditions used.³³

2.6 Kinetics Studies of the migratory-insertion reaction

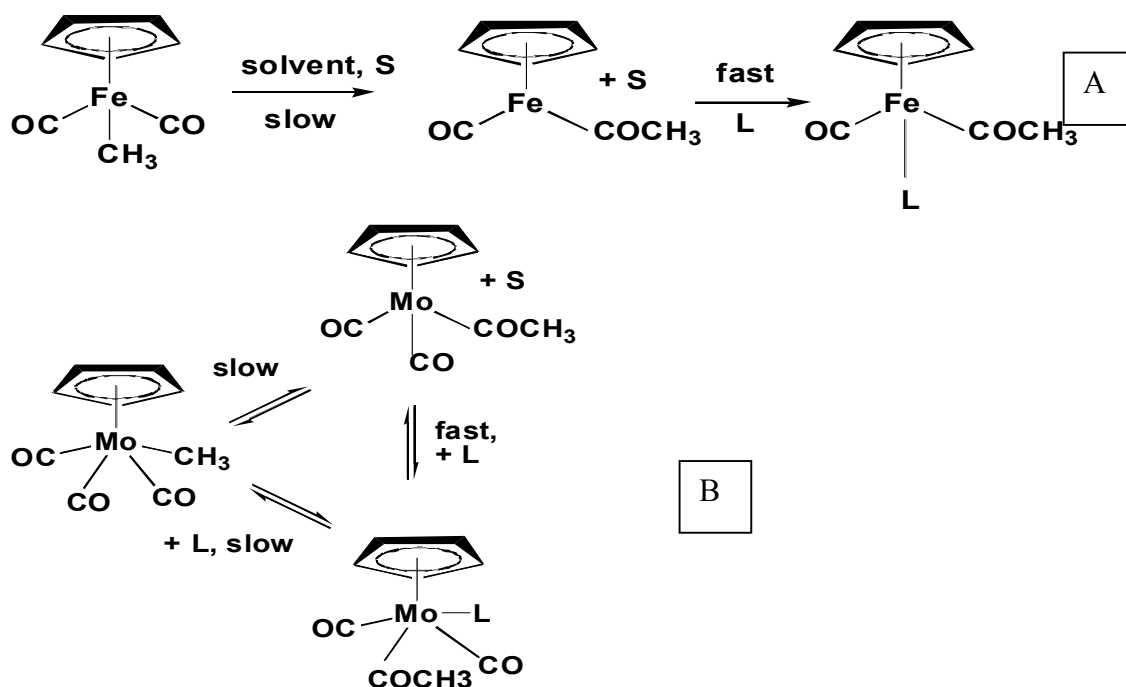
The first piano-stool compounds studied kinetically were the aforementioned alkylmanganese and alkyliron complexes.¹⁹ Butler and co-workers specifically studied the kinetics of the reaction of $CpFe(CO)_2CH_3$ and $CpMo(CO)_3CH_3$ with a variety of ligands (phosphines and phosphites).²⁸ This was accomplished by

monitoring the changes in the infrared spectra in the appropriate CO stretching region of the particular compounds.²⁸

They found the rates for reactions of both the Mo and Fe complexes with the ligands to be first order in all of the different solvents (THF, toluene, nitromethane and dimethylformamide) that were employed.²⁸ The kinetic study of $\text{CpFe}(\text{CO})_2\text{CH}_3$ revealed a dependence of the reaction on the concentration of the ligand used. This differed from reaction with $\text{CpMo}(\text{CO})_3\text{CH}_3$ which showed no dependence on ligands in most solvents.²⁸ Notably only the reaction in tri-*n*-butylphosphine showed a linear dependence on the phosphine concentration.²⁸

2.7 Proposed mechanism of migratory-insertion reaction

A two-step mechanism was proposed and a rate law was determined.¹⁹



Scheme 2.5 The two-step mechanisms (A and B) of a migratory-insertion reaction

The most valuable result obtained from the $\text{CpMo(CO)}_2\text{CH}_3$ study was that (i) the solvent plays a vital role in the reaction and (ii) the role of the nucleophilicity of the ligand.²⁸ The rate of the reaction followed the sequence: $\text{P}(n\text{-C}_4\text{H}_9)_3 > \text{P}(n\text{-OC}_4\text{H}_9)_3 > \text{P}(\text{C}_6\text{H}_5)_3 > \text{P}(\text{OC}_6\text{H}_5)_3$ which was expected from the strength of the nucleophilicity of the ligand.²⁸ The Mo system showed a faster reaction rate than that of the Fe system.²⁸ Bergman and Wax also showed that CO migrations were what they termed “solvent catalysed”, when they studied the dependence upon THF concentration with the rate of reaction with $\text{CpMo(CO)}_3\text{Me}$ and PPh_2Me .³⁴

2.8 Ligand bonding

2.8.1 Steric effects of the ligands

The size of the ligand also affects the interaction of the ligands with the metal centre. Tolman proposed the “cone angle” to give an indication of a steric effect.³⁵ The cone angle increased in the order³⁵:



Cone angles were initially measured for a $\text{Ni(CO)}_3\text{L}$ (L = phosphine) system using a space-filling model approach.³⁵ This was then modified in order to determine cone angles of other systems.³⁶

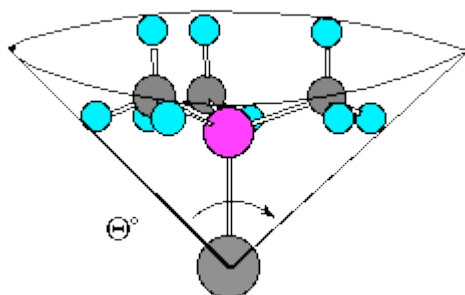


Figure 2.1. Cone angle(Θ°) representation³⁷

Tolman had also acknowledged that his cone angle concept had some limitations. These include: the space-filling models were not flexible and there were set tetrahedral geometries around the carbon and phosphorus atoms, while in real molecules, the ligands are indeed flexible and distortions may occur.³⁸ Other variations of the cone angle concept were introduced which will not be discussed here.³⁸

Another method used to quantify a steric effect is by measurement of a solid angle. Mathematically the solid angle, Ω , at a point O of a surface can be defined as:

$$\Omega = \int_s \frac{\mathbf{r} \cdot d\mathbf{S}}{r^3}, \dots\dots\dots 2.3$$

where $\mathbf{r}$ is the position vector of an element of the surface with respect to O and r is the magnitude of $\mathbf{r}$. There are three important factors that the integrand covers: the size of the element of surface, its inclination to the line joining the element to O, and the distance from O. In common terms the 'solid angle can be viewed as the surface area of that part of a solid projected onto the surface of a sphere'.

Unlike the Tolman cone angle, the solid angle is additive, meaning, that the solid angle of a ligand, can be dissected into the solid angles of individual substituents that make up that ligand. A summary of differences between the Tolman cone angle and solid angle are displayed in **Table 2.2**.³⁶

Table 2.2: Summary of differences between Tolman cone angle and solid angle

θ	Ω
Facile to measure. Initially requires a physical scale model of the ligand for calculation. Currently possible to generate θ using molecular drawing software (e.g. ALCHEMY)	Requires algorithm which is now available.
Requires known bond lengths, angles and atom sizes.	Requires known bond lengths, angles and atom sizes.
Measures in degrees only.	Measures in degrees, steradians, percentage occupancy of sphere or effective radius in angstroms.
Non additive. Composites must be re-built. Only rotation about the M-P(N,C) bond. Gives ligand profile.	Additive. A composite can readily be calculated. Can be used to generate radial profiles, yielding variation in Ω with distance.
Does not readily take account ligand meshing	Readily takes into account inter- and intraligand meshing

Most authors, including Tolman, agreed that both steric and electronic properties determine the reactivity of the phosphine ligand with the organometallic compound.^{23,38} A parameter, Z , was introduced to determine the combined effects (steric and electronic) of a ligand by the use of an equation:

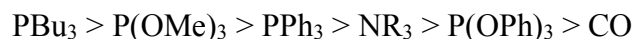
$$Z = a\theta + b\nu + c \dots\dots\dots 2.4$$

where, θ and ν are the steric and electronic parameters, respectively, and, a , b and c are regression coefficients. The equation used implied that the effects were additive. The evaluation of Z is then determined by an appropriate choice of θ and ν terms.

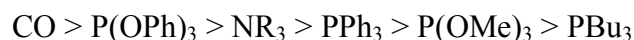
2.8.2 Electronic effects of the ligands

The metal centre in molybdenum piano stool complexes of the type $\text{CpMo}(\text{CO})_3\text{X}$ has a low formal oxidation state (2+) that allows bonding to a variety of ligands.²³ For CO attached to the metal, there would be σ donation from the carbon to the metal and π -back bonding, from the filled d -orbitals on the metal to the CO antibonding orbitals.²³ Atwood states that a synergic interaction occurs due to the enhancement of one type of bonding by the other.²³

There has been much debate on the relative strength of the two types of bonding when L = phosphines and phosphites.²³ The sequence for the substitution of organometallic compounds was found to be:



for σ -donation, and



for π -acceptance.

Tolman also defined electronic effects by the electronic parameter, ν (also referred to as the Tolman Electronic Parameter, TEP). Tolman used the frequency of the A_1 carbonyl mode of $Ni(CO)_3L$ in CH_2Cl_2 to evaluate ν and to create a table of electronic parameters for various phosphine ligands. A selected list of phosphines with their TEP is shown in **Table 2.3**. This $\nu(CO)$ value was originally determined for the Ni system, but the value obtained is in principle transferable to any metal and to any metal complex.

Table 2.3: A selection of phosphines and their associated Tolman Electronic Parameters³⁵

Phosphine	Tolman Electronic Parameter, ν / cm^{-1}
$P(OEt)_3$	2076.3
PPh_3	2068.9
PMe_3	2064.1
PCy_3	2056.4
PF_3	2110.8

Tolman also introduced an equation that could be used to calculate the electronic parameter for other ligands that had not been measured experimentally. A substituent contribution, χ_i , can be added according to **equation 5.4**, to estimate the electronic parameter for any PR_3 ligands that has not been measured.

$$\text{For } PX_1X_2X_3 \quad \nu = 2056.1 + \sum_{i=1}^3 \chi_i \dots\dots\dots 2.5$$

where (X_1 , X_2 and X_3 are the substituents on the P atom).

2.9 Solvent-free chemistry

Most organometallic chemistry has been studied using reactions in a solvent.³⁹ Tanaka and Toda, have quoted the Greek philosopher, Aristotle who said, “No Coopora nisi Fuida,” which means “No reaction occurs in the absence of solvent,” as the guiding principle behind many, if not most, chemical reactions.⁴⁰ This, according, to Tanaka and Toda, has had a major impact on the development of science.⁴⁰ Most reactions that are performed today still include solvents although there may be no evidence for the need of a solvent in the reaction.⁴⁰

Comparative studies involving experiments done in solution and those done in the solid-state had revealed the vital role that solid-state chemistry has to play in modern science.⁴⁰ Although solid-state organic chemistry has been explored for the past hundred years, organometallic chemists have, in general, had little interest in this aspect of chemistry.³⁹ Reactions in the solid-state have proven to take place more efficiently, with far higher yields, and more selectively, both stereochemically and enantioselectively, than the identical reaction taking place in solution.⁴⁰ The subtraction of the use of the solvent in chemical reactions, that is, performing reactions solvent-free, is an exciting possibility that opens the door to “greener” chemistry. Green chemistry offers a paradigm shift for chemists to drive towards cleaner and safer technologies.^{40, 41}

2.9.1 Green chemistry

Green chemistry is defined by the US Environmental Protection Agency (EPA): “to promote the innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture and use of chemical products.”⁴² The “12 Principles of Green Chemistry,” stipulate how green chemistry can be made viable in the modern world.⁴³

The 12 Principles of Green Chemistry⁴³

1. Prevention.

It is better to prevent waste than to treat or clean up waste after it has been created.

2. Atom Economy

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. Less Hazardous Chemical Synthesis

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to people or the environment.

4. Designing Safer Chemicals

Chemical products should be designed to affect their desired function while minimizing their toxicity.

5. Safer Solvents and Auxiliaries

The use of auxiliary substances (e.g. solvents or separations agents) should be made unnecessary whenever possible and innocuous when used.

6. Design for Energy Efficiency

Energy requirements of chemical processes should be recognised for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. Use of Renewable Feedstocks

A raw material or feedback should be renewable rather than depleting whenever technically and economically practicable.

8. Reduce Derivatives

Unnecessary derivatization (use of blocking groups, protection/de-protection, and temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9. Catalysis

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Design for Degradation

Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. Real-time Analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for the real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention

Substances and forms of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

These 12 principles can be used as a guide when planning and designing chemical processes typically in industry.^{42, 3, 43} It has become a necessity for industrial companies to comply with safety regulations legislated by governments.⁴² The chemist plays a major role in ascertaining the best route for an environmentally feasible industrial process.⁴²

2.9.2 Solvent-free reactions

It is interesting to note that a very feasible route would be the elimination of a solvent in a chemical process (principles 1 and 5 above). Organic solvents are on

the list of toxic chemicals or have the potential of being hazardous due to the high volumes produced by industry.⁴¹ There is the hope that solvent-free chemistry can be applied to more processes and will become industrially applicable in the future.

2.9.2.1 The advantages of using solvent-free reactions⁴¹

- (i) no reaction medium is needed to collect, purify and recycle
- (ii) compounds formed are sufficiently pure so that there is no need to further purify products by extensive chromatography, and in some cases recrystallisation
- (iii) sequential solvent-free reactions are possible resulting in high yields
- (iv) reactions are fast, sometimes needing a few minutes while in organic solvents they may take hours
- (v) no need for specialised equipment; simple grinding techniques may be employed⁴⁴
- (vi) energy use is much lower
- (vii) need for pre-formed salts and metal-metalloid complexes can be disregarded
- (viii) functional-group protection-deprotection can be avoided
- (ix) lower capital outlay for equipment in setting up industrial processes
- (x) batch size reductions and cost savings are achievable.

2.9.2.2 The disadvantages of using solvent-free reactions

The major disadvantages of solvent-free chemistry is the formation of “hot spots”. It is known that heat is released when two components are ground together and this heat is credited to the occurrence of “hot spots”, which are points of rapid reaction, and hence rapid heat loss. The old paradigm of using a reaction medium or a solvent to act as a heat sink or heat transfer agent is noted.⁴¹ These “hot spots” have the potential of uncontrollable reactions, and that there may be problems associated with the handling of a solid or highly viscous material.⁴¹ The diffusion process would also cause a problem owing to solid product formation, that would impede the reactant contact. The way around these problems is via the design of the reactor, where the expertise of the engineer and chemist is called upon.⁴¹

2.9.2.3 In Summary

Solvent use has many implications like the cost associated with extraction of the solvent, storage, and ultimately, in the safe removal of the solvent.⁴² Before a solvent can be used it is imperative to assess the full life cycle of the solvent to predict its cost and environmental impact in a “cradle to the grave approach”.^{42,45}

2.10 Environmentally-friendly processes

There has been a move to stop the use of volatile organic compounds (VOCs) as solvents, because of their link in causing many health problems, such as conjunctival irritation and allergic skin reaction.⁴² There are various alternatives to VOCs and so-called green solvents, like isopropanol and ethyl acetate, have been suggested as apposed to dichloromethane and hexane which are quite harmful^{42,45}

2.10.1 Solvent-free processes

Examples of these are the use of simple grinding, UV light, microwaves or ultrasound.

2.10.1.1 Simple Grinding / ball-milling

When solid-state reactions are activated by grinding or milling they are termed mechanochemical reactions.⁴⁴ Simple grinding techniques, requiring only a mortar and pestle, are currently employed in numerous chemical laboratories.^{42,44} The commercialised process used in industry is called ball-milling and is commonly used for grinding ores.⁴² This process is also used to grinding materials in research laboratories. For example, Huang and co-workers made chromium thiosulphate, a $M_2P_2S_6$ type complex that exhibits semiconducting and

magnetic behaviour, via a grinding process, rather than the conventional ceramic method.⁴⁶ This complex took only 1 hr of grinding to form.⁴⁶

2.10.1.2 Microwave irradiation

Microwaves have wavelengths between 1 mm and 1 m.⁴² The mechanism by which heat is imparted to a substance is complex. A process called dipolar polarization, explains why some substances when exposed to microwave irradiation will heat up, i.e. have a dipole moment, while others will not (do not have a dipole moment). For substances that contain ions heating mechanism is by conduction. These ions will move through the solution under the electric field, undergoing frequent collisions, with this kinetic energy being converted to heat. Energy is transferred by the mechanism called dielectric loss, which explains why substance with similar polarity heat up at different rates.

A feature of microwave heating is that materials can be heated selectively, and the heat becomes uniformly distributed throughout the reaction medium with time. A heating rate of 10 °C per second can be achieved and thus the total reaction time can be shortened using microwave heating when compared to the conventional heating. Microwave heating have been used for the synthesis of many compounds.⁴⁷⁻⁴⁹ Microwave irradiation is sometimes a method of choice because of the faster reaction time and improved selectivity.⁴⁵

Ardon *et al.* showed that Mo(CO)_6 , a common starting material for Mo systems, can react with some mono- and bidentate amines and phosphines to give tetracarbonyl complexes (**Figure 2.6**).⁵⁰ Interestingly, the reaction with PPh_3 depended on the stoichiometry of the reaction, i.e. one equivalent of PPh_3 gave the monosubstituted $\text{Mo(CO)}_5(\text{PPh}_3)$ complex.⁵⁰ The reaction was performed in diglyme and THF solution for 40 min and the product obtained in an 85 % yield upon a cooling and filtering process. They also explored similar reactions with W(CO)_6 and Cr(CO)_6 , which were not as successful as the Mo system and the yields were lower and reaction times were longer than Mo(CO)_6 (**Figure 2.2**).

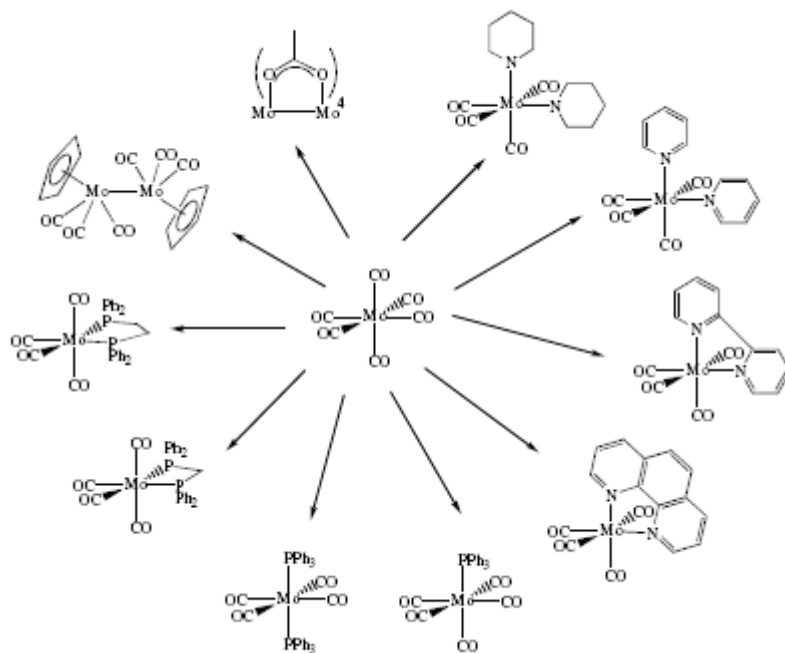


Figure 2.2 Microwave accelerated reactions of Mo(CO)_6

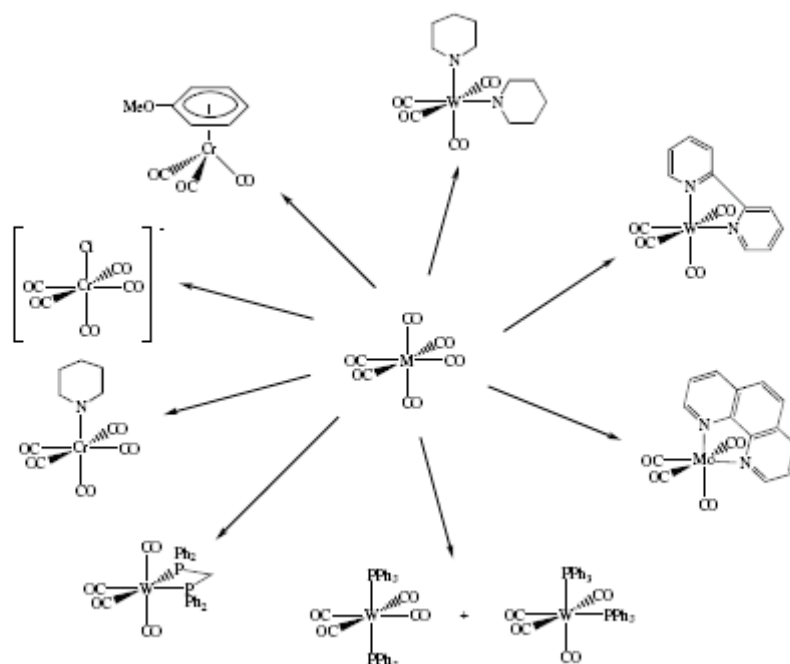


Figure 2.3 Microwave accelerated reactions of $\text{W}(\text{CO})_6$ and $\text{Cr}(\text{CO})_6$

2.10.1.3 Ultrasound

Sonochemistry is the field of chemistry in which ultrasound is used in chemical reactions.⁵¹ Ultrasound is the term given to sound waves that have frequencies higher than 18 kHz.⁴² Molecules begin to oscillate around their mean position when a sound wave passes through a liquid medium. Sonochemical effects originate from cavitation.⁵² This phenomenon is defined as the formation, growth and subsequent violent collapse of microbubbles, resulting in incredibly high temperatures and pressures of approximately 5000 K and 1000 atm respectively being generated at millions of points in the reaction system.^{52,53} Importantly, during cavitation, hydrogen atoms and hydroxyl radicals form, and react to make hydrogen peroxide, which further enhances redox reactions.^{52,53} Sonochemistry can for example be used to treat waste water.⁴⁹

Sweet *et al.* had subjected $\text{Fe}(\text{CO})_5$ and trimethylphosphine (or triethylphosphine) (1:1) solution, to ultrasound and produced a black powder of FeP , that could be used as a semi-conductor.⁵⁴ It was previously found by Suslick *et al.* that sonication of metal carbonyls, like $\text{Fe}(\text{CO})_5$ and $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), in the presence of PPh_3 allowed the substitution by the phosphines ligands.⁵⁵

2.10.2 Supercritical fluids

Supercritical fluids (SCF), such as carbon dioxide and water, are substances that exist above their critical pressure and temperature, being in a single condensed state with the benefits of properties of a gas and a liquid.⁴²

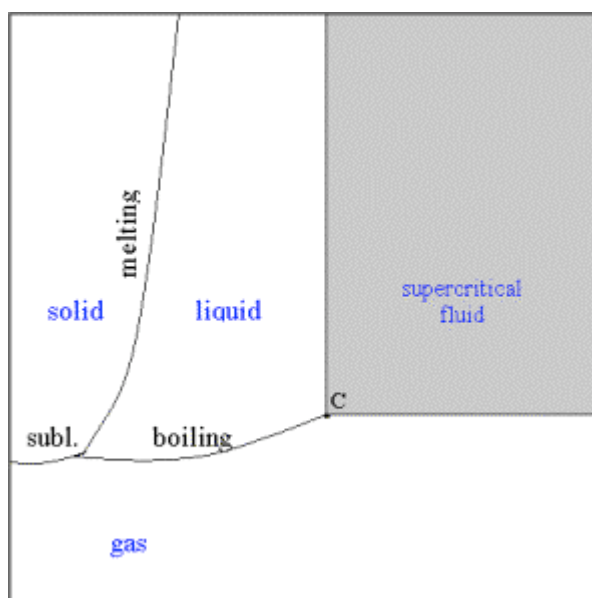


Figure 2.4: Phase diagram showing the supercritical fluid region and the critical point, C .⁵⁶

The advantage of a SCF is the increased reaction rate and solubility of the solvent.⁴² Interestingly, Harrod Research have developed SC propane and SC dimethylether for the hydrogenation of fatty acid esters, which turns out to be 100 times more productive than the conventional gas-liquid technique.⁴⁵

Howdle *et al.* showed that organometallic chemistry usually performed using matrix isolation or cryogenic solvents could be done at room temperature using SCFs.⁵⁷ They used the miscibility of H₂ and N₂ with scXe to generate dinitrogen and dihydrogen half-sandwich complexes of transition metals in Group 6, 7 and 8. The use of a supercritical solvent has provided a general route to a new class of dihydrogen complexes, (C_nR_n)M(CO)₂(H₂) (n = 6, M = Cr; n = 5 M = Mn; n = 4, M = Fe) which can be generated in spectroscopic quantities.

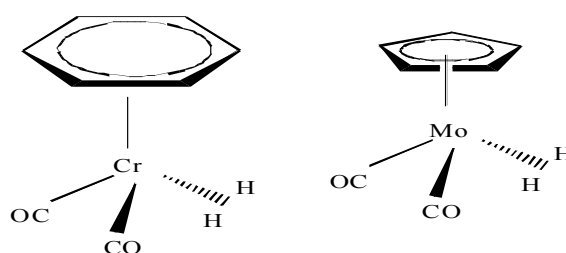


Figure 2.5 Some organometallic complexes of the type, (C_nR_n)M(CO)₂(H₂), synthesized by the use of SFCs

2.10.3 Water as a solvent

The advantages and disadvantages of the use of water as a solvent are displayed in **Table 2.4**⁴².

Table 2.4: Advantages and disadvantages of the use of water as a solvent

Advantages	Disadvantages
Non-toxic	Distillation is energy intensive
Opportunity for replacing VOCs	Contaminated waste streams may be difficult to treat
Naturally occurring	High specific capacity – difficult to heat or cool rapidly
Inexpensive	
Non-flammable	
High specific capacity-exothermic reactions can be safely controlled	

The potential use of water as a solvent was first discovered in the 80s by Breslow.⁵⁸ He showed that the hydrophobic effect of water can increase the rate of some organic reactions.⁵⁸ Bigi and co-workers investigated the use of water in Knoevenagel condensations, which are important in C-C bond formation, and found that water gave a 60 % yield as apposed to a 30 % yield using ethanol.⁵⁸

Organometallic reactions have conventionally not used water as a solvent because M-C bonds in organometallic compounds can be hydrolysed in water.⁵⁹ However, not all organometallic compounds deteriorate in water, and those have drawn interest owing to the various advantages of the use of water as a solvent, like less cost, environmentally-friendliness, and high heat capacity.⁵⁹ Molybdocenes, like $\text{Cp}'_2\text{Mo}(\text{OH})(\text{H}_2\text{O})^+$ (see **Figure 2.6**), were investigated extensively owing to their homogenous catalytic reactivity.⁶⁰

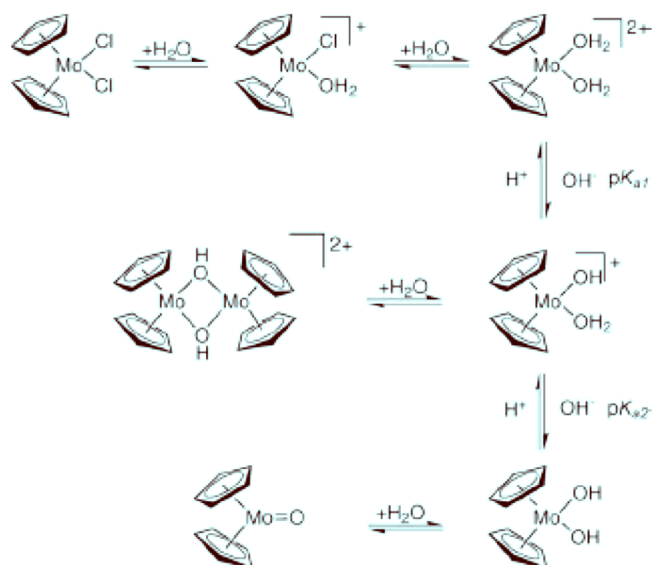
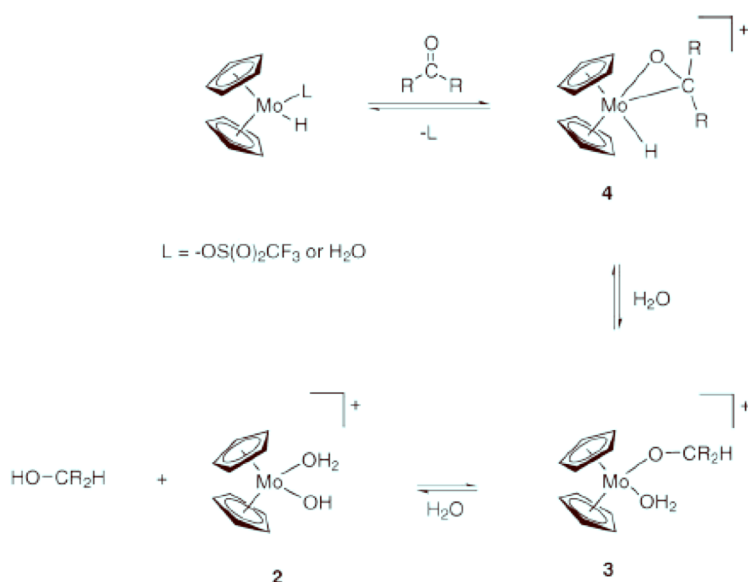


Figure 2.6: Equilibria of the various molybdocene species in aqueous solution.

One of the reactions catalysed by a molybdocene species, $\text{Cp}_2\text{MoH}(\text{OTf})$, is the hydrogenation of ketones (see **Scheme 2.6**).⁶⁰



Scheme 2.6: Proposed mechanism for the catalytic hydrogenation of ketones using $\text{Cp}_2\text{Mo}(\text{H})(\text{OTf})$.

2.10.4 Ionic liquids

Ionic liquids are salts that are liquid at low temperatures (many at room temperature or below) and that in a molten form are composed wholly of ions. The advantage of ionic liquids is that, as solvents, they have very low vapour pressure, low melting points and the ability to act both as a catalyst and a solvent.^{42,43} In the 90s “melt catalysts” were developed on an industrial pilot scale.⁴³ These “melt catalysts”, a type of liquid-supported organometallic chemistry, combine both homogenous and heterogenous catalysis principles.⁴³ A company called Texaco transformed syngas into acetic acid, esters, alcohols and glycol by using a ruthenium based “melt catalyst” which was dispersed in bromide ionic liquid.

2.10.5 Fluorous biphasic solvents

Fluorous biphasic solvents are those hydrocarbon solvents that are immiscible with organic solvents at room temperature.^{42,43} The application of this property is to have reactant and catalyst soluble in the fluorous phase at the reaction temperature and that the product will separate at room temperature.^{42,43}

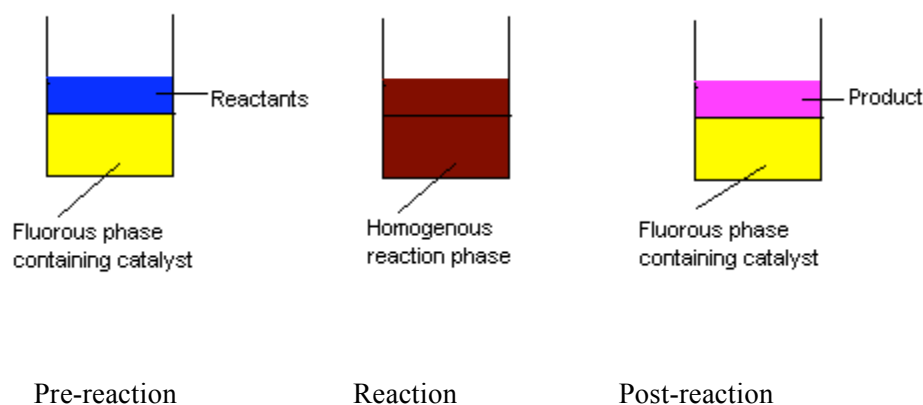


Figure 2.7: Concept of fluororous biphasic reactions

2.10.6 Conclusion of environmentally-friendly processes

The practicality of the removal of solvent from an entire industrial process, although most ideal, can increase energy costs that may occur owing to problems associated with poor heating, insufficient mass transfer and viscosity issues.⁴⁴

Jenck and co-workers have presented case studies that show that industrial sustainable chemistry through the use of green chemistry can be efficiently achieved.⁴⁵ Industrially sustainable chemistry, as defined by the Organisation for Economic Cooperation and Development (OECD), is the continuous innovation, improvement and utilisation of clean technologies to lower pollution and reduce the consumption of resources.⁴⁵

2.11 Solvent-free chemistry

Solid state work can be considered to fall under the realm of solventless or solvent-free chemistry.⁴¹ According to Rothenberg *et al.*, the reaction between two solids can be divided into 3 types of reactions as depicted in **Figure 2.8**.⁶¹

- (1) Solid-phase reaction
- (2) solvent-free reaction
- (3) solid-state reaction

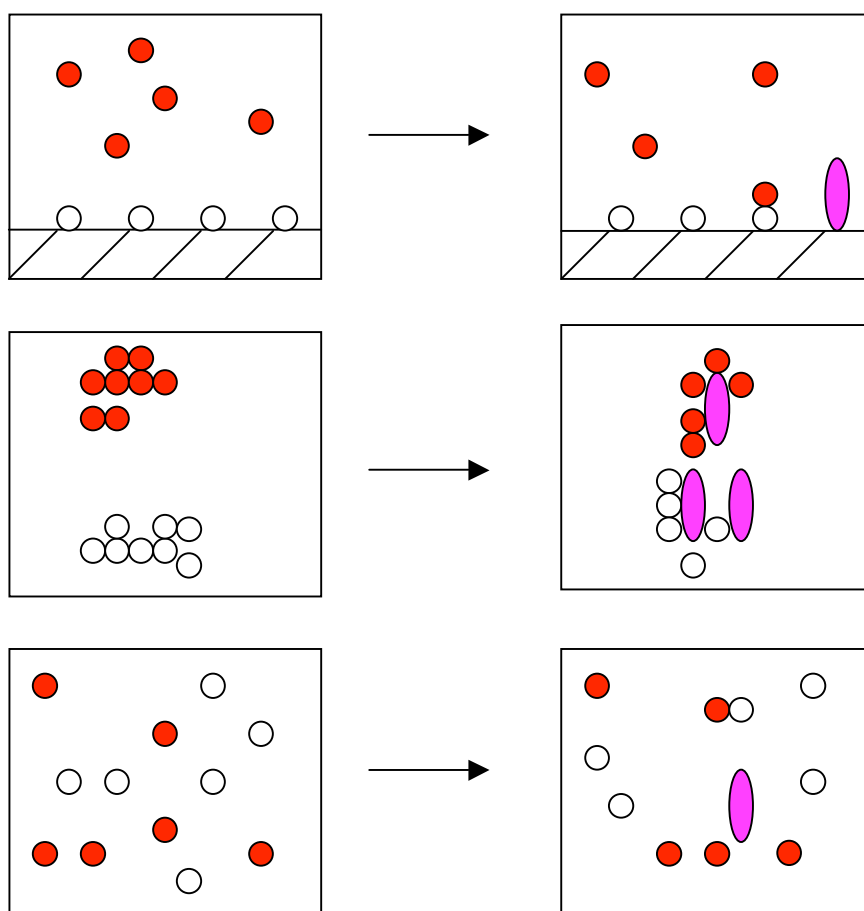


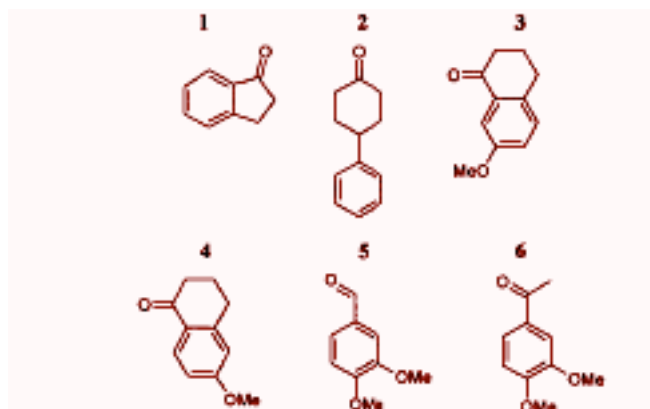
Figure 2.8: Diagrammatic representation of solid-phase reaction (top), solvent-free reaction (middle) and solid-state reaction (bottom)

In a solid-phase reaction molecules react in a liquid phase with a solid substrate, while a solvent-free reaction allows the neat reaction between components without the presence of a solvent. A solid state (or solid-solid) reaction differs from the others in that two solid components interact to produce a solid product without a liquid or vapour phase medium.

Rothenburg *et al.*, discussed the aldol condensation, which entailed the synthesis of α , β -unsaturated ketones from two carbonyl compounds, like aldehyde and ketone or ketone and ketone in the presence of a strong base.⁶¹ When two components are ground together (without the base) a melt occurs (see **Table 2.5** below). This melt occurred below the individual components melting points, hence a eutectic melt, and sometimes above room temperature.⁶¹ When the base catalyst is added to this system, the aldol condensation is only observed if there has been a melt in the system. Thus, they concluded that the reaction between the two solids was only possible if a melt occurred.⁶¹

Table 2.5: The solid ketones and aldehydes shown below (1 - 6) that when mixed produce a melt that is necessary for adol condensation reaction

	6	5	4	3	2
1	melt	melt	partial melt	melt	melt
2		melt			
3	melt	melt			
4		partial melt			
5	melt				



2.12 Solid state chemistry

The development of techniques such as X-ray powder diffraction, solid state NMR spectroscopy and Diffuse Reflective Infrared Fourier Transform spectroscopy (DRIFTS) can be used to study solid state reactions.⁶² One of the first organometallic solid state reaction to be studied, was reported by Vaska in 1966, which involved the reaction of $\text{IrX}(\text{CO})(\text{PPh}_3)_2$, where X is a halogen, with HY , where Y is also a halogen to give $\text{IrX}(\text{H})(\text{Y})(\text{CO})(\text{PPh}_3)_2$.⁶³

A solid state reaction occurs between adjacent crystal lattices that are restricted in motion, and relies on defects in the crystal.^{3,62,64} The defects create an avenue for bond breakage or bond formation to and in so doing facilitates the solid-state reaction. A reaction cavity formed by the rigid environment surrounding each molecule directs the reaction pathway.⁶⁵ The success of the reaction depends on the intimate contact between the reacting solids.⁶² At the initial point of contact, the product forms and the reaction occurs at the boundary of the two solids, and the reaction continues by diffusion.^{62,3}

Hill studied and proposed a mathematical model for the diffusion mechanism.³ In basic terms, he suggested that there existed germ nuclei at the reaction interface which capture ions of the reaction product that diffuse in special paths in front of the interface to become activated.³ Interestingly, Welsh states that the reaction is facilitated by some type of liquid or vapour phase that must be present in the reaction system to allow the migration of molecules.⁶² The complexity of the reaction pathway is, thus, apparent.^{48,62}

Thermodynamics

A solid state reaction will favour the pathway that requires the least energy. Thus the kinetic product (rather than the thermodynamic product) will be formed.⁶⁴ The thermodynamics of the reaction is constant throughout the process.⁶² It is noted that most solid state reactions do not go to completion.⁶² The entropy change for solid-solid reactions is negligible, and the reaction is generally exothermic.⁶² The rate of the reaction, proposed by Tammann and Langmuir, should be directly proportional to the surface area of the reaction interface.³

2.13 Crystal engineering

2.13.1 Introduction to crystal engineering

Organometallic crystal engineering is still in its infant stages and deals with the design and synthesis of a crystal from its building blocks using the knowledge of

intermolecular interactions.^{65,66} Organic chemists have been at the forefront of this kind of work and successful endeavours have been for the past 30 years.⁶⁷ Braga and fellow researchers are prolific in crystal engineering as reflected in the extent of their publications.⁶⁶⁻⁸⁵ Crystal engineering forms a bridge between materials chemistry (which is the synthesis, processing, characterisation, understanding and exploitation of compounds that have useful or potentially useful properties and applications⁸⁶) and supramolecular chemistry (which refers to the area of chemistry which focuses on the non-covalent bonding interactions of molecules to assemble molecules into multimolecular complexes⁸⁶).⁶⁷ Apart from the synthesis of novel compounds, the materials produced may also be used to⁸⁷:

- (i) Trap small molecules (applications in catalysis, filtering, storage etc.)
- (ii) Sense the absorption of small molecules (applications in detection devices, gas-sensors, etc.)

Organometallic complexes are particularly attractive in crystal engineering because they can develop supramolecular aggregate systems by the combination of intra- and inter-molecular bonds between the organic entity of the organometallic complex. The complex can have variable valence states and magnetic properties associated with core metal atom/s.⁷⁰

Thus, organometallic complexes provide the crystal engineer with a variety of structural and chemical possibilities that can be utilized to design a solid with pre-

specified physical and chemical properties.⁷⁰ The design relies largely on the interaction between the organometallic molecules via hydrogen bonding, ionic interactions or van der Waals forces.⁶⁷

2.13.2 Hydrogen Bonding

Hydrogen bonding is defined as the bond between an H atom and more electronegative non-metallic atoms, and one of the examples can be seen in the structure of ice in **Figure 2.9**.⁸⁸

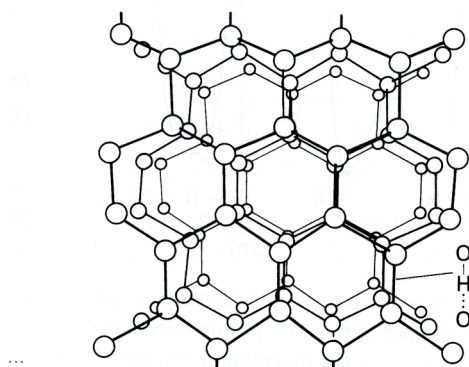


Figure 2.9 Structure of ice⁸⁸

Hydrogen bonds are stronger than van der Waals forces by an order of magnitude, having a strength of 20 kJ/mol, and they are directional.⁶⁷ Hydrogen bonds can be formed by carboxyl groups, O-H...O and amido groups etc. In **Figure 2.10**, the organometallic fragment $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+$ that was attached to organic components via O-H...O and C-H...O hydrogen bonds.

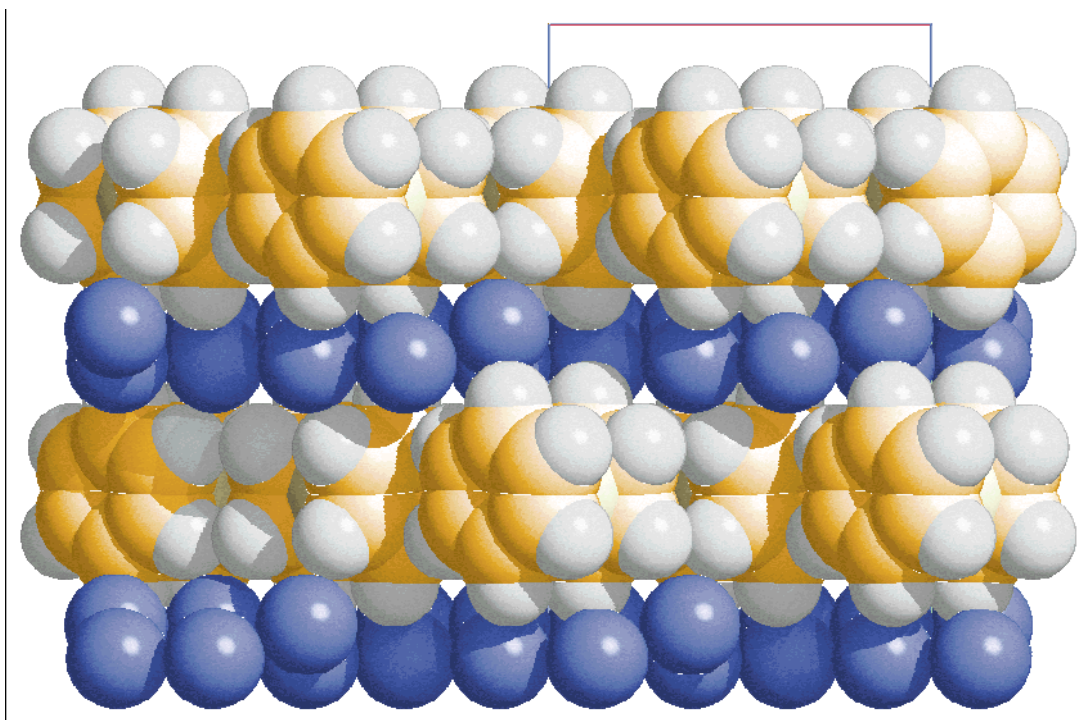


Figure 2.10. Space filling representation of crystalline $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]\text{·}[\text{OH}]^-\text{·}3\text{H}_2\text{O}$. The crystal is comprised of a stacking sequence of layers containing $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ cations intercalated with $([\text{OH}]^-\text{·}3\text{H}_2\text{O})_n$ layers of hydrogen bonded H_2O molecules and OH^- groups.

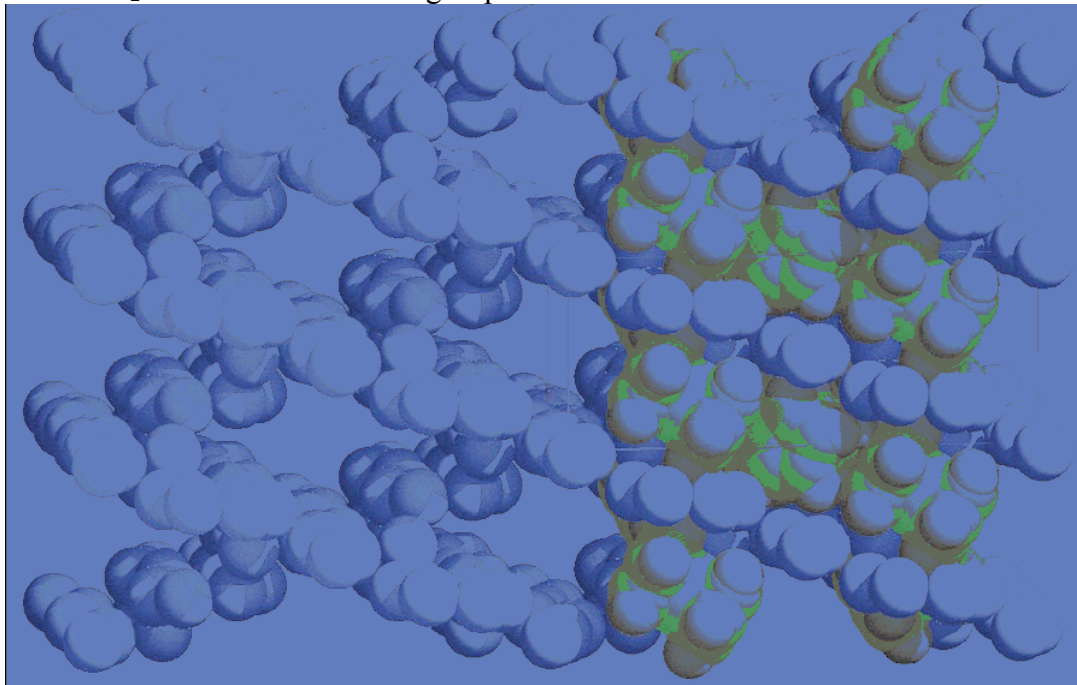


Figure. 2.11 Space filling representation of crystalline $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+\text{·}[\text{OH}]^{2-}\text{·}4\text{H}_2\text{O}$. The $[\text{OH}]^{2-}\text{·}4\text{H}_2\text{O}$ system forms a three-dimensional structure, which consists of hydrogen, bonded zigzagged chains of disordered ‘ice-like’ hexagonal rings linked *via* oxygen atoms.

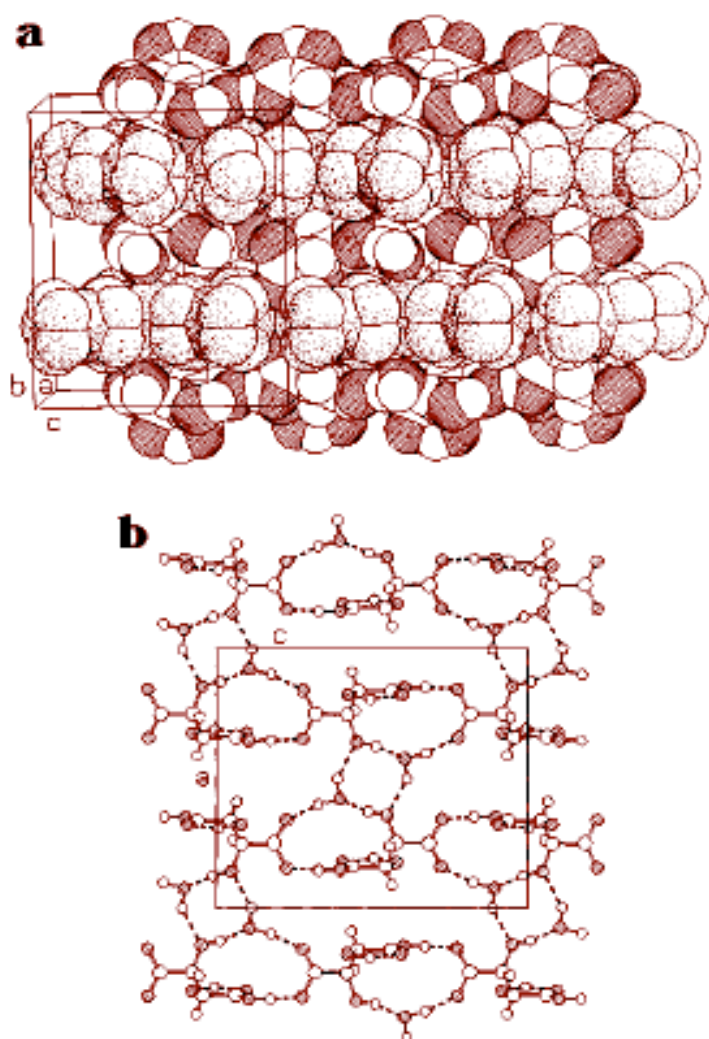


Figure 2.12 (a) The space-filling diagram of the crystalline structure $[\text{Cp}^2\text{Co}]^+[\text{D, L-HTA}]\cdot\text{H}_2\text{O}$ (H^+ are omitted for clarity). (b) A $(-\text{OH})_4$ tetramer formed from two hydroxyl groups (belonging to two tartrate ions) and two H_2O molecules. Note how the H_2O molecules bridge the parallel chains of the tartrate ions.

Braga and colleagues say that intermolecular interactions between closed-shell atoms and interactions between molecular fragments and ligands are sufficiently strong to allow for crystal engineering.⁶⁶

2.14 Mechanisms of reactions between two solids

The complexity of solid state reactions is revealed by the many models for the mechanism of a reaction.

Solid-solid models were introduced by Tamhanker and Doraiswamy based on product layer diffusion and nucleation growth.⁸⁹ Merzhanov investigated the solid state reaction between pure Mo and B powders, and found that a reaction only took place in the presence a small amount of oxide.⁸⁹ This prompted him to say that the volatile oxide forms sub-oxides that *act as carriers* that carry the reactants to the reaction sites, thus facilitating the reaction.⁸⁹ Rastogi *et al.* were interested in solid state reactions between naphthalene and picric acid.⁹⁰

2.14.1 Early work on Mechanism of Reaction between Two solids

The beauty of the reaction, between solid naphthalene and solid picric acid, was that the kinetics of the reaction was followed by the movement of the coloured interface of the product in a capillary tube.⁹⁰ This was done by placing the two powdered reactants side by side in a capillary tube and noting the distance moved by the boundary after different time intervals (**Figure 2.13**).⁹⁰

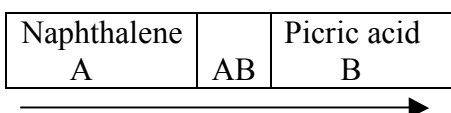


Figure 2.13. Diagram of reaction in capillary tube

They found that only the naphthalene diffused through the product layer.⁹⁰ They defined the rate of the advance of the product layer as:

$$\varepsilon^2 = 2k_i t e^{-p\varepsilon} \dots\dots\dots 2.6$$

where ε is the thickness of the product layer and at any time, t , while k_i and p are constants.⁹⁰ They were still uncertain of the mechanism of the reaction, but from the kinetic data they knew it was diffusion controlled.⁹¹

Therafter they suggested three different mechanisms that could explain the reaction⁹¹ :

- (i) the mechanism of chemical reactions between between the reactants
- (ii) the mechanism of propagation of reaction across the product layer
- (iii) the mechanism of propagation of reaction in individual grain once a coating of naphthalene-picric acid compound is formed on the surface.

2.14.2 Proposed mechanism by Rastogi *et al.*⁹¹

Pictorially, the reaction was envisioned as follows: the initial stages of the reaction occurs at the boundary of the naphthalene (N) and picric acid (P) molecules (**Figure 2.14.1**), thereafter, diffusion of the hydrocarbon takes place across the product layer (**Figure 2.14.2**) by vapour phase, surface migration of grain boundary diffusion (**Figure 2.14.3**). Eventually, propagation of the reaction occurs in the individual picric acid grains (**Figure 2.14.4**).

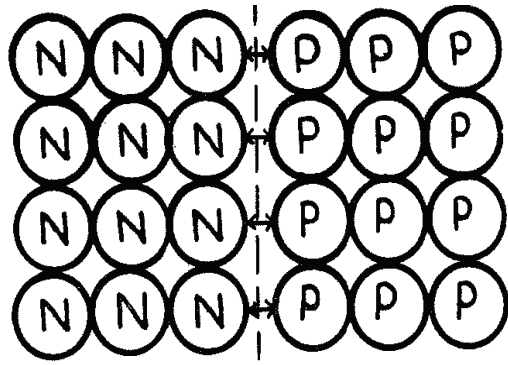


Figure 2.14.1: Reaction occurring at the boundary

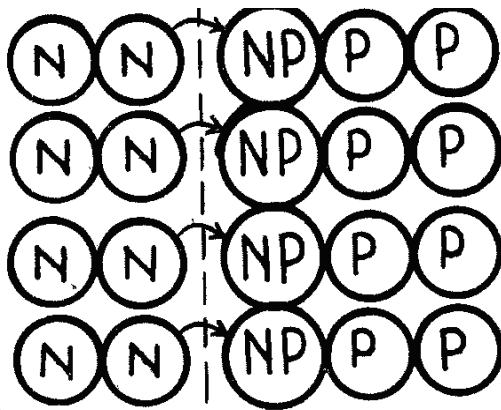


Figure 2.14.2: Diffusion across the product layer

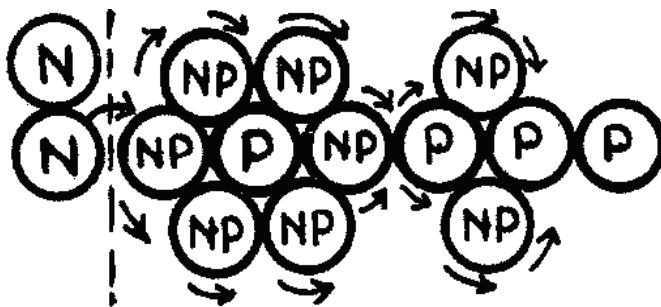


Figure 2.14.3: Visualization of surface migration or grain boundary diffusion

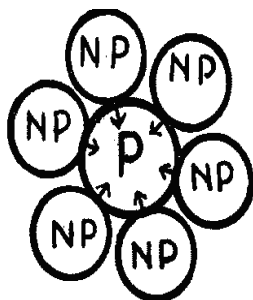


Figure 2.14.4: Propagation of reaction

2.14.3 Mechanism of Diffusion

They also considered various mechanisms for the diffusion process: (1) bulk diffusion; (2) lattice diffusion; (3) grain boundary diffusion; (4) surface diffusion and (5) vapour phase diffusion. They presented reasons as to why each possibility may be ruled out in favour of surface diffusion.

Bulk diffusion can involve disruption of molecules from their equilibrium position or it can allow diffusion through defects in the crystal lattice, and this cannot be the case here since it necessitates a higher energy of activation than that observed. Lattice diffusion was also eliminated. In the presence of ultraviolet light, the π -electrons should be elevated to higher electronic levels thus causing reaction velocity and lattice diffusion to accelerate. No change in reaction velocity was observed. There was also no reaction temperature for picrate formation.

2.14.3.1 Evidence for vapor phase diffusion

Vapor phase diffusion was favoured according to the the following observations.

(a) The hydrocarbons which have vapour pressure diffuse through the product layer, whereas picric acid does not. (b) The reaction still proceeds even if there is an empty space between the two reactants in the capillary tube. (c) The reaction was also studied by forming tablets of each reactant, and then placing them next to each other. The picric acid tablet was found to be covered with a fine layer of picrate.

2.14.3.2 Evidence against vapor phase diffusion

Unfortunately, there was also evidence against vapour diffusion. In order to justify a vapour diffusion mechanism, the diffusion coefficient should be proportional to the vapour pressure, and the activation energy should be the same as, or greater than, the heat of sublimation. It was observed that the activation energy was less than the heat of sublimation. The observations (b) and (c) that were given in favour of vapour diffusion cannot be generalized to other hydrocarbons. Reaction kinetics showed that the reaction rate increases with particle size. This disproves a vapour phase diffusion since the surface area of both reactants increase in the same way which should have the same overall reaction rate. These results indicate that surface migration may be playing a part in the reaction.

2.14.4 Model for Surface Diffusion

Further studies by Rastogi *et al.* on the solid state reactions between picric acid and substituted hydrocarbons were performed. They designed a model for surface diffusion of two reactants, A and B, adjacent to each other (**Figure 2.15**).⁹¹

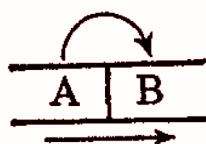


Figure 2.15: Model for surface diffusion between adjacent reactants A and B

The reaction progresses in the direction of the arrow and the surface migration of A is depicted by the curved arrow. They derived the mathematical equation for surface migration:

$$k_i = 4n\pi r^2 D_0 e^{-E/RT} \dots\dots\dots 2.7$$

where D_0 is the diffusion coefficient, E is the energy of activation, n is the number of particles of B, and r is the radius of the particle B. The elucidation of the mechanism of surface migration depends largely on the shape and size of the particles.⁸⁹

2.14.5 Factors that Control Surface Migration

Rastogi *et al.* suggest that surface migration is favoured by symmetrical and planar molecules, since they have the ability to move over the surface with more

ease than unsymmetrical molecules.⁹¹ The surface may also not be smooth, thus causing the unsymmetric particles to become entangled on the surface impeding the reaction.⁹¹ They studied molecules with varying symmetry and different sizes.⁹¹ They confirmed that surface migration was imperative in solid state reaction and that bulky molecules migrated with greater difficulty than smaller molecules as expected.⁹¹ They envisioned surface migration as follows: a disturbance is created when a surface of a reactant diffuses into another.⁹¹ The molecules at the surface have the tendency to vaporise or drift on the surface and this tendency is affected by the asymmetry of the molecules.⁹¹

2.14.6 Role of surface area contacts

The role of surface area contacts was also investigated by Richter and Viljoen.⁹² They stipulated three factors that determine the rate of a solid state reaction, $aA(s) + bB(s) \rightarrow cC$, which is as follows: the concentration of A and B atoms that could interact, the fraction of them that has sufficient energy and the frequency of interacting events.⁹² The reaction only takes place between different surface atoms (A/B) and is impeded by A/A, B/B, A/C and B/C contacts.⁹² They suggest a rhombohedral form of molecules as the best estimation that would incorporate different aspect ratios of variable shapes and sizes. Particle size of the product is also of concern, since if the product is a solid, it forms an intermediate layer between reactants. Thus, it competes with A/B contacts, and if C becomes a solid immediately after its formation, then the process becomes diffusion-controlled,

and if it is first volatile and then condenses, it affects the A/B contact in a different manner.

2.14.7 Proposed Mechanism of a Solid State Reaction by Paul and Curtin⁹³

Paul and Curtin described a solid state reaction as occurring in five stages: (a) unreacted crystal; (b) loosening of molecules at the reaction site; (c) molecular change; (d) solid solution formation and (e) separation of product (**Figure 2.16**)⁹³

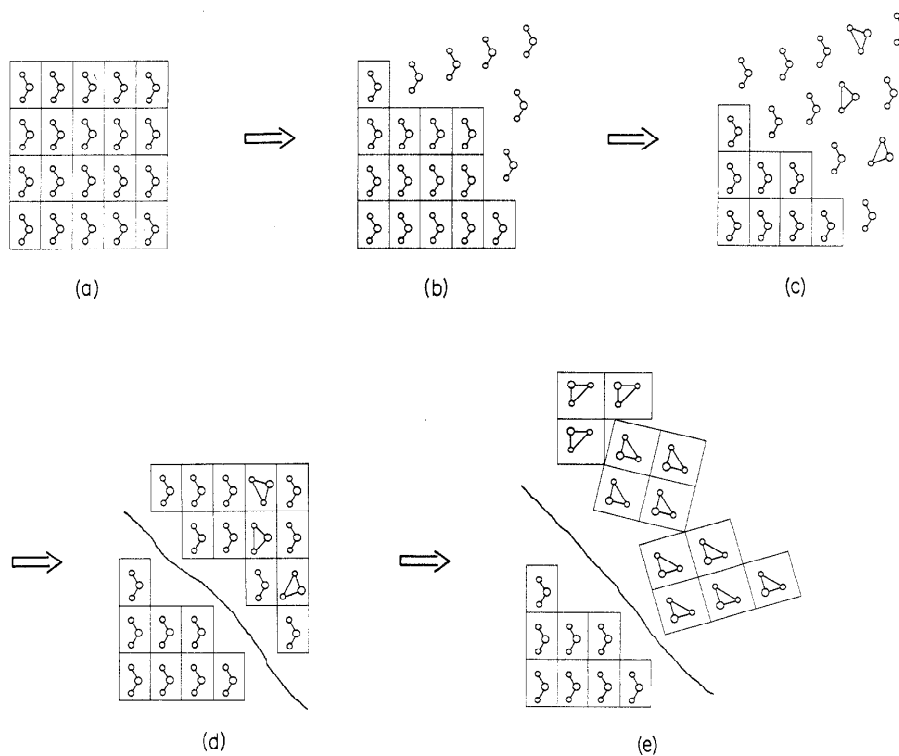


Figure 2.16 The five stages of a solid-state reaction

The unreacted crystal has tightly packed molecules that have no freedom of movement to facilitate a reaction. The system requires a loosening or partial unpacking of the crystal in order to allow a reaction.

Molecular change. The authors state that this stage has a counterpart in solution chemistry. Molecular change causes the formation of the product molecules embedded in the matrix of the starting material.

Solid solution formation. Molecules of the product form in the parent crystal until the “solubility” is exceeded and nucleation causes the crystallization of a separate phase.

Separation of the Product. The product may be randomly oriented or with a net orientation that is dictated by the starting material.

Molecular loosening. Studies using x-ray and neutron diffraction techniques and also, nuclear magnetic relaxation of the molecular motion of molecular crystals have shed light on the subject of molecular loosening. For example, alkanes do not move at low temperatures, but with an increase in temperature, rotation of the terminal methyl groups occurs, and interestingly, at a few degrees below its melting point, the entire hydrocarbon chain begins to rotate. There are two classes of solids, “plastic crystals” and “ionic crystals” that provide valuable insight on solids that have the molecular freedom of the liquid state. It has been noted in some studies, for example those by Kitaigorodskii *et al.*, that reaction change can be observed at various nucleation sites on the crystal which then completely covers the entire crystal.

For example, Kitaigorodskii *et al.* showed that the conversion of monoclinic to triclinic *p*-dichlorobenzene, began at a nucleation site, and eventually spread throughout the crystal and was easily followed using a polarizing microscope. Paul and Curtin have suggested that the spread is anisotropic meaning that it is fast in the plane normal to the morphological crystal axis and slow in the direction of this axis. The reaction is also slow when moving from one layer to the next.

The nucleation process has been linked to defects in the crystal as discussed above. It has been observed by various researchers, like Hartshorne *et al.* and Kitaigorodskii *et al.* that the growth of crystals can be induced by pricking a crystal with a pin or introducing a little of the reaction product. This has yet to be observed in thermally induced reactions and photochemical reactions, but Paul and Curtin have shown in their studies that crystal defects play a major role in these reactions too.

Molecular change. Molecular change is one of the stages of a solid state reaction in which there is a change in the covalent bonding if there is one in the molecules reacting. Studies to find rate equations for the special features of solid state reactions, like nucleation, have not been very successful. It has been found that the behaviour of individual crystals may be different to the average behaviour of the crystal. Paul and Curtin point out that many molecules undergo a chemical reaction upon melting, but none have been investigated as solid state reactions. Luty and Eckhardt state that a solid state reaction by its nature must undergo a phase change which is indicative of its collective properties.⁶³

Solid Solution Formation. At the reaction stage, the initial product molecules that form appear as a solid solution in the parent crystal. Studies on the accumulation of the amount of substance in a crystalline matrix, has led to a “solubility” table that depicts the amount of guest molecule that can be incorporated into a crystalline host material without altering the structure of the crystal. An example from the “solubility” table, indicating that 12 mol % of acridine is the maximum amount that can be incorporated in anthracene to form a solid solution. Interestingly, 45 mol % of acridine can be grown from the vapour of metastable crystals of anthracene. It was found that the inability to keep a stable solid solution early in the reaction, can be salvaged when the product is allowed to accumulate as a metastable solid solution, which can then diffuse out forming its own crystals.

Separation of product phase. The final stage of a solid state reaction the product slowly separates into its own crystalline state.

Paul and Curtin define the eutectic temperature of the mixtures of the starting material and the products, as the temperature below which a reaction may be said to occur in the solid state. They have proposed that for reactions that occur in inert solvents at a temperature approximately 60 - 100 °C below the reactants melting point, that there is a great possibility that the reaction may occur in the solid state. This may be more difficult to define.

2.14.8 Are solid state reactions, melt reactions?

Many reactions that appear to be going through a solid state reaction, in fact are actually occurring through a melt reaction. This had been suggested by Paul and Curtin and recently with more recent papers.

Example 1

It has been recently been shown that organic reactions that were supposedly a solid-solid reaction actually occurred in the liquid phase.⁶⁰ Rothenberg and co-workers had studied the solvent-free aldol condensation reaction previously reported by Toda and co-workers (see above). During the grinding process of the two complexes, they observed that a melt formed below the ambient temperature at which the experiment was carried out (see **Figure 2.17** for full explanation). Consequently they proposed that “the existence of a liquid phase is a prerequisite for reaction in these systems”.⁶⁰ The elevated kinetics were explained by the occurrence of reaction in the melt.



Figure 2.17: 4-aminotoluene and 2-hydroxy-3-methoxybenzaldehyde were ground separately. (i) Immediate orange liquid phase forms upon mixing at room temperature. (ii) Mixing with glass rod after 2 minutes, the entire mass is a homogenous liquid. (iii) Solid, orange azomethine product crystallizes from the liquid as the reaction proceeds and the entire mass is a wet crystalline solid in less than 10 minutes.

Example 2

Another example of what was initially thought to have been a solid state reaction is the CO substitution reaction of $\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{Br}$ with phosphines.⁹⁴ The kinetics of the reaction was studied using NMR spectroscopy, and DSC profiles of the reaction were also obtained. All data indicated a well-behaved solid state reaction. The authors then decided to monitor the reaction under the optical microscope. To their amazement, they found that the substitution began at 39 °C, which was well below the melting point of any of the reactants' ($\text{Mn complex} = 130\text{ °C}$, $\text{PPh}_3 = 78\text{ °C}$).⁹⁴ An set of photographs was obtained from the optical microscopy data (**Figure 2.18**) which clearly revealed this phenomenon.

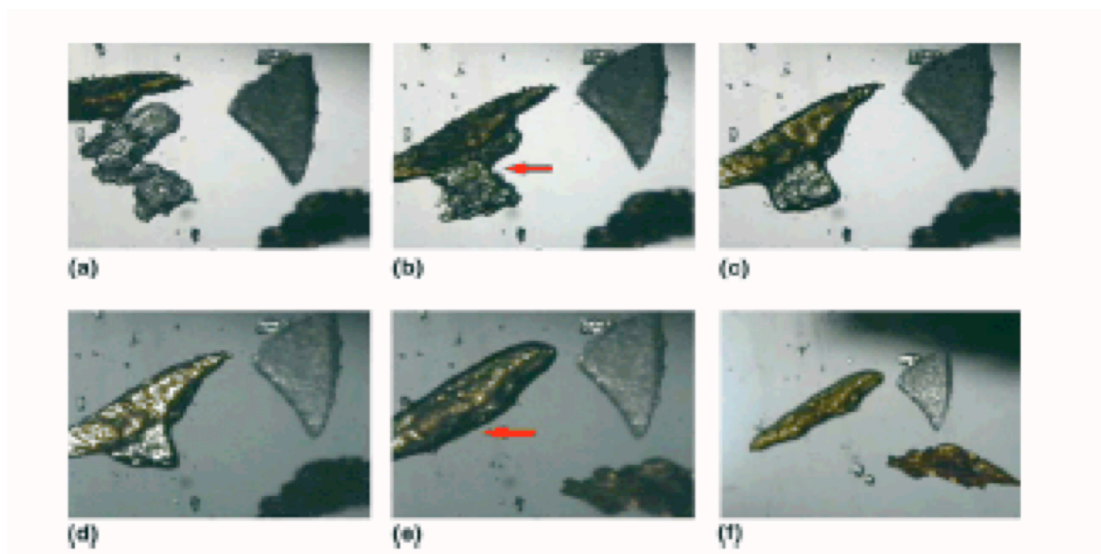


Figure 2.18: Photographs of the reaction between Mn complex and PPh_3 (a) Mn complex and phosphine place in contact, and apart; (b) red arrow indicates a melt of the phosphine; (c) and (d) continuation of melt; (e) red arrow indicates the crystallisation of product, (f) end of reaction showing crystallised product and Mn complex and phosphine still apart.⁹⁴

Their findings were as follows. The reaction only occurred at the interface of the reactants where the two crystals touched (**Figure 2.18a**). At the interface the PPh_3 melted and reacted with the Mn complex (**Figure 2.18b**). If the reactants did not touch they did not react in the temperature range of 35 - 65 °C (see **Figure 2.18f**). It appeared as if the PPh_3 was consumed in the reaction (**Figure 2.18c** and **2.18d**), which was followed by crystallization of the product from the melt (**Figure 2.18e**). Another phosphine, $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$ (150 °C) with a higher melting point than the Mn complex (132 °C) was also studied. Here the Mn complex melted at 65 °C at the point of contact with the phosphine, and then their proposed product crystallised out from the melt.

It was found that in both reaction the products had melting points higher than the reactants, and that as the products crystallised from the melt, it impeded the reaction. A secondary pathway was imperative to continue the reaction and this was facilitated by the diffusion of the reactant (eg. PPh_3 has a high vapour pressure and sublimates easily).⁹⁴ A fall in the rate of the reaction was observed towards the end of the reaction. They concluded that the initial reaction may be a solid-solid reaction at the interface, then the melt reaction ensued, and finally the reaction was controlled by the diffusion of the reactant/s.⁹⁴ All this suggests a complicated mechanism for a melt reaction.

2.15 Conclusion

- ☞ The literature survey revealed the origin of organometallic chemistry with migratory-insertion reactions in particular, with the objective of performing these reactions using solvent-free procedures.
- ☞ The generality of solvent-free chemistry was revealed.
- ☞ The methodology has been used in organic, inorganic and organometallic studies to produce novel products, and the benefits were numerous.
- ☞ Detailed methods, particularly in organometallic chemistry, were described.
- ☞ It was found, in most cases, that the solvent-free reaction goes through a melt phase, and a detailed study of melt reactions was explored.

2.16 References

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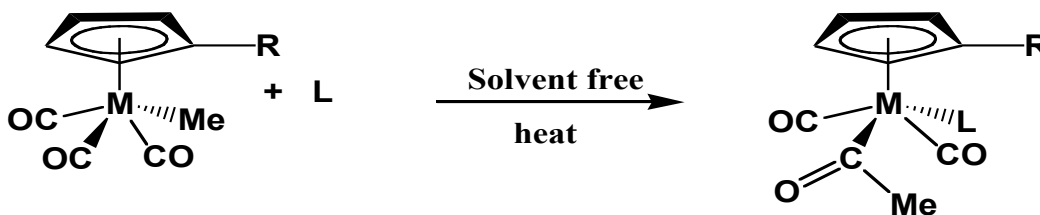
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CHAPTER 3: SYNTHESIS AND CHARACTERISATION OF SOME MOLYBDENUM AND TUNGSTEN COMPLEXES

3.1 Introduction

Piano-stool complexes have been subject to investigation owing to their ability to undergo various interesting reactions, such as, *cis-trans* isomerizations, migratory-insertions reactions, and decarbonylation reactions that are pivotal steps in various catalytic steps. As stated before our focus was to shed more light on migratory-insertion and decarbonylation reactions. The overall plan is outlined in **Scheme 3.1**. The initial step was to synthesize piano-stool complexes of the type, $(\text{CpR})\text{M}(\text{CO})_3\text{Me}$ (R = organic group). These complexes were air- and moisture-sensitive and proved quite tricky to reproduce.



Scheme 3.1. The general migratory-insertion reaction between the starting material, $(\text{CpR})\text{M}(\text{CO})_3\text{Me}$ ($\text{M} = \text{Mo}, \text{W}$) and L (L = phosphines).

Another exciting feature of this migratory-insertion reaction, as found by fellow colleagues, was that it could be carried out without a solvent. The added benefits of no waste, cleaner reactions and easy preparation were also appealing. A systematic investigation of migratory-insertion reactions using different conditions, such as temperature, mole ratio, and ligands, was carried out (see **Chapters 4, 5 and 7**).

Once complexes of the type $(\text{CpR})\text{M}(\text{CO})_2(\text{L})\text{COMe}$, were made, the consequent decarbonylation reaction was afforded. This reaction was carried out to produce complexes of the type, $(\text{CpR})\text{M}(\text{CO})_2(\text{L})\text{Me}$, and an investigation of the reaction conditions as stated above was also carried out (see **Chapter 6 and 7**).

The various procedures used in the characterization of $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$, $(\text{CpR})\text{M}(\text{CO})_2(\text{L})\text{COMe}$ and $(\text{CpR})\text{M}(\text{CO})_2(\text{L})\text{Me}$ complexes in this study are summarized below.

Characterization procedures

(a) Fourier Transform Infrared spectroscopy (FTIR)¹

Molecules have energy distributed throughout their structure, thus causing bonds to stretch and contract, atom/s to move and other molecular vibrations to occur. The amount of energy in a molecule is quantized, and so stretching and bending modes occur at specific frequencies. When a molecule is irradiated with electromagnetic radiation, energy is absorbed when the frequency of radiation matches the frequency of the vibrational motion. Since each frequency absorbed by a molecule corresponds to a specific molecular motion of a molecule it can be detected in an IR spectrum.

Interpretation of these motions reveals the types of bonds, i.e. functional groups, present in the molecule.

(b) ^1H -Nuclear Magnetic Resonance spectroscopy (^1H -NMR)¹

In the presence of a magnetic field, positively charged nuclei, that are tiny magnets themselves, orient themselves parallel or anti-parallel to the external field. The parallel state is slightly lower in energy. When the electromagnetic radiation is at a particular frequency, energy absorption occurs and the lower energy state “flips” to the higher energy state. When this “flip” occurs the magnetic nuclei are in resonance with the applied radiation – this is termed nuclear magnetic resonance (NMR). The nuclei in the molecules are surrounded by electrons, whose magnetic fields act in opposition to the applied field so that the effective field actually felt by the nucleus is a bit smaller than the applied field i.e. shielding occurs. Since each specific nucleus in a molecule is in a slightly different electronic environment, each nucleus is shielded to a slightly different extent and the effective magnetic field is not the same for each nucleus. Thus, a characteristic signal is detected for different nuclei.

(c) Differential Scanning Calorimetry (DSC)²

DSC is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material as the two specimens are subjected to identical temperatures in an environment heated or cooled at a controlled rate. There are 2 types of DSC systems in common use, namely, power-compensation and heat-flux. The latter was be used in this project. This

technique involves the sample and reference being controlled by a low-resistance heat-flow path (a metal disc). The assembly is enclosed in a single furnace. Enthalpy or heat capacity changes in the sample causes a difference in its temperature relative to the reference. The temperature difference is recorded and related to the enthalpy change in the sample using calibration experiments.

(d) Column chromatography³

Chromatography is a method of extraction where one phase is held in place, while another moves past it. The technique involves packing a column with solid particles, e.g., silica gel, and a solvent e.g., hexane. The sample mixture (solute) is dissolved in a little solvent and added to a column. The sample is washed down the column with continuous solvent flow. If a solute contained in the sample mixture is more strongly adsorbed than others, it spends a smaller time in free solution i.e. moves down the column slower. This effectively separates the crude sample mixture into its components.

(e) X-ray diffraction (XRD)⁴

XRD allows the study of atomic arrangements in crystalline material. A crystal was described by Buerger in 1956 as a “region of matter within which the atoms are arranged in a 3 dimensional translationally periodic pattern”. In order to interpret XRD data the following aspects are required:

- Conventions of lattice description, unit cells, lattice planes, d-spacing and Miller indices

- Crystal structure and symmetry elements
- The reciprocal lattice

The technique uses the interference of short wavelength particles (e.g. neutrons) or photons (x-rays) reflected from planes of atoms in crystalline materials to yield 3-dimensional structural information at the atomic level. The detector is set at a given angle, which picks up reflections of diffraction from the crystalline sample that satisfy Bragg's law ($\lambda = 2d\sin\theta$, where d is the spacing between atomic planes in the crystalline phase (d -spacing)). The intensity of the diffracted X-rays is measured as a function of diffraction angle 2θ and the crystalline orientation of the sample.

In this study, NMR spectra were recorded on a Bruker AC 300 spectrometer using CDCl_3 as the solvent. DRIFTS spectra were collected on a Bruker Tensor 27 FTIR spectrometer equipped with a Thermo Spectra-Tech Collector II. DSC profiles were collected on a Dupont Instrument 910 differential scanning calorimeter. Melting points were determined on a Kofler hot stage melting point apparatus. CHN analyses were performed at the CSIR, Pretoria.

3.2 Experimental Procedure

The Cp dimer was first cracked. Cracking involved the dimer being thermally reduced to its monomeric unit, which is highly unstable at room temperature. All techniques involving these air-sensitive materials were performed under dry nitrogen.

All chemicals used were dried appropriately using distillation and drying overnight in molecular sieves.

3.2.1 Synthesis of the starting material molybdenum complexes (CpR)Mo(CO)₃Me (R = ring substituent)

As stated above the starting material, (CpR)Mo(CO)₃Me (R = organic group) was prepared with a variation of literature procedures.⁵⁻¹² A list of the starting materials with the NMR and IR spectroscopic analyses is tabulated in **Table 3.1**.

3.2.2 Synthesis of CpMo(CO)₂(L)COMe (L = P(*p*-FC₆H₄)₃, P(*p*-MeC₆H₄)₃, P(*p*-OMeC₆H₄)₃, PPh₃)

The prepared CpMo(CO)₃Me (38 mmol) was added to L (42 mmol) in a 50 ml round-bottom flask, which had been flushed with N₂. The reaction was carried out in a 80 °C oil-bath for 2 hrs for P(*p*-FC₆H₄)₃ and P(*p*-OMeC₆H₄)₃. For P(*p*-MeC₆H₄)₃ the reaction was performed for 6 hrs. Note that no solvent was used for this experiment.

3.2.3 Synthesis of (CpMe)Mo(CO)₂(L)COMe (L = PPh₃, P(*p*-FC₆H₄)₃, P(*p*-MeC₆H₄)₃ and P(*p*-OMeC₆H₄)₃)

The prepared (CpMe)Mo(CO)₃Me (18 mmol) was added to L (20 mmol) in a 50 ml round-bottom flask, which had been flushed with N₂. The reaction was carried out in a 90 °C oil-bath. Note that no solvent was used for this experiment. For PPh₃, 100 % conversion was achieved in 15 minutes, while P(*p*-MeC₆H₄)₃ and P(*p*-OMeC₆H₄)₃)

showed 100% product after 1 hr. For the $P(p\text{-FC}_6\text{H}_4)_3$ ligand, the migratory-insertion insertion took place in 30 minutes.

3.2.4 Synthesis of $(\text{CpCOH})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{L} = P(p\text{-FC}_6\text{H}_4)_3$, $P(p\text{-MeC}_6\text{H}_4)_3$ and $P(p\text{-OMeC}_6\text{H}_4)_3$)

The prepared $(\text{CpCOH})\text{Mo}(\text{CO})_3\text{Me}$ (34 mmol) was added to L (37 mmol) in a 50 ml round-bottom flask, which had been flushed with N_2 . The reaction was carried out in a 90 °C oil-bath for 2 hrs for $P(p\text{-FC}_6\text{H}_4)_3$ and PPh_3 , and for 4 hrs for $P(p\text{-OMeC}_6\text{H}_4)_3$ and $P(p\text{-MeC}_6\text{H}_4)_3$. Note that no solvent was used for this experiment.

3.2.5 Synthesis of $(\text{CpCOMe})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{L} = P(p\text{-FC}_6\text{H}_4)_3$, $P(p\text{-MeC}_6\text{H}_4)_3$ and $P(p\text{-OMeC}_6\text{H}_4)_3$)

The prepared $(\text{CpCOMe})\text{Mo}(\text{CO})_3\text{Me}$ (33 mmol) was added to L (36 mmol) in a 50 ml round-bottom flask, which had been flushed with N_2 . The reaction was carried out in a 90 °C oil-bath for 2 hrs for $P(p\text{-FC}_6\text{H}_4)_3$ and PPh_3 , and for 4 hrs for $P(p\text{-OMeC}_6\text{H}_4)_3$ and $P(p\text{-MeC}_6\text{H}_4)_3$. Note that no solvent was used for this experiment. See **Table 3.5** for the results.

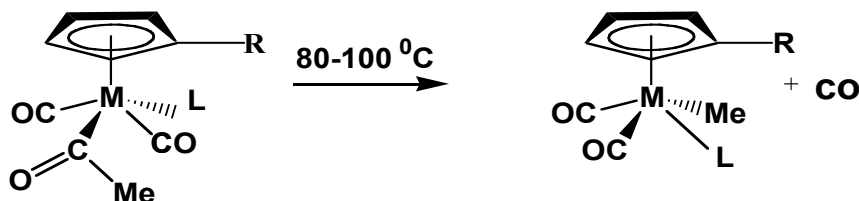
3.2.6 Synthesis of $\text{CpW}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{L} = P(p\text{-FC}_6\text{H}_4)_3$, $P(p\text{-MeC}_6\text{H}_4)_3$ and $P(p\text{-OMeC}_6\text{H}_4)_3$)

The prepared $\text{CpW}(\text{CO})_3\text{Me}$ complex (29 mmol) was added to L (32 mmol) in a 50 ml round-bottom flask, which had been flushed with N_2 . The reaction was carried out in a 60 °C oil-bath for 4 hrs for $P(p\text{-FC}_6\text{H}_4)_3$ and $P(p\text{-OMeC}_6\text{H}_4)_3$. For $P(p\text{-MeC}_6\text{H}_4)_3$

the reaction was performed for 6 hrs. Note that no solvent was used for this experiment.

3.3.7 Attempted synthesis of $(\text{CpR})\text{M}(\text{CO})_2(\text{L})\text{Me}$ (For $\text{M} = \text{Mo}$, $\text{R} = \text{H}$, Me , COH , COMe , for $\text{M} = \text{W}$, $\text{R} = \text{H}$; $\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ and $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$)

The prepared $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R} = \text{H}$, Me , COH , COMe) (s) was mixed in KBr (1 %) and added to L (s) in KBr (1 %). The reaction was carried out in a the DRIFTS cell at 50°C to produce the insertion complex of the type $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ (as above), the reaction temperature was then increased to 80°C , to produce the complex of the type, $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{Me}$, which is the decarbonylated product. Note that no solvent was used for this experiment.



Scheme 3.2: The decarbonylation reaction of $(\text{CpR})\text{M}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{M} = \text{Mo}$, $\text{R} = \text{H}$, Me , CHO , COMe or $\text{M} = \text{W}$, $\text{R} = \text{H}$ and $\text{L} = \text{PPh}_3$, $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$)

3.3 Results and Discussion

3.3.1 Synthesis of the starting material metal complexes (CpR)M(CO)₃Me (M = Mo, R = H, Me, COMe, COH ; M = W, R = H)

The different procedures for synthesis of the starting material of the type, (CpR)M(CO)₃Me, were found in the literature⁵⁻¹², and a variation of these procedures was used here. These starting materials were used to perform migratory-insertions reactions and decarbonylation reactions. A summary of the analysis of the starting material is found in **Table 3.1** below.

Table 3.1. Starting material, (CpR)M(CO)₃Me (M = Mo, R = H, Me, COMe, COH; M = W, R = H) analyses using IR and NMR spectroscopy and melting points

Complex	¹ H-NMR / ppm			ν (CO) / cm ⁻¹	Melting point / °C
	Cp	R-Cp	M-Me		
CpMo(CO) ₃ Me (s)	5.29,s	-	0.37, s	2017, 1945	100-101
(CpMe)Mo(CO) ₃ Me (s)	5.14-5.16,d	1.94,s	0.30, s	2015, 1934	50-51
(CpCOMe)Mo(CO) ₃ Me (s)	5.67,t 5.43,t	2.32,s	0.42, s	2025, 1957, 1684	82-85
(CpCOH)Mo(CO) ₃ Me (s)	5.68,t 5.51,t	9.63,s	0.44, s	2030, 1954, 1703	106-110
CpW(CO) ₃ Me	5.39, s	-	0.44, s	2016, 1940	82-84

Table 3.2: Table of some expected spectroscopic data for (CpR)M(CO)₃Me complexes (M = Mo, R = H, COH, COMe; M = W, R = H)

Complex	¹ H-NMR / ppm		ν (CO) / cm ⁻¹
	Cp	M-Me	
CpMo(CO) ₃ Me (s) ¹³	5.30, s	0.37, s	2018, 1927
(CpCOMe)Mo(CO) ₃ Me (s) ¹⁴	5.78 5.39	0.45	2020, 1920, 1665
(CpCOH)Mo(CO) ₃ Me (s) ¹⁴	5.72 5.52	0.45	2020, 1920, 1680
CpW(CO) ₃ Me ¹³	5.30, s	0.37, s	2018, 1927

The starting material tabulated above were yellow-orange in colour, except for (CpCOH)Mo(CO)₃Me, which was orange-brown. The crystal structure of the latter complex was elucidated and this data is discussed in **Chapter 8**. The methyl-substituted Cp complex had the lowest melting point of ~ 50 °C. All had ν (CO) at ~ 2020 cm⁻¹ and ~ 1945 cm⁻¹.

Starting materials, (CpR)M(CO)₃Me complexes (M = Mo, R = H, COH, COMe; M = W, R = H) were compared to those found in literature in **Table 3.2**. All the ¹H NMR compared well with the literature data (all done in CDCl₃).^{13, 14} However, the IR data for R = COH and COMe differed owing to the method of analysis. The authors used KBr press for the R = COH and for R = COMe a melted sample was used.¹⁴

3.3.2 Synthesis of $\text{CpMo(CO)}_2\text{(L)COMe}$ ($\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ and $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$, PPh_3)

$\text{CpMo(CO)}_3\text{Me}$ was the starting material used to perform migratory-insertion reactions to produce complexes of the type, $\text{CpMo(CO)}_2\text{(L)COMe}$ in 80 - 100 % yield. The crystal structures of some of these complexes with the following phosphines were solved: PPh_3 (by Churchill and Fennessey¹⁵), $\text{P}(p\text{-FC}_6\text{H}_4)_3$ and $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$ (see **Chapter 8**). All products were confirmed by the shift of the 5.29 ppm signal to ~ 5.0 ppm and the appearance of the ~ 2.60 ppm signal (Me-CO) in the $^1\text{H-NMR}$ spectra. In IR spectroscopy the product was confirmed by the disappearance of the 2017 cm^{-1} peak and the appearance of the $\sim 1620\text{ cm}^{-1}$ peak(C=O). These solid, yellow products are summarized in **Table 3.3**. See **Appendix A1** for additional information.

Table 3.3: Spectroscopic data and melting points of $\text{CpMo(CO)}_2\text{(L)COMe}$

L	$^1\text{H-NMR}$ / ppm			$\nu(\text{CO}) / \text{cm}^{-1}$	m.p. / $^\circ\text{C}$
	C_5H_5	$\text{CH}_3\text{-CO}$	Other		
$\text{P}(p\text{-FC}_6\text{H}_4)_3$ (s)	5.01, s	2.59, s	7.14-7.15,m	1938, 1853, 1630	143-145
$\text{P}(p\text{-MeOC}_6\text{H}_4)_3$ (s)	5.00,s	2.61,s	6.86-6.94,m 3.82, 3.84	1933, 1847, 1628	173-175
$\text{P}(p\text{-MeC}_6\text{H}_4)_3$ (s)	4.98,s	2.60,s	7.12-7.23,m	1938, 1852, 1620	169-171
PPh_3 (s)	4.98,s	2.60, s	7.19-7.22, m	1933, 1852, 1631	140-143

Table 3.4: Table of some expected spectroscopic data for $\text{CpMo(CO)}_2(\text{L})\text{COMe}$ from literature¹³

L	¹H-NMR / ppm			$\nu(\text{CO}) / \text{cm}^{-1}$
	C_5H_5	$\text{CH}_3\text{-CO}$	Other	
PPh_3	5.00, s	2.61, s	7.43, m	1938, 1852, 1597
$\text{P}(p\text{-MeOC}_6\text{H}_4)_3$	5.00, s	2.61, s	6.89-7.25, m	1936, 1841, 1594

Table 3.4 lists the ^1H -NMR and IR spectroscopic data found by Adeyemi and Coville, which compared very well with our data.

3.3.3 Synthesis of $(\text{CpMe})\text{Mo(CO)}_2(\text{L})\text{COMe}$ ($\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ and $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$, PPh_3)

The starting material $(\text{CpMe})\text{Mo(CO)}_3\text{Me}$ was used to perform migratory-insertion reactions to produce complexes of the type, $(\text{CpMe})\text{Mo(CO)}_2(\text{L})\text{COMe}$ in 100 % yield. All of the complexes resulted in suitable crystals that were solved using X-ray diffraction, and a full account of this information can be found in **Chapter 8**. All products were confirmed by the shift of the 5.10 ppm doublet to a $\sim 4.60 - 4.90$ ppm doublet and the appearance of the ~ 2.60 ppm signal (Me-CO) in the ^1H -NMR spectra. In IR spectroscopy the product was confirmed by the disappearance of the 2015 cm^{-1} peak and the appearance of the $\sim 1600 \text{ cm}^{-1}$ peak(C=O) (see **Table 3.3**). These were also solid, yellow products.

Table 3.5: Spectroscopic data and melting points of (CpMe)Mo(CO)₂(L)COMe

L	¹ H-NMR(ppm)			ν (CO)	m.p.
	C ₅ H ₄	CH ₃ -CO	Other		
PPh ₃ (s)	4.68-4.87,d	2.63,s	7.43,m	1926, 1832, 1609	125-127
P(<i>p</i> -FC ₆ H ₄) ₃ (s)	4.67, 4.86,d	2.60,s	7.02- 7.28,m	1937, 1843, 1620	120-123
P(<i>p</i> -MeC ₆ H ₄) ₃ (s)	4.64, 4.84,d	2.62,s	7.14 - 7.30,m	1937, 1846, 1620	120-122
P(<i>p</i> -MeOC ₆ H ₄) ₃ (s)	4.65, 4.85,d	2.62,s	6.86 - 6.94,m 3.82,3.84	1933, 1842, 1607	153-155

3.3.4 Synthesis of (CpCOH)Mo(CO)₂(L)COMe (L = P(*p*-FC₆H₄)₃, P(*p*-MeC₆H₄)₃ and P(*p*-OMeC₆H₄)₃, PPh₃)

The starting material (CpCOH)Mo(CO)₃Me was used to perform migratory-insertion reactions to produce complexes of the type, (CpCOH)Mo(CO)₂(L)COMe in 60 - 80 % yield. Products were confirmed by the shift of the ~ 5.50 ppm doublet to a ~ 5.10 ppm doublet and the appearance of the ~ 2.60 ppm signal (Me-CO) in the ¹H-NMR spectra. In IR spectroscopy the product was confirmed by the disappearance of the 2030 cm⁻¹ peak and the appearance of the ~ 1620 cm⁻¹ peak(C=O). The data for these solid, brownish-yellow products are summarised in **Table 3.6**. See **Appendix** for additional information.

Table 3.6: Spectroscopic data and melting points of (CpCOH)Mo(CO)₂(L)COMe

L	¹ H-NMR / ppm			ν (CO) / cm ⁻¹	m.p. / °C
	C ₅ H ₄	CH ₃ -CO	Other		
PPh ₃ (s)	5.17, 5.16,d	2.60, s	9.78, s 7.05-7.33,m	1943, 1859, 1692, 1627	149-151
P(<i>p</i> -MeOC ₆ H ₄) ₃ (s)	5.08,s	2.61, s	9.80, s 6.86-6.94, m 3.80, s	1943, 1859, 1690, 1624	135-138
P(<i>p</i> -FC ₆ H ₄) ₃ (s)	5.17, 5.16,d	2.59, s	6.96-7.36,m 9.78, s	1946, 1865, 1690, 1628	105-109
P(<i>p</i> -MeC ₆ H ₄) ₃ (s)	5.12, 5.18, d	2.60, s	7.12-7.76,m 9.71, s	1940, 1865, 1689, 1622	132-136

3.3.5 Synthesis of (CpCOMe)Mo(CO)₂(L)COMe (L = PPh₃, P(*p*-FC₆H₄)₃, P(*p*-MeC₆H₄)₃ and P(*p*-OMeC₆H₄)₃)

The starting material (CpCOMe)Mo(CO)₃Me was used to perform migratory-insertion reactions to produce complexes of the type, (CpCOMe)Mo(CO)₂(L)COMe in 60 - 80 % yield. Products were confirmed by the shift of the ~ 5.50 ppm doublet to a ~ 5.00 ppm doublet and the appearance of the ~ 2.60 ppm signal (Me-CO) in the ¹H-NMR spectra. In IR spectroscopy the product was confirmed by the disappearance of the 2025 cm⁻¹ peak and the appearance of the ~ 1620 cm⁻¹ peak (C=O). The data for these solid, brownish-yellow products are summarised in **Table 3.7**.

Table 3.7: Spectroscopic data and melting points of (CpCOMe)Mo(CO)₂(L)COMe

Complex	¹ H-NMR / ppm			ν (CO) / cm ⁻¹	m.p. / °C
	C ₅ H ₄	CH ₃ -CO	Other		
PPh ₃ (s)	5.00, d	2.62, s	7.31-7.46, m	1938, 1857, 1681, 1622	140-153
P(<i>p</i> -MeC ₆ H ₄) ₃ (s)	5.00, d	2.61, s	7.12-7.56, m	1940, 1857, 1681, 1625	157-160
P(<i>p</i> -MeOC ₆ H ₄) ₃ (s)	4.99, d	2.61, s	6.86-7.60, m 3.80	1935, 1853, 1678, 1623	152-154
P(<i>p</i> -FC ₆ H ₄) ₃ (s)	5.01, d	2.59, s	6.91-7.64, m	1938, 1859, 1681, 1627	146-150

3.3.6 Synthesis of CpW(CO)₂(L)COMe (L = PPh₃, P(*p*-FC₆H₄)₃, P(*p*-MeC₆H₄)₃ and P(*p*-OMeC₆H₄)₃)

The starting material CpW(CO)₃Me was used to perform migratory-insertion reactions to produce complexes of the type, CpW(CO)₂(L)COMe in 50-80 % yield. Products were confirmed by the shift of the ~ 5.39 ppm singlet to a ~ 5.00 ppm singlet and the appearance of the ~ 2.60 ppm signal (Me-CO) in the ¹H-NMR spectra. In IR spectroscopy the product was confirmed by the disappearance of the 2016 cm⁻¹ peak and the appearance of the 1620 - 1660 cm⁻¹ peak (C=O). The data for these solid, reddish-yellow products are summarised in **Table 3.8**. The data for L = PPh₃ compared well to that found in the literature (¹H NMR / ppm 5.00, d, C₅H₄; 2.61, s, CH₃-CO, IR / cm⁻¹ ν(CO): 1938, 1853, 1600). See **Appendix** for additional information.

Table 3.8: Spectroscopic data and melting points of $\text{CpW(CO)}_2\text{(L)COMe}$

L	$^1\text{H-NMR}$ / ppm			$\nu(\text{CO})$ / cm^{-1}	m.p. / $^\circ\text{C}$
	C_5H_4	$\text{CH}_3\text{-CO}$	Other		
$\text{P}(p\text{-MeC}_6\text{H}_4)_3$ (s)	5.08, d	2.61, s	7.12-7.24, m	1932, 1852, 1657	218-220
$\text{P}(p\text{-MeOC}_6\text{H}_4)_3$ (s)	5.08, d	2.61, s	6.86-6.96, m 3.80, s	1931, 1851, 1640	185-190
$\text{P}(p\text{-FC}_6\text{H}_4)_3$ (s)	5.01, d	2.59, s	7.05-7.21, m	1938, 1849, 1623	145-147
PPh_3	5.01, d	2.59, s	7.05-7.36, m	1934, 1854, 1588	-

3.3.7 Attempted synthesis of $(\text{CpR})\text{M(CO)}_2\text{(L)Me}$ (For $\text{M} = \text{Mo}$, $\text{R} = \text{H}$, Me , COH , COMe , for $\text{M} = \text{W}$, $\text{R} = \text{H}$; $\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ and $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$)

The synthesis of the pure decarbonylated complexes of the type, $(\text{CpR})\text{M(CO)}_2\text{(L)Me}$ proved to be difficult owing to decomposition of the material over the long periods and high temperatures that were required to make them. Decarbonylated species were obtained in spectroscopic quantities. Confirmation of the presence of decarbonylated products were shown by IR spectra, in which the $\sim 1600\text{ cm}^{-1}$ peak disappeared, and in the NMR spectra, which the $\sim 2.60\text{ ppm}$ peak disappears and the signal for the hydrogens on the Cp ring shift slightly up field. An example of an NMR spectrum of the decarbonylated product, $\text{CpMo(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{Me}$ is shown in the **Appendix A2**.

Kinetic data for the decarbonylation reaction generated by NMR spectroscopy was also attempted, but the solvent for NMR analysis caused inconsistent data. This study

was abandoned, and kinetics by DRIFTS proved to be a more suitable alternative (see **Chapter 6**).

3.4 Conclusion

Organometallic complexes of the type, $(\text{CpR})\text{M}(\text{CO})_3\text{Me}$ ($\text{M} = \text{Mo}$, $\text{R} = \text{H}$, Me , COH , COMe ; $\text{M} = \text{W}$, $\text{R} = \text{H}$) were synthesized and used as the starting materials for a kinetic study of migratory-insertion reaction. All complexes were solids at room temperature. The yields were approximately 40 – 60 %. The kinetic study lead to the synthesis of complexes of the type, $(\text{CpR})\text{M}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{M} = \text{Mo}$, $\text{R} = \text{H}$, Me , COH , COMe ; $\text{M} = \text{W}$, $\text{R} = \text{H}$; $\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ and $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$, PPh_3). Mo complexes were obtained in good yield of > 80 %, while W complexes had > 60 % yield (from NMR spectra). These complexes were orange-yellow solids. They were used in the kinetic study of the decarbonylation reaction, which produced compounds of the type, $(\text{CpR})\text{M}(\text{CO})_2(\text{L})\text{Me}$, some in yields of < 50 % (from NMR spectra). The poor yields were due to the decomposition of the material over long periods and high temperatures. A 78 % yield of $(\text{CpR})\text{M}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{Me}$ obtained in spectroscopic quantity revealed that these decarbonylated complexes were red in colour.

3.5 References

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CHAPTER 4: THE USE OF NMR SPECTROSCOPY TO STUDY THE SOLVENT-FREE INSERTION REACTION OF Mo COMPLEXES

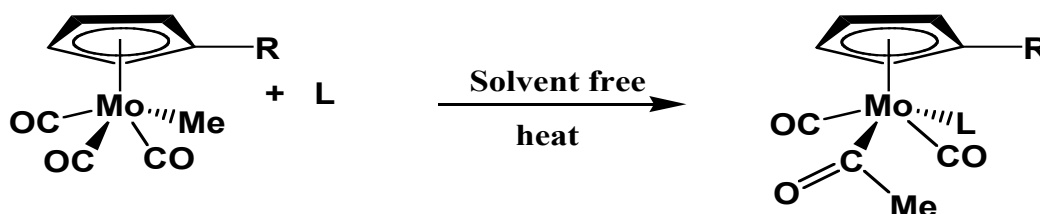
4.1 Introduction

Nuclear magnetic resonance (NMR) is a spectroscopic technique that provides information about the atom inter-connections in a molecule. NMR spectroscopy works by detecting the energy absorption accompanying the transition between spin states that occur when a molecule is placed in a strong magnetic field and irradiated with radiofrequency waves.¹ NMR spectroscopy works on the principle that atoms i.e. nuclei, like ^1H , ^{13}C and ^{31}P , act like tiny magnets which can interact with an external magnetic field, and thus a picture of the specific compound can be mapped out.¹

4.2 Experimental

4.2.1 NMR spectroscopic study of the migratory-insertion reaction of $(\text{CpMe})\text{Mo}(\text{CO})_3\text{Me}$ and PPh_3

(CpMe)Mo(CO)₃Me (0.11 mM, 0.030 g) and PPh₃ (0.11 mM, 0.029 g) were placed in a 50 ml round bottom flask, and this mixture was dissolved in drops of dried dichloromethane (5 ml). The solvent was removed in vacuo to give a solid. The flask was flushed with nitrogen and placed in a 42 - 43 °C oil bath. The reaction is depicted in **Scheme 4.1**. Samples were removed after different time intervals from the reaction flask for NMR spectroscopic analysis.



Scheme 4.1: The solvent-free insertion reaction between (CpR)Mo(CO)₃Me (R = H, Me, COH) and L (L = PPh₃, P(*p*-FC₆H₄)₃) at the required temperature.

4.2.2 NMR spectroscopic study of the migratory-insertion reaction of (CpCOH)Mo(CO)₃Me and P(*p*-FC₆H₄)₃

(CpCOH)Mo(CO)₃Me (0.26 mM, 0.078 g) and *para*-fluoro-triphenylphosphine (0.29 mM, 0.095 g) were placed in a 50 ml round bottom flask and mixed together using a spatula. The flask was flushed with nitrogen and placed in a 74 - 75 °C oil bath. The reaction is depicted in **Scheme 4.1**. Samples were removed from the reaction flask for NMR spectroscopy analysis at different time intervals

4.2.3 NMR spectroscopic study of the migratory-insertion reaction of $\text{CpMo(CO)}_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$

$\text{CpMo(CO)}_3\text{Me}$ (0.21 mM, 0.054 g) and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (0.21 mM, 0.066 g) were placed in a 50 ml round bottom flask and mixed together using a spatula. The flask was flushed with nitrogen and placed in a 72 - 73 °C oil bath. The reaction is depicted in **Scheme 4.1**. Samples were removed from the reaction flask for NMR spectroscopy analysis at different time intervals.

4.3 Results

4.3.1 The investigation of the migratory-insertion reaction of $(\text{CpMe})\text{Mo(CO)}_3\text{Me}$ and PPh_3 using NMR spectroscopy

The conversion of $(\text{CpMe})\text{Mo(CO)}_3\text{Me}$ to the insertion product, $(\text{CpMe})\text{Mo(CO)}_2(\text{PPh}_3)\text{COMe}$ can be easily monitored using NMR spectroscopy. The NMR spectrum for $\text{Cp(Me)Mo(CO)}_3\text{Me}$ and the inserted $(\text{CpMe})\text{Mo(CO)}_2(\text{PPh}_3)\text{COMe}$ showed that the required complexes were formed as indicated in **Section 3**. The change in position of the Cp hydrogens from ~5.10 to ~4.60 ppm, was used to identify the migratory-insertion reaction (see **Appendix A1**). The reaction progress was followed using NMR spectroscopy by following the

disappearance of the Cp hydrogens at ± 5.10 ppm (15, 30, 45, 60, 120, 180, 240 minutes).

Initially (0 min), the $(\text{CpMe})\text{Mo}(\text{CO})_3\text{Me}$ is assumed to comprise 100 % of the reactant material. At the end of the reaction (240 min), the NMR spectrum showed absence of $(\text{CpMe})\text{Mo}(\text{CO})_3\text{Me}$ (all converted to insertion product). **Figure 4.1** shows the reaction conversion of $(\text{CpMe})\text{Mo}(\text{CO})_3\text{Me}$ to $(\text{CpMe})\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{COMe}$.

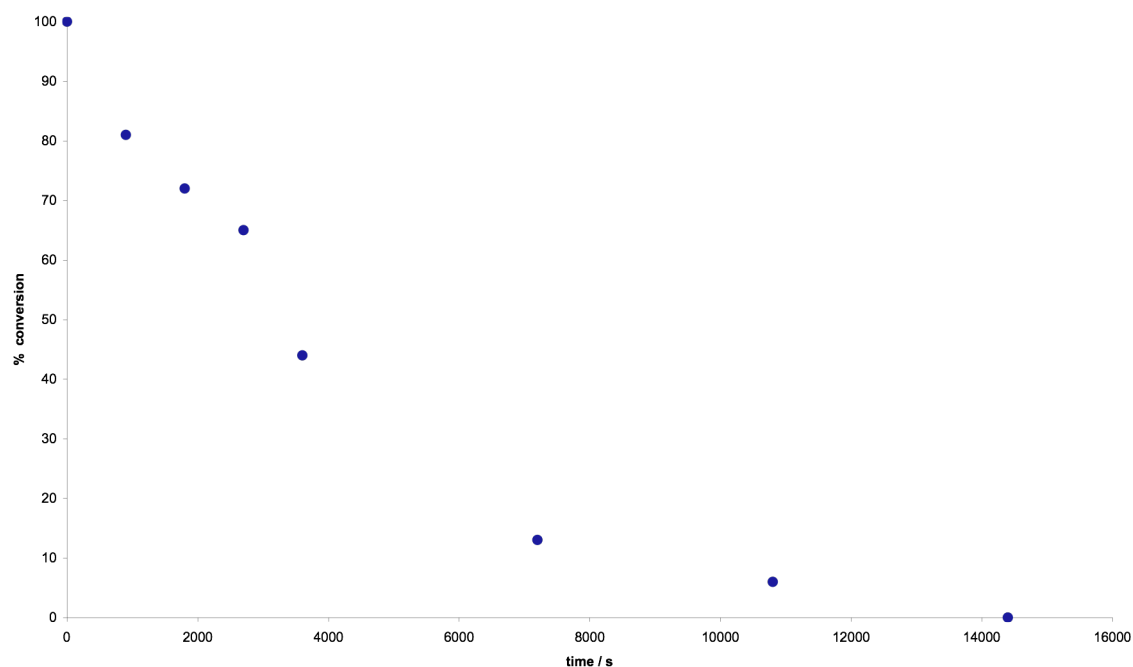


Figure 4.1: The graph of the % reactant conversion over time for the solvent-free reaction between $(\text{CpMe})\text{Mo}(\text{CO})_3\text{Me}$ and PPh_3

Thereafter, the reaction was assumed to be first-order and a rate plot of $\ln(A - a)$ against time was constructed (see **Figure 4.2**). The rate plot was consistent with the assumption of a first order reaction.

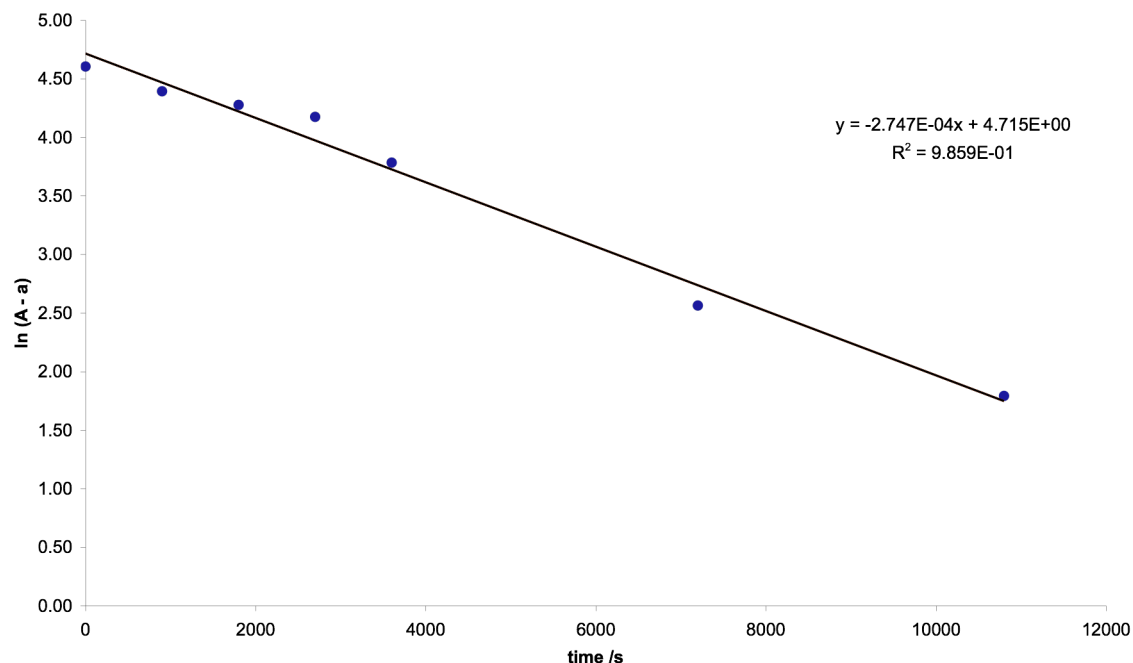


Figure 4.2: The rate plot for the first order solvent-free reaction between $(\text{CpMe})\text{Mo}(\text{CO})_3\text{Me}$ and PPh_3

4.3.2 NMR spectroscopic study of the migratory-insertion reaction of $(\text{CpCOH})\text{Mo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$

The kinetics of the reactions of $(\text{CpCOH})\text{Mo}(\text{CO})_3\text{Me}$ undergoing migratory-insertion with $\text{P}(p\text{-FC}_6\text{H}_4)_3$, were studied using a similar method of analysis as above. Progress of the reaction between $(\text{CpCOH})\text{Mo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ was

followed using the disappearance of the 5.6 ppm signal on the NMR spectrum.

Figure 4.3 shows the % reactant conversion over time for the reaction between $(\text{CpCOH})\text{Mo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ at 75 °C. The data obtained were assumed to be first order, and the $\text{Ln}(A-a)$ against time was plotted (**Figure 4.4**).

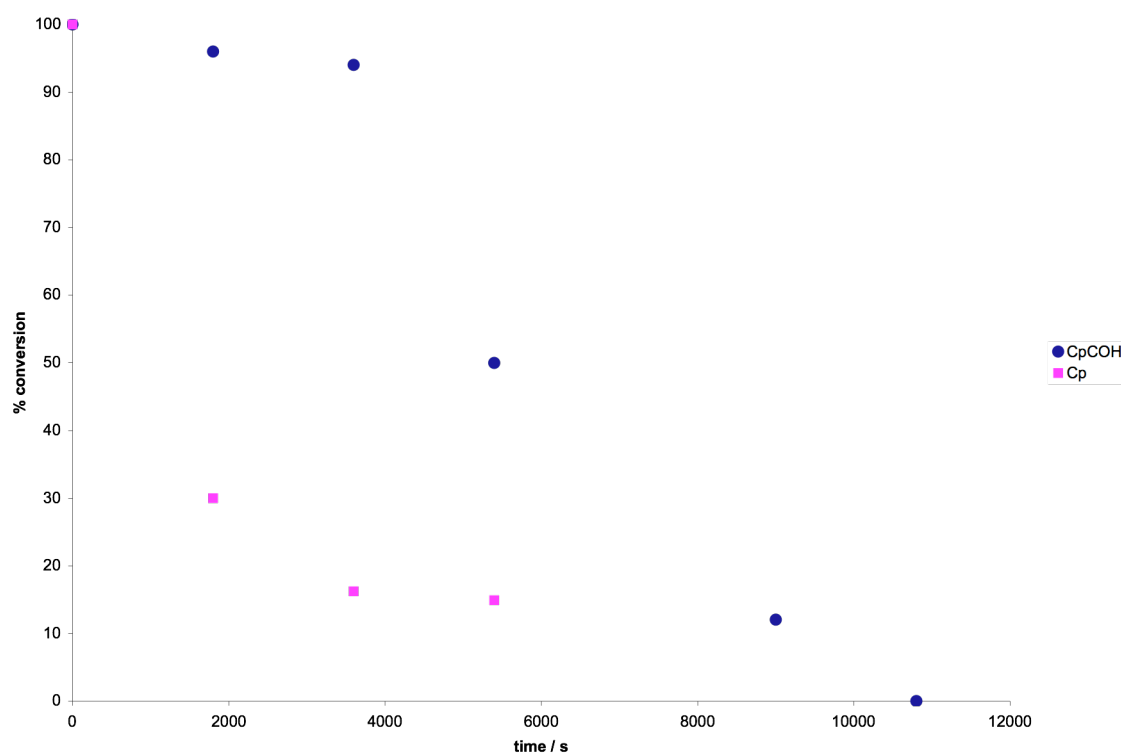


Figure 4.3: The graph of the % reactant conversion over time for the solvent-free reaction between $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R} = \text{H}, \text{COH}$) and $\text{P}(p\text{-FC}_6\text{H}_4)_3$

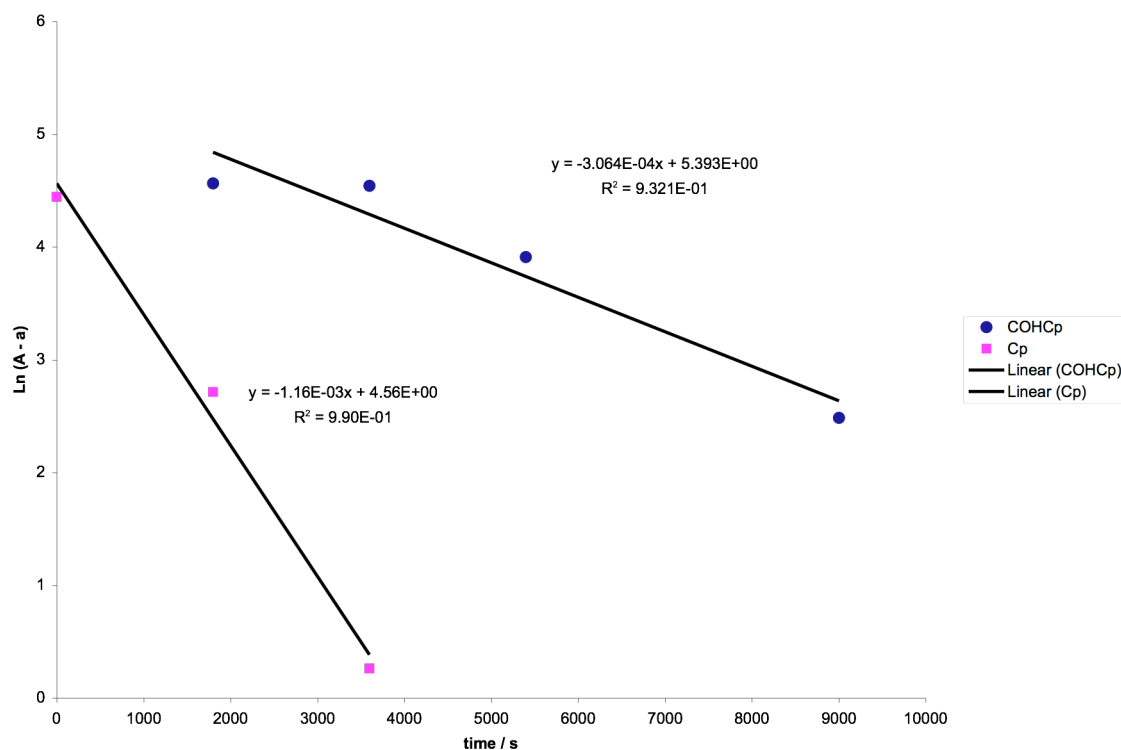


Figure 4.4: The rate plots for the solvent-free reaction between $(\text{Cp})\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R} = \text{H}, \text{COH}$) and $\text{P}(p\text{-FC}_6\text{H}_4)_3$

The rate plot approximately followed a first order reaction, although a low correlation factor ($R = 0.93$) was obtained.

4.3.2 NMR spectroscopic study of the migratory-insertion reaction of $\text{CpMo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$

The kinetics of the reactions of $\text{CpMo}(\text{CO})_3\text{Me}$ undergoing migratory-insertion with $\text{P}(p\text{-FC}_6\text{H}_4)_3$, were studied using a similar method of analysis as stated above. The reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ was followed using the

disappearance of the ± 5.10 ppm signal of the NMR spectra. The % reactant conversion against time graph is depicted in **Figure 4.3**. The data was also assumed to be first-order and the $\ln(A-a)$ against time plot was constructed (see **Figure 4.4**). The plot revealed that the reaction was indeed first order and a good correlation factor ($R = 0.99$) was obtained.

A summary of the rate constants obtained for three different migratory-insertion reactions studied (including the work done by Adeyemi and Coville²) at the specific temperatures is displayed in **Table 4.1**.

Table 4.1: The rate constants for the migratory-insertion reactions of the specific Mo complex with the phosphine ligand at specific temperatures

Complex	Ligand	Temperature / °C	k / s ⁻¹	R
(CpMe)Mo(CO) ₃ Me	PPh ₃	42 - 43	2.75×10^{-4}	0.99
(CpCOH)Mo(CO) ₃ Me	P(<i>p</i> -FC ₆ H ₄) ₃	74 - 75	3.06×10^{-4}	0.93
CpMo(CO) ₃ Me	P(<i>p</i> -FC ₆ H ₄) ₃	72 - 73	11.6×10^{-4}	0.99
CpMo(CO) ₃ Me*	PPh ₃	40	0.18×10^{-4}	

Note: * Obtained from Adeyemi and Coville²

4.4 Discussion

In all three reactions a temperature was chosen to ensure the reactions were in the melt. The reaction of (CpMe)Mo(CO)₃Me with PPh₃ in a 1:1 mole ratio at 40 °C

revealed a rate constant of $2.75 \times 10^{-4} \text{ s}^{-1}$. This was compared to a similar experiment done by Adeyemi and Coville², but using $\text{CpMo(CO)}_3\text{Me}$. They found their rate constant to be $0.181 \times 10^{-4} \text{ s}^{-1}$ (1:1 ratio; 40 °C).² The increased rate for the $(\text{CpMe})\text{Mo(CO)}_3\text{Me}$ reaction with PPh_3 can be attributed to the methyl group adding more electron density to the Cp ring, thus strengthening the Cp-Mo bond. This then weakens the Mo-Me bond, allowing a faster CO insertion reaction.

The steric³ and electronic parameters⁴ that define the effect of the R group on the rate of the reaction are displayed in **Table 4.2**. Additionally, the phosphine ligand also plays a role in the rate of the reaction. Both, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ and PPh_3 , have the same cone angle of 145° ⁵, thus their steric effect can be ignored. However, they do differ electronically, since $\text{P}(p\text{-FC}_6\text{H}_4)_3$ and PPh_3 have electronic parameters of 2071.3 and 2068.9 cm^{-1} , respectively.⁵ $\text{P}(p\text{-FC}_6\text{H}_4)_3$ is defined as electron-withdrawing, while PPh_3 is used as the reference ligand in this case.⁶

The reaction of $\text{CpMo(CO)}_3\text{Me}$ with $\text{P}(p\text{-FC}_6\text{H}_4)_3$ in a 1:1 mole ratio at 75 °C revealed a rate constant of $11.6 \times 10^{-4} \text{ s}^{-1}$. This was fast when compared to the reaction of $(\text{CpCOH})\text{Mo(CO)}_3\text{Me}$ with $\text{P}(p\text{-FC}_6\text{H}_4)_3$ in a 1:1 mole ratio at 75 °C. The latter experiment had an observed rate constant of $3.06 \times 10^{-4} \text{ s}^{-1}$. The substituent on the Cp ring (R group) seems to play a role in the rate of the reaction because at similar reaction conditions the rate decreases when R changes from H to COH. The steric and electronic effect of the R group is significant in this reaction.

The aldehyde group (COH) attached to the Cp ring in (CpCOH)Mo(CO)₃Me withdraws electron density from the ring. The H atom, as mentioned above, has no electron withdrawing or donation ability in relation to -COH. The steric effects (quantified by the Tolman cone angle, $\theta^{3,5}$, and solid angles, Ω_{av}^3) and electronic factors,⁴ F (combination of inductive and resonance effects), σ_I (inductive effects) and σ_R (resonance effects), are listed in **Table 4.2**. Note that the two methods of measuring the Tolman cone angles, θ_1 and θ_2 , will be discussed in **Chapter 5**.

Table 4.2: The cone angles, solid angles for C₅H₄R³ and electronic factors for CH₂R⁴

R	θ_1 (°)	θ_2 (°)	Ω_{av} (°)	F	σ_I	σ_R
H	128	55	131	0.03	0	-
COH	140 ^a	40 ^a	140 ^a	0.33	-	0.23

^a calculated using STERIC (see **Chapter 5**)

The large difference exists between the cone angles, especially the Tolman cone angles. There is also a great difference between their electronic factors. It can be seen from the above table that the two complexes differ significantly both sterically and electronically. This thus impacts on the rate of the migratory-insertion reaction.

4.5 Conclusions

The important issues that arose from this study indicated that the magnitude of the study of the migratory-insertion reaction of $(\text{Cp})\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R} = \text{H}$ or organic group) with L (phosphine) required :

- 1) More data points before 50 % conversion in order to plot adequate rate plots.
- 2) An *in-situ* technique, such that the reactants are not exposed to air or solvent that aids in decomposition.
- 3) In order to provide conclusive data on ligand and R group effects, *a number of reactions* under various conditions, such as at different temperature and mole ratios and with different Mo complexes and different phosphines, must be done.

4.6 References

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CHAPTER 5: THE USE OF DRIFTS TO STUDY THE SOLVENT-FREE MIGRATORY-INSERTION REACTION OF Mo COMPLEXES

5.1 Introduction

The study of the kinetics of the solvent-free migratory-insertion reaction between solid $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R} = \text{H}, \text{Me}, \text{CHO}, \text{COMe}$) and solid phosphines using NMR spectroscopy was shown to be successful (see **Chapter 4**). Some of the reactions appeared to occur in the solid state. In particular the study entailed the reaction of solid phosphines (e.g. $\text{P}(p\text{-FC}_6\text{H}_4)_3$) with $(\text{CpR})\text{Mo}(\text{CO})_3\text{CH}_3$ ($\text{R} = \text{H}, \text{Me}, \text{CHO}, \text{COMe}$) at temperatures *below the melting points of the reactants and products*.¹ However, it is difficult to imagine a mechanism that would allow for an insertion reaction between two solids. Indeed, it was established that the migratory-insertion occurred via a melt phase that took place below the melting points of both reactants, i.e. the reaction occurred in a eutectic melt.¹ To further explore this phenomenon the reaction has been studied using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and Optical Microscopy.

5.1.1 DRIFTS technique to study the migratory-insertion reaction

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is a technique that can be used to study solid samples by collecting and analyzing

scattered infrared (IR) energy.² Diffuse reflectance is also known as Kubelka-Munck reflection after the two scientists who developed the theory of radiation transport in scattering media.³ When an IR beam enters a sample, it can either be reflected off the surface of a particle or be transmitted through a particle. The IR energy reflecting off the surface is typically lost. The IR beam that passes through a particle can either reflect off the next particle or be transmitted through the next particle. This transmission-reflectance event can occur many times in a solid sample, and this increases the pathlength of the IR beam. Finally, the scattered IR energy is collected by a spherical mirror, which is focused onto the detector. The detected IR light is partially absorbed by particles of the sample, generating the sample information.

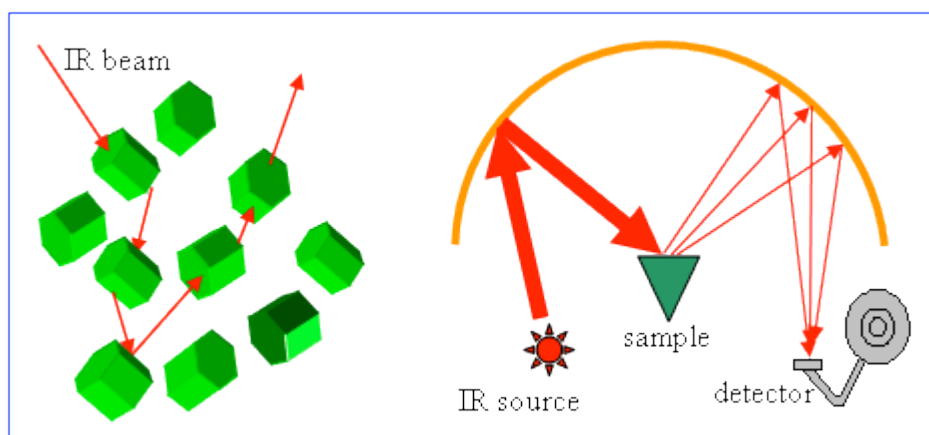


Figure 5.1: The representation of the pathway of the IR beam from the source through the sample and to the detector²

The optical properties of a sample are then defined by its absorption and scattering coefficients in the Kubelka-Munck equation shown below³:

$$f(R_{\infty}) = (1 - R_{\infty})^2 / 2 R_{\infty} = K/S \dots\dots\dots 5.1$$

where R_{∞} is the degree of reflection on the sample surface at infinite thickness, K is the absorption modulus and S the scattering modulus.

The DRIFTS spectra are dependent on various sample preparation parameters as well as on geometric optical effects of the spectral measurement such that spectra of the same sample differ depending on the accessories used.⁴ Parameters that are important in spectral acquisition include sample preparation method,⁵ particle size,^{6,7} packing density^{8,9} and reaction mixture homogeneity.¹⁰ It is critical that the above parameters are kept constant in investigations to obtain experimentally reproducible results.

DRIFTS can be used for studies of fine particles and powders, as well as rough surfaces.² Thus, the application of DRIFTS is prevalent in the chemical industry. It has been used for the analysis of catalysts¹¹, mechanistic studies¹², and characterization of samples.^{13,14} The technique has also found use in forensic science.^{15,16} Quantitative analysis using DRIFTS has also been used for some time.^{17,18}

Herein we report the first attempt to study a solvent-free organometallic migratory-insertion reaction using DRIFTS. It is shown that a solvent-free reaction can be followed using this time and temperature controlled, *in situ*, infrared technique. Another, vital part of the study was to study the influence of the incoming ligand, i.e. a phosphine, on the reaction.

5.1.2 The study of steric and electronic effects

Tertiary phosphines have been known to bind to metals since the last century and since then their place in organometallic chemistry has been affirmed. Much research has gone into investigating the possible influence of a phosphine ligand on the physicochemical properties of compounds.¹⁹ This influence has been narrowed down to two important factors: a steric hindrance and an electronic affect.¹⁹ Both of these effects are brought about by changes in the nature of the substituents on the phosphine ligand.¹⁹ Quantitative physical measures of the steric effects of phosphines can be achieved using ligand cone angles (θ) of space filling CPK molecular models²⁰⁻²² or solid angles.^{20,22} There are other methods to quantify steric size (see **Chapter 2**) and these include molecular mechanics, chemical methods (NMR spectroscopy or a modified Taft steric parameter) and molecular volume approaches.²² Historically, organic chemists use chemical methods, while inorganic chemists use the physical approach of cone angles and solid angles.²²

Electronic effects have also been quantified. This can be achieved by IR spectroscopy, e.g. by measuring the A_1 carbonyl stretching frequencies (ν) in $\text{Ni(CO)}_3\text{L}$ complexes (the Tolman electronic parameter).²¹ The electronic effect can also be measured from pK_a values, (for HPR_3^+) as derived from half wave neutralization potentials in nitromethane (ΔHNP), by enthalpies of protonation, by measuring ^{13}C NMR chemical shifts of $\text{Ni(CO)}_3\text{L}$ complexes or by using Quantitative Analysis of Ligand Effects (QALE) approaches¹⁹ (see **Chapter 2**).

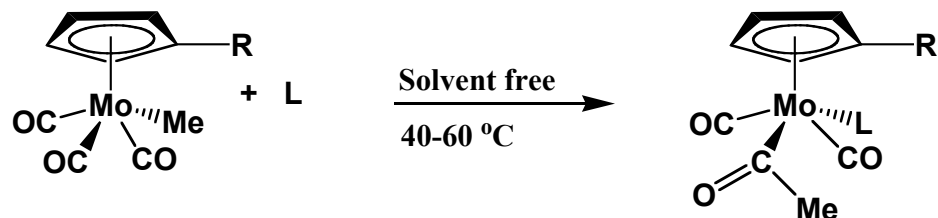
5.1.3 Optical photomicroscopy techniques to study reactions

Optical microscopy has been used to study reaction mechanisms in the past.²³ The following reaction mechanisms were elucidated using this technique: thermal dehydration of barium chlorate monohydrate $[(\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O})]$ and the thermal decomposition of KMnO_4 ²⁴, RbMnO_4 ²⁵ and CsMnO_4 ²⁶, $\text{Ni}(\text{MnO}_4)_2$ ²⁷ and $\text{Cu}(\text{MnO}_4)_2$.²⁸ The latter was also found to take place in the melt. The technique had also been used to study the kinetics of dehydration of potassium tartrate hydrates.²⁹ Solid-state organometallic isomerisation reactions of $(\text{CpR})\text{M}(\text{XYZW})$ ($\text{R} = \text{H}$, alkyl; $\text{M} = \text{Re}$, W , Mo ; $\text{X}, \text{Y}, \text{Z}, \text{W} = \text{CO}$, Br , I , RCN , PR_3 , $\text{P}(\text{OR})_3$) were studied using the same technique.³⁰ Manzini and Coville recently found that an organometallic substitution reaction which was thought to be a solid-state reaction, was actually a melt reaction once the reaction was seen under an optical microscope.³¹ Thus, optical microscopy allows a microscopic view of the reaction progress provided that the required reaction conditions can be accounted for.

5.1.4 Aim of this study

The aim of this study was to perform the solvent-free migratory-insertion reaction between $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R} = \text{H}$, Me , CHO , COMe), and L ($\text{L} = \text{PPh}_3$, $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$) (**Scheme 5.1**) using DRIFTS. The rate of the reaction was monitored by varying reaction conditions such as reactant,

mole ratios and the temperature of the reaction. The influence of diluents (e.g. KBr) on the reaction progress, was also investigated.



Scheme 5.1: The general migratory-insertion reaction between $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R} = \text{H}, \text{Me}, \text{CHO}, \text{COMe}$), and L ($\text{L} = \text{PPh}_3, \text{P}(p\text{-OMeC}_6\text{H}_4)_3, \text{P}(p\text{-FC}_6\text{H}_4)_3, \text{P}(p\text{-MeC}_6\text{H}_4)_3$)

5.2 Experimental

5.2.1 Migratory-insertion reaction studied by DRIFTS

$(\text{CpR})\text{Mo}(\text{CO})_3\text{CH}_3$ ($\text{R} = \text{H}, \text{Me}, \text{CHO}, \text{COMe}$), hereafter referred to as the Mo complex, was synthesized as discussed in the synthesis of piano-stool complexes in **Chapter 3**. The solid phosphines, $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, PPh_3 and $\text{P}(p\text{-FC}_6\text{H}_4)_3$, were obtained from Sigma-Aldrich and Strem chemicals.

5.2.1.1 Sample preparation for DRIFTS analysis

The Mo complex (0.01 g - 0.02 g) was mixed in KBr (1.0 g) to produce a 1 - 2 % starting material in KBr that acted as a reference material. Similarly, the solid

phosphine (0.01 g - 0.4 g) was mixed with 1 g - 2 g KBr to produce 1 % - 20 % ligand in KBr.

Components were ground together in air using a mortar and pestle for ≈ 10 minutes to achieve a particle size in the range of 60 – 80 μm as determined by optical microscopy.

5.2.1.2 Steps in the analysis process

1. Equal amounts (≈ 5 mg) of finely ground KBr and ligand / KBr sample were mixed together in a vial using a micro spatula.
2. A background spectrum was recorded.
3. Equal amounts of a ligand / KBr sample and starting material/KBr sample were quickly mixed together in another vial using a micro spatula.
4. The mixture was placed in the DRIFTS cell.
5. The sample in the cell was heated to the required temperature.
6. IR spectra were recorded as a function of time at pre-set time intervals.

Preliminary studies using DRIFTS, using information obtained from previous work by Manzini on Mn complexes³², showed that:

- 1) KBr acted as an effective diluent for the reactants.
- 2) Only a small percentage (e.g. 1 - 2 %) of reactant in KBr was necessary in the reaction mixture to ensure that requisite spectra could be obtained that allowed for direct measurement of the course of the reaction.

5.2.2 Investigation of the effect of temperature on the migratory-insertion reaction between $\text{CpMo(CO)}_3\text{Me}$ and phosphine ligand, $\text{P}(p\text{-FC}_6\text{H}_4)_3$

A mixture of 1 - 2% powdered $\text{CpMo(CO)}_3\text{Me/KBr}$ and 1 – 20 % powdered $\text{P}(p\text{-FC}_6\text{H}_4)_3/\text{KBr}$ were mixed together in a 1:1 or 1:10 molar ratio. The mixture was then placed in the DRIFTS cell and the IR spectra recorded at temperatures of 40, 50 and 60 °C for pre-set time intervals.

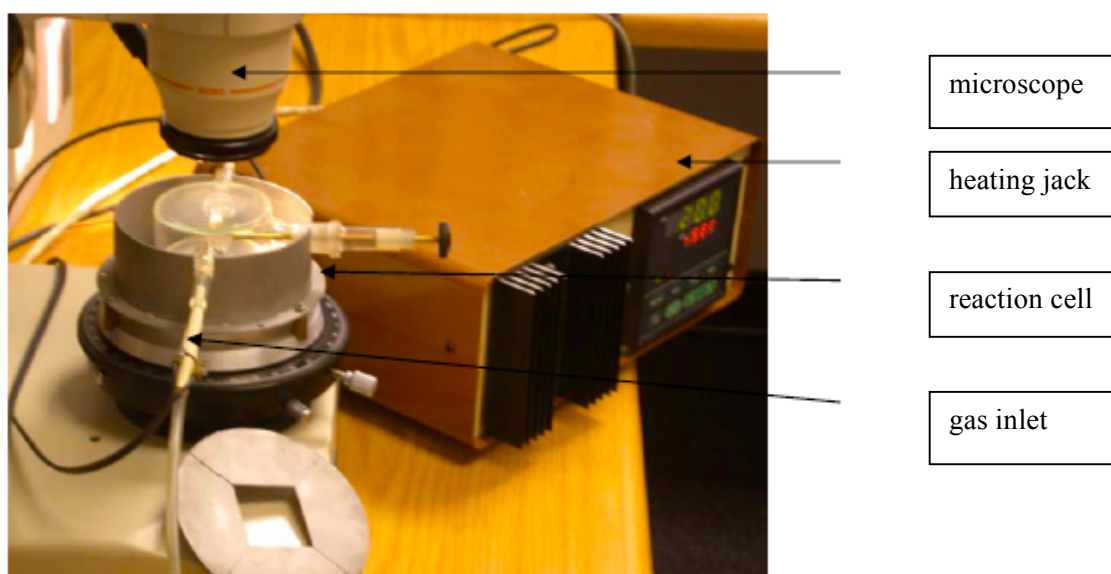
5.2.3 Investigation of the effect of molar ratio on the migratory-insertion reaction between $\text{CpMo(CO)}_3\text{Me}$ and phosphine ligand, $\text{P}(p\text{-FC}_6\text{H}_4)_3$

A mixture of 1 – 2 % powdered $\text{CpMo(CO)}_3\text{Me/KBr}$ and 1 – 20 % powdered $\text{P}(p\text{-FC}_6\text{H}_4)_3/\text{KBr}$ were mixed together in specified molar ratios (1:1, 1:5 and 1:10). The mixture was then placed in the DRIFTS cell and the IR spectra recorded at a temperature of 50 °C at pre-set time intervals.

5.2.4 Investigation of the migratory-insertion reaction between $(\text{CpCOMe})\text{Mo(CO)}_3\text{Me}$ and L ($\text{L} = \text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ and PPh_3 using optical photomicroscopy

The optical microscopy apparatus consisted of the following: reaction cell, heating jacket, and a microscope (**Figure 5.2a**). The A heating stage which was previously designed by Bogadi *et al.* to enable the observation of a reaction at a microscopic level was used.³³ The reaction cell contained a chamber (**Figure**

5.2b) in which a thermocouple was attached to a glass slide (**Figure 5.2c**). Desired samples, crystals or powders, were placed on the glass slide. The reaction cell allowed for the inlet of a gas. A camera was attached to the microscope, which allowed photographs of the reaction to be taken.



a



Figure 5.2: The reaction chamber under the optical microscope with heating apparatus (**a**), reaction cell (**b**) and heating slide (**c**) used for photomicroscopic analysis

5.2.5 Investigation of the effect of different ligands on the migratory-insertion reaction between $\text{CpMo(CO)}_3\text{Me}$ and phosphine ligands, L (L = $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, PPh_3)

Both of 1 - 2% powdered $\text{CpMo(CO)}_3\text{Me/KBr}$ and 1 - 20% powdered L/KBr , (L = $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, PPh_3), were mixed together in a 1:10 molar ratio. Then the mixture was placed in the DRIFTS cell and the IR spectra recorded at 40 °C and pre-set time intervals.

5.2.6 Investigation of the effect of a substituent, R, on the Cp ring, on the migratory-insertion reaction between $(\text{CpR})\text{Mo(CO)}_3\text{Me}$, (R = H, Me, CHO, COMe) and phosphine ligands, L (L = $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, PPh_3)

Samples of 1 - 2% powdered $(\text{CpR})\text{Mo(CO)}_3\text{Me/KBr}$ (R = H, Me, CHO, COMe) and 1 - 20% powdered L/KBr , (L = $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, PPh_3), were mixed together in a 1:10 molar ratio. Then the mixture was placed in the DRIFTS cell and the IR spectra recorded at 40 °C for pre-set time intervals.

5.2.7 Investigation of the effect of the diluent in the migratory-insertion reaction between $\text{CpMo(CO)}_3\text{Me}$ and phosphine ligand, $\text{P}(p\text{-FC}_6\text{H}_4)_3$

This study was done using the same procedures as before, only the diluent in which the reactants were mixed were changed. The diluents used were: KBr, KI, KCl, K_2SO_4 , NaCl, Na_2SO_4 , CaSO_4 , CaO, MgO, Al_2O_3 , silica and sucrose. The migratory-insertion reaction was performed using a 1:1 mixture of $\text{CpMo(CO)}_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ at the constant temperature of 50 °C with the above diluents.

5.3 Results and Discussion

5.3.1 Investigation of the migratory-insertion reactions using DRIFTS

A study of the kinetics of the insertion reaction of $(\text{CpR})\text{Mo(CO)}_3\text{Me}$ ($\text{R} = \text{H}, \text{Me}, \text{CHO}, \text{COMe}$) and L ($\text{L} = \text{P}(p\text{-OMeC}_6\text{H}_4)_3, \text{P}(p\text{-FC}_6\text{H}_4)_3, \text{P}(p\text{-MeC}_6\text{H}_4)_3, \text{PPh}_3$) was done using DRIFTS. Temperatures of 40 °C and above were chosen for the reaction since (i) little if any reaction occurred at temperature below 40 °C, (ii) this temperature was lower than the melting points of the piano-stool complexes and the ligands. Reactions were performed using a range of Mo complex : ligand molar ratios ranging from 1:1 to 1:10.

The reaction was monitored in the $\nu(\text{CO})$ and $\nu(\text{COR})$ region of the IR spectrum since the starting Mo complex had absorptions at 2020 and 1945 cm^{-1} , while the product had absorptions at ~1945, ~1840 and ~1600 cm^{-1} .

Initially spectra were recorded on pure reactant to ascertain the correct absorptions peaks for the Mo complex. For example, the Mo complex absorption peaks occur at 2020 cm^{-1} and 1945 cm^{-1} . The conversion to the insertion product was observed by the disappearance of the 2020 cm^{-1} absorption peak (one CO band) and the appearance of the $\sim 1845\text{ cm}^{-1}$ and $\sim 1600\text{ cm}^{-1}$ (R-C=O) absorption peaks. The band at $\sim 1945\text{ cm}^{-1}$ remained a constant feature as it was associated with both reactant and product.

A typical example of the spectra of the starting material and the insertion product is shown for $L = \text{P}(p\text{-FC}_6\text{H}_4)_3$ in **Figure 5.3**. As can be seen the IR band at 1956 cm^{-1} could not be used for the analysis.

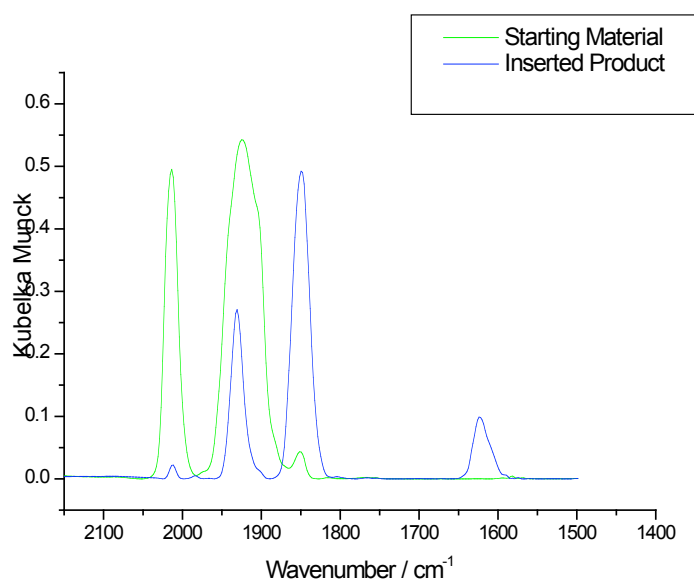


Figure 5.3: Spectra showing the starting material, $(\text{CpMe})\text{Mo}(\text{CO})_3\text{Me}$ and the insertion product, $(\text{CpMe})\text{Mo}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$

The reaction changes were thus easily monitored using DRIFTS and a typical set of spectra obtained during the course of a reaction for the migratory-insertion of $(\text{CpMe})\text{Mo}(\text{CO})_3\text{M}$ with $\text{P}(p\text{-FC}_6\text{H}_4)_3$ to give $(\text{CpMe})\text{Mo}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ is shown in **Figure 5.4**.

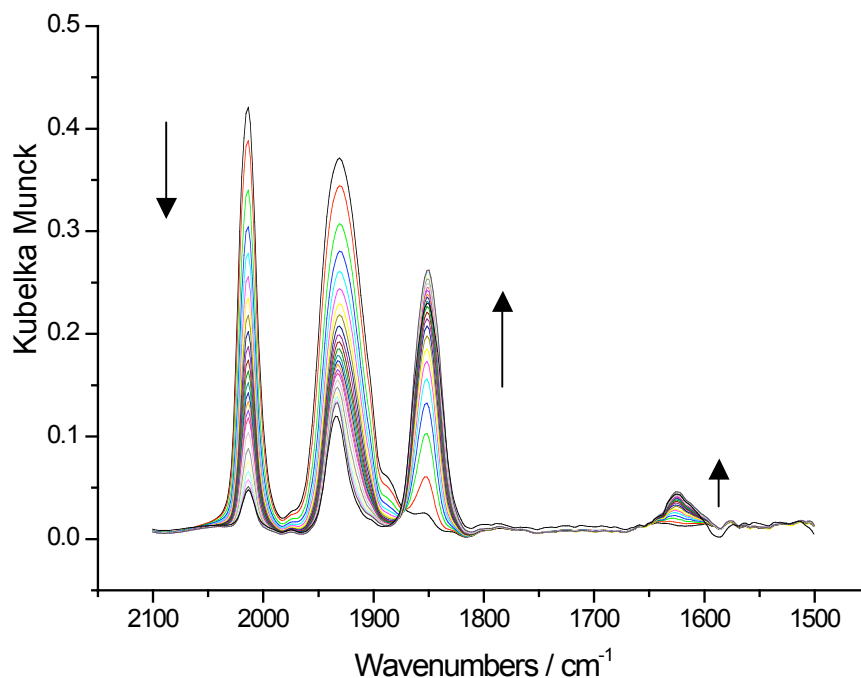


Figure 5.4: DRIFTS spectra showing the typical conversion of $(\text{CpMe})\text{Mo}(\text{CO})_3\text{Me}$ to $(\text{CpMe})\text{Mo}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$.

This data was used to plot a conversion graph shown in **Figure 5.5**. This was done by following the gradual disappearance of the 2020 cm^{-1} absorption peak, as it changed from 100 % to close to 20 % ($\approx 5000\text{ min}$) as the migratory-insertion

progressed and the reactant converted to product. Thus, the % conversion is actually a measure of the % reactant (which is 100 % at time 0).

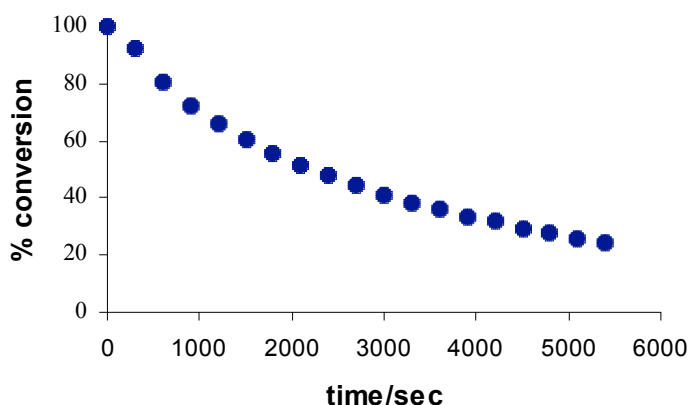


Figure 5.5: $(\text{CpMe})\text{Mo}(\text{CO})_3\text{Me}$ conversion to $(\text{CpMe})\text{Mo}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$.

The data was then re-plotted making the assumption that the rate of the reaction was first order. The above data was used to construct the rate plot ($\ln (A - a)$) against time, where 'A' represents the % reaction conversion at a specific time, and 'a' is the % unconverted reactant at the end of the reaction shown in **Figure 5.6**. As can be seen the rate data are consistent with first order kinetics. Further attempts to plot the data according to other rate law equations (e.g. second order) did not give a good fit to the data.

Similar data and plots were obtained for the other reactions monitored in this study and the actual data will be discussed in the sections below.

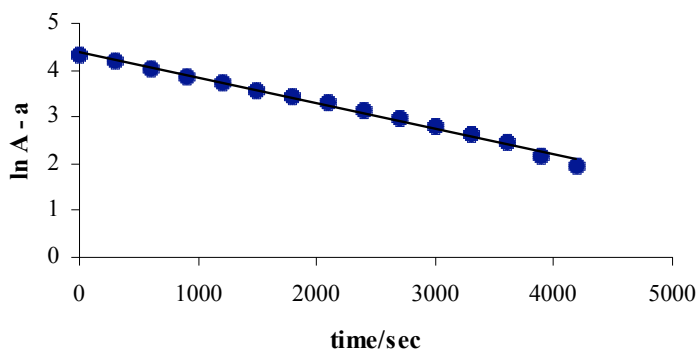


Figure 5.6: First order kinetic plot for the conversion of $(\text{CpMe})\text{Mo}(\text{CO})_3\text{Me}$ to $(\text{CpMe})\text{Mo}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$.

5.3.1.2 Comparison of the NMR and DRIFTS techniques

The insertion reaction between $(\text{CpMe})\text{Mo}(\text{CO})_3\text{Me}$ and PPh_3 (1:1, 40 °C) was used to evaluate the data from the DRIFTS technique with the equivalent NMR data described in **Chapter 5**. The identical reaction conditions were used but the DRIFTS data was collected in the presence of KBr. The kinetics were studied as discussed before. The rate of the reaction from the DRIFTS study was found to be $2.40 \times 10^{-4} \text{ s}^{-1}$, which compared well to the rate found by the NMR spectroscopic technique ($2.75 \times 10^{-4} \text{ s}^{-1}$, **Chapter 4**).

Some comments can be made about the use of the two techniques.

- (i) DRIFTS proved to be a faster and more efficient method to study the migratory-insertion reaction than did NMR spectroscopy (**Chapter 4**). Simple mixing procedures were employed to allow the powdered Mo complex to interact

with the powdered ligand. Once mixed the material was then inserted into the DRIFTS microcup. Thereafter, the reaction was controlled via the heat controller and the Optics software of the DRIFTS instrument. This was in contrast to the NMR spectroscopic studies. In this procedure the Mo complex and the ligand are weighed out into numerous individual NMR tubes and then placed in an oil bath at a pre-set temperature. After regular time intervals, a designated NMR tube was removed from the oil bath, the sample dissolved in CH_2Cl_2 , and the NMR spectrum for the mixture was recorded.

(ii) In the DRIFTS technique, in principle, an infinite number of data points can be recorded. In the NMR spectroscopic approach one data point per test tube can be collected. Thus the data collection in the DRIFTS approach is superior to that in the NMR approach.

(iii) It is important to note that the Mo complexes were found to slowly decompose in CH_2Cl_2 when left at room temperature in the solvent, even in the presence of N_2 .

5.3.2 An investigation of the effect of temperature on the migratory-insertion reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and phosphine ligand, $\text{P}(p\text{-FC}_6\text{H}_4)_3$

Temperature is the measure of the average kinetic energy of particles, and addition of heat to a sample is a common method used to initiate a reaction or speed it up.³⁴ The effect of temperature was used to obtain information on the migratory-insertion reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (1:1 and 1:10 molar ratios) in the DRIFTS monitored reaction. The DRIFTS spectra were

recorded at temperatures of 40, 50 and 60 °C using otherwise identical reaction conditions. The data showing the effect of temperature on the reaction as a function of molar ratio for the reaction are shown in **Figure 5.7** (1: 1 ratio) and **Figure 5.9** (1:10 ratio, first 12 minutes). The rate plots (assuming first order kinetics) are shown in **Figure 5.8** (1:1 molar ratio, first 20 minutes) and **Figure 5.10** (1:10 molar ratio). The data gave good rate plots for the early parts of the reaction when the assumption was made that the reaction obeyed a first order rate law except for the data at 40 °C (1:1 ratio) which suggests a more complicated mechanism (see later).

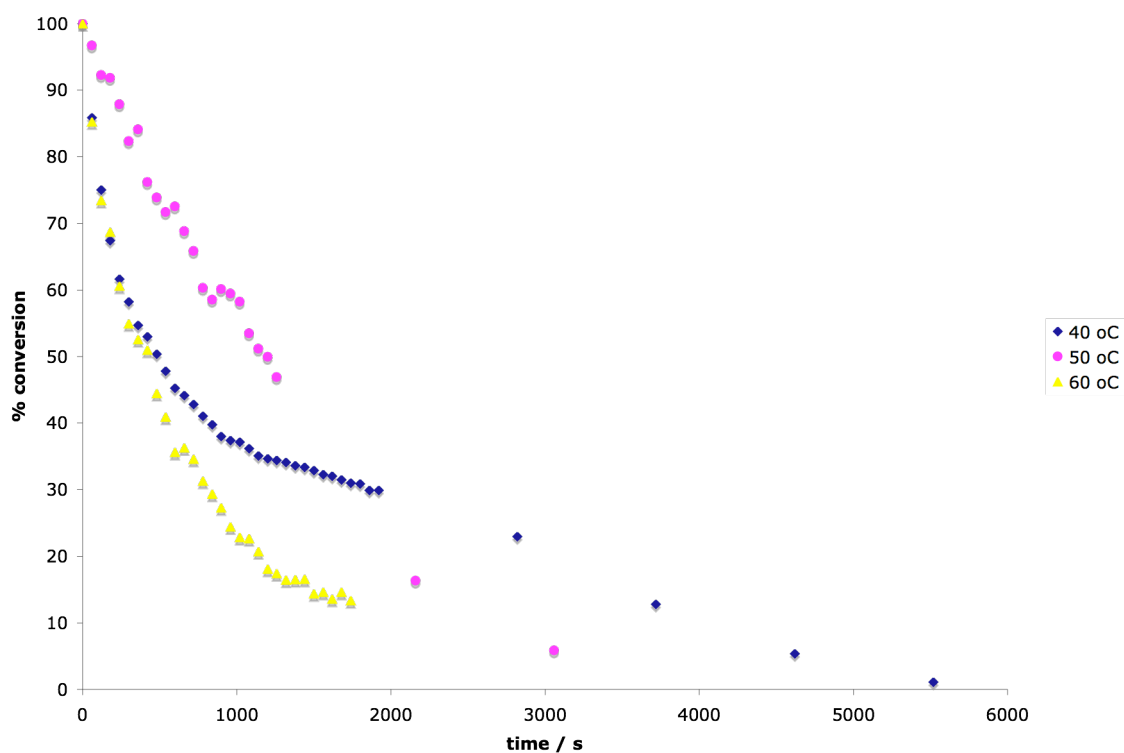


Figure 5.7: The conversion plot for migratory-insertion reaction between $\text{CpMo(CO)}_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (1:1) at varying temperatures.

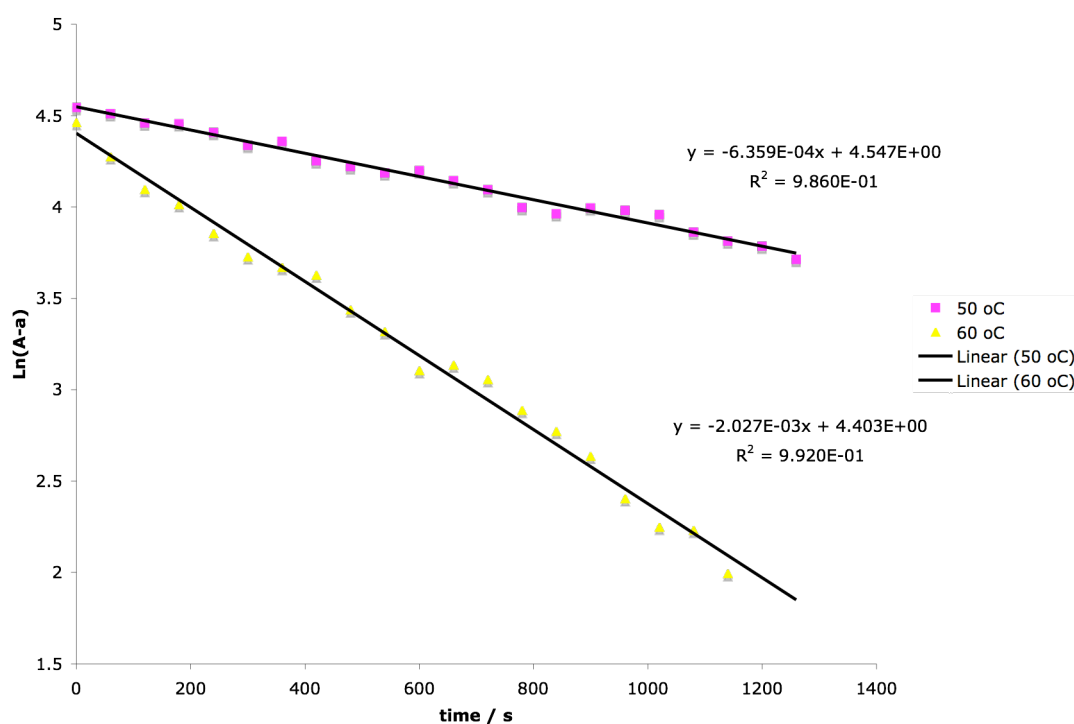


Figure 5.8: The first-order rate plot for migratory-insertion reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (1:1) at varying temperatures.

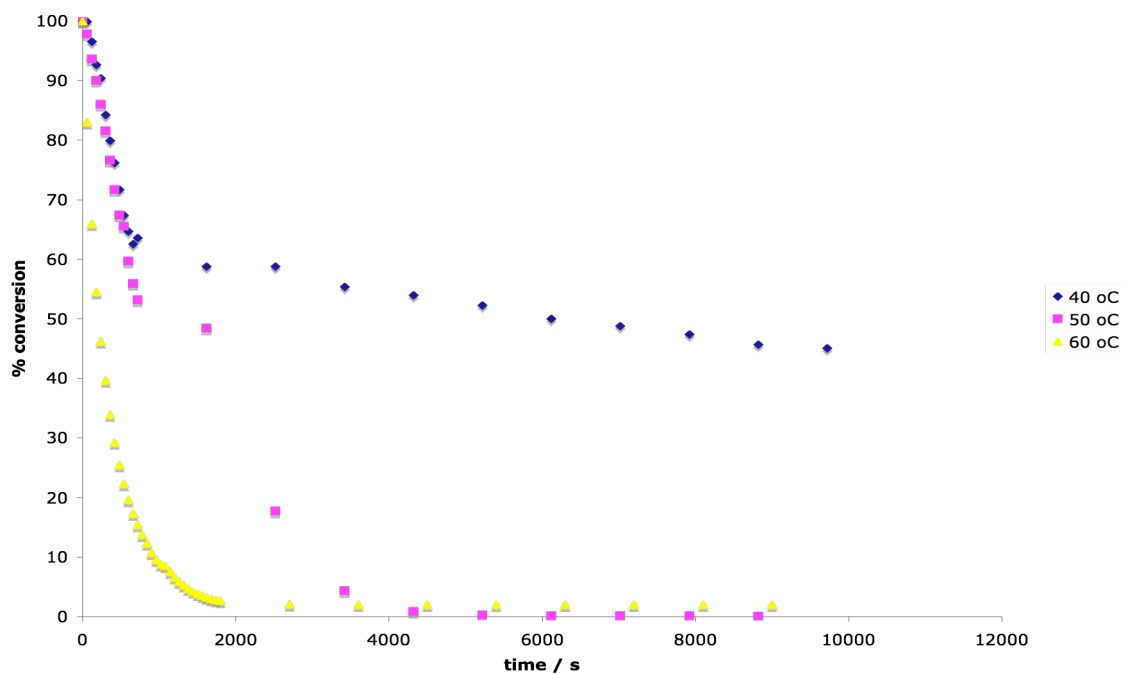


Figure 5.9: The conversion plot for migratory-insertion reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (1:10) at varying temperatures.

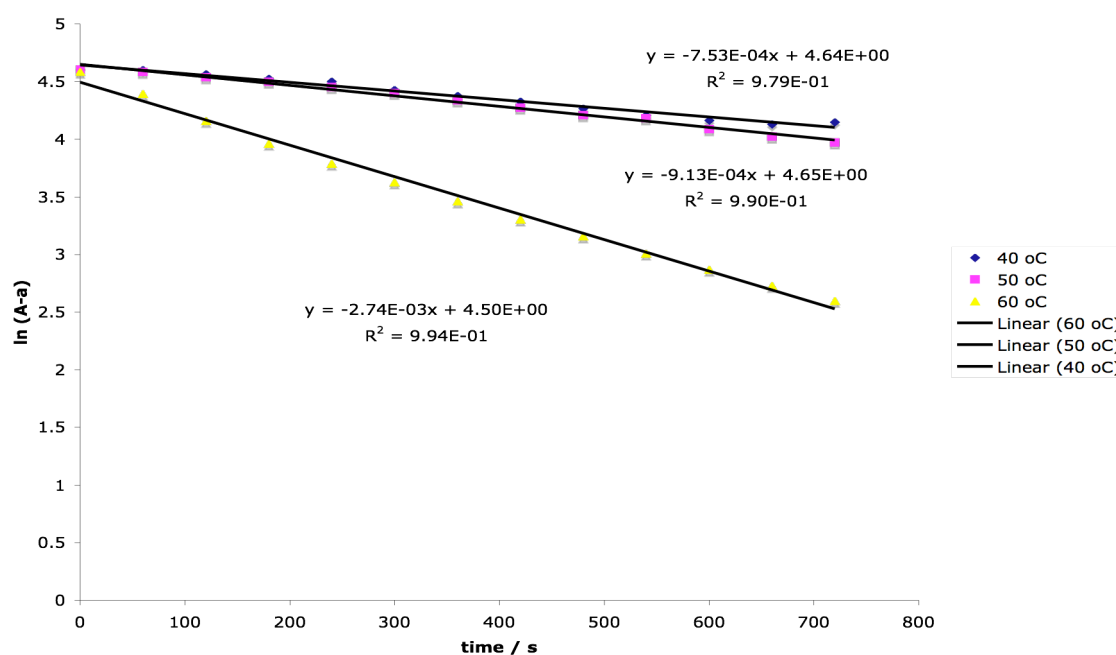


Figure 5.10: The first order kinetic plot for migratory-insertion reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (1:10) at varying temperatures.

Table 5.1: Rate constants for the migratory-insertion between $\text{CpMo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ at different temperatures and at molar ratios of 1:1 and 1:10

Ratio	Temperature/ °C	Rate constant (s^{-1})	% R^2	Ratio	Rate constant (s^{-1})	% R^2
1:1	40	-		1:10	7.53×10^{-4}	98
1:1	50	6.36×10^{-4}	99	1:10	9.38×10^{-4}	99
1:1	60	20.3×10^{-4}	99	1:10	25.2×10^{-4}	99

A summary of these results is displayed in **Table 5.1**. It can also be seen this table that the % R^2 values ($R^2 = 100\%$ for a straight line) were $> 98\%$ for all reactions. The overall data shows that the rate of the migratory-insertion reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ is generally well behaved.

The data in **Table 5.1** (1:10 mole ratio) was used to construct Arrhenius plots ($\ln k$ vs $1/T$) shown in **Figure 5.11** to obtain the activation energy for the migratory-insertion reaction using the different mole ratios. The activation energy for the 1:10 mole ratios was found to be 52.0 kJmol^{-1} . The Arrhenius plot shows that there is some scatter in the data, suggesting that there are complexities when analyzing the data (see later).

More significant was the analysis of the full set of data over the whole reaction. **Figures 5.7 and 5.9** show that at 50 and 60 °C, the reaction curves are smooth while the data at 40 °C show a clear discontinuity after about 1000 seconds. This is especially true for the data at the 1:10 ratio. The use of optical microscopy (see later) revealed that as the reaction progressed the product precipitated from the melt and it was this effect that resulted in a slower reaction after a long reaction time. At the higher temperature the product was soluble in the melt even after 50 % conversion. This information suggests a reason for the poor data obtained at 40 °C for the 1:1 mole ratio. This finding suggests that the data obtained at 40 °C might contain a different contribution to the rate data and could then impact on any activation energies measured.

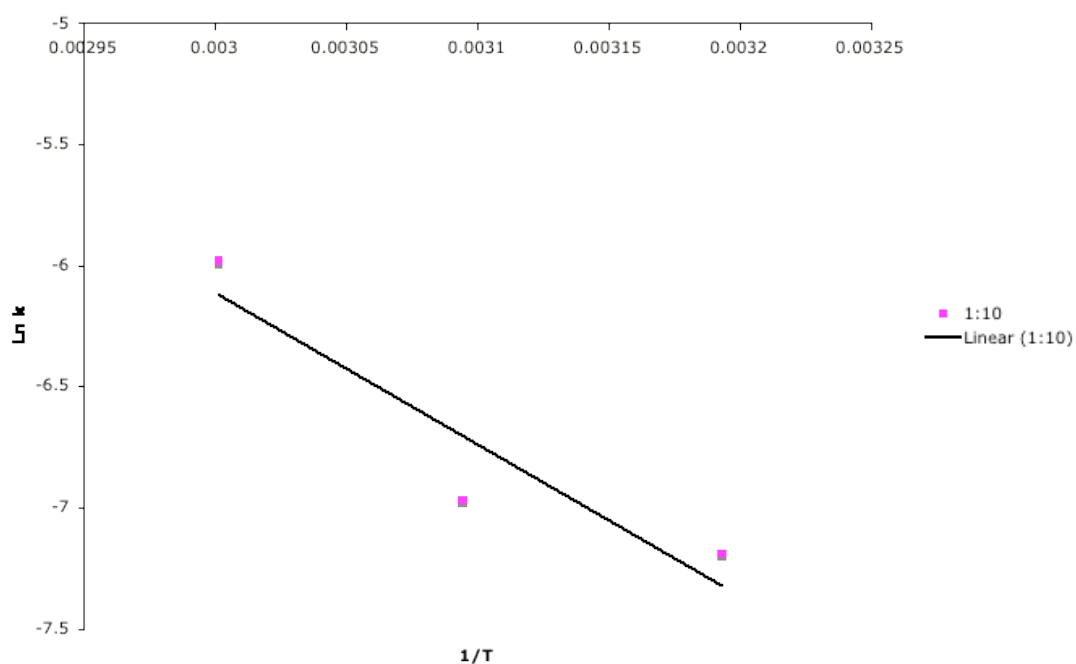


Figure 5.11: Arrhenius plot for the migratory-insertion reaction between $\text{CpMo(CO)}_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ at 50 °C for 1:0 mole ratio, where the activation energy was 52.0 kJmol^{-1} .

5.3.3 Investigation of the effect of molar ratio on the migratory-insertion reaction between $\text{CpMo(CO)}_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$

The comparison of the data for the different mole ratios (i.e. Mo complex : ligand) yielded some interesting issues. Firstly, at 40 °C the rate increase doubled from a 1:1 to 1:10 mole ratio, indicating that as the metal complex to ligand ratio increased, the rate of the reaction increased. However, as explained earlier, this data is affected by diffusion issues. At both 50 and 60 °C, the reaction is well behaved and here the rate constant also increased as the molar ratio changed from 1:1 to 1:10. At these temperatures the reaction is in the melt and all metal complex particles should be in contact with the ligand. The rate of the reaction

was dependent on the molar ratio and the reaction fitted a pseudo first-order reaction mechanism.

A DRIFTS study of $\text{CpMo(CO)}_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ in a 1:5 molar ratio was also recorded at a temperature of 50 °C. As can be seen excellent results were obtained (**Figure 5.12**). The conversion graphs for the three ratios (1:1, 1:5, 1:10) for $\text{P}(p\text{-FC}_6\text{H}_4)_3$ a 50 °C are shown in **Figure 5.12**, while the corresponding rate plots are given in **Figures 5.13**. **Table 5.2** lists the rate constants for both 50 and 60 °C data.

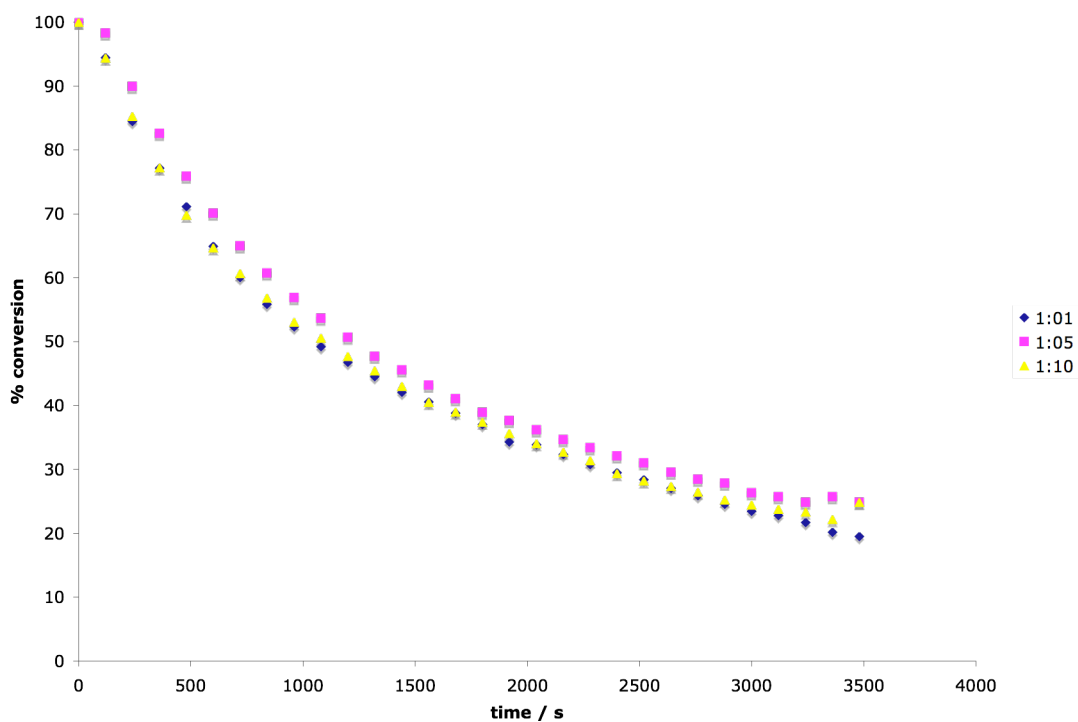


Figure 5.12: The conversion plot for the migratory-insertion reaction between $\text{CpMo(CO)}_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ at 50 °C at varying molar ratios.

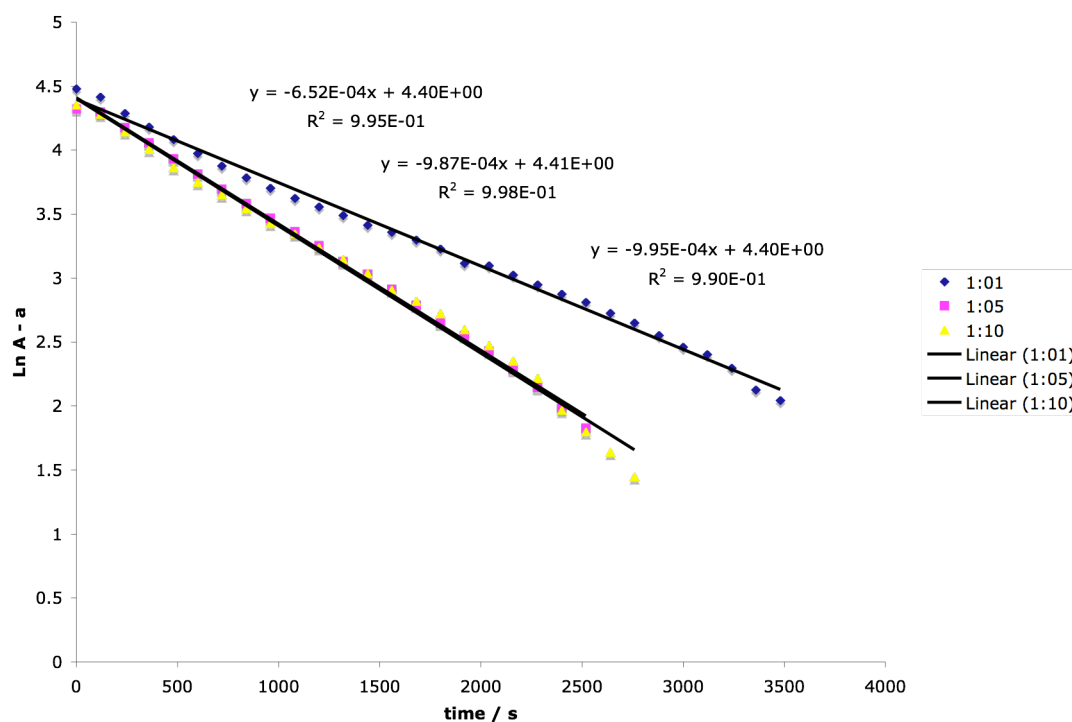


Figure 5.13: The rate plot for migratory-insertion reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ at 50 °C at varying molar ratios.

Table 5.2: Rate constants for the migratory-insertion reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and phosphine ligand, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ at different molar ratios at 50 and 60 °C

Molar Ratio	Rate constant (s^{-1}) 40 °C	% R^2	Rate constant (s^{-1}) 50 °C	% R^2	Rate constant (s^{-1}) 60 °C	% R^2
1:1	12.5×10^{-4}	95	6.52×10^{-4}	100	20.3×10^{-4}	99
1:5	8.62×10^{-4}	91	9.87×10^{-4}	100	-	
1:10	7.53×10^{-4}	98	9.95×10^{-4}	99	25.2×10^{-4}	99

The results showed that the rate of the migratory-insertion reaction increased as the mole ratio (Mo complex to the ligand ratio) increased from a 1:1 to a 1:5 mole ratio. Also, 1:5 and 1:10 mole ratios gave similar rate constants. This revealed

that at 50 °C and at high molar ratios the reaction is independent of ligand concentration i.e. there is sufficient ligand to ensure the reaction is independent of any operational constraints.

The same mole ratio investigation was compared at 40 °C. As can be seen in **Figure 5.14**, the plot of conversion versus time for the reaction at 40 °C is quite different when compared to the data obtained at 50 °C. Indeed the slowest reaction occurred with the largest molar ratio! The break in the data at ~ 1000 seconds for the 1:5 ratio relates to an instrumental effect and not a chemical issue. The break in the data for the 1:1 rate data at ~ 1000 s is suggestive of two competing reactions taking place in the melt.

The rate plots for the reaction are depicted in **Figures 5.15** (first 600 seconds), and **5.16** (first 1000 seconds) and **5.17** (after 1000 seconds), respectively.

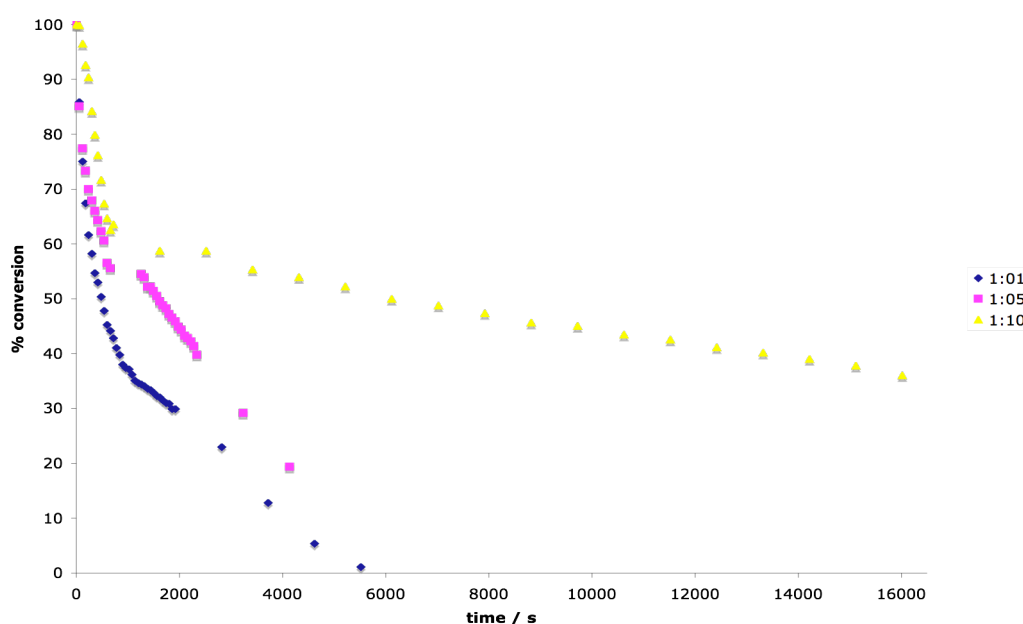


Figure 5.14: The conversion plot for migratory-insertion reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ at 40 °C at varying molar ratios.

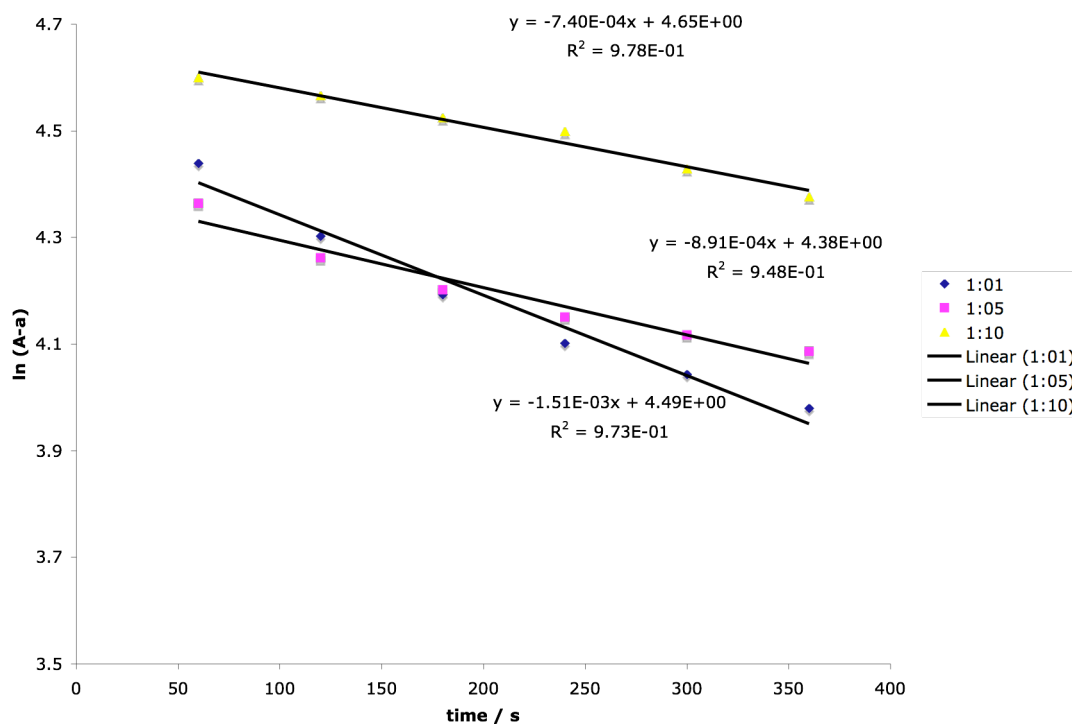


Figure 5.15: The first order kinetic rate plot for the first 5 minutes of the migratory-insertion reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ at 40°C at varying molar ratios.

The data gave good rate plots when the assumption was made that the reaction occurred by a first order rate law. The rate constants extracted from the reactions are given in **Table 5.3**.

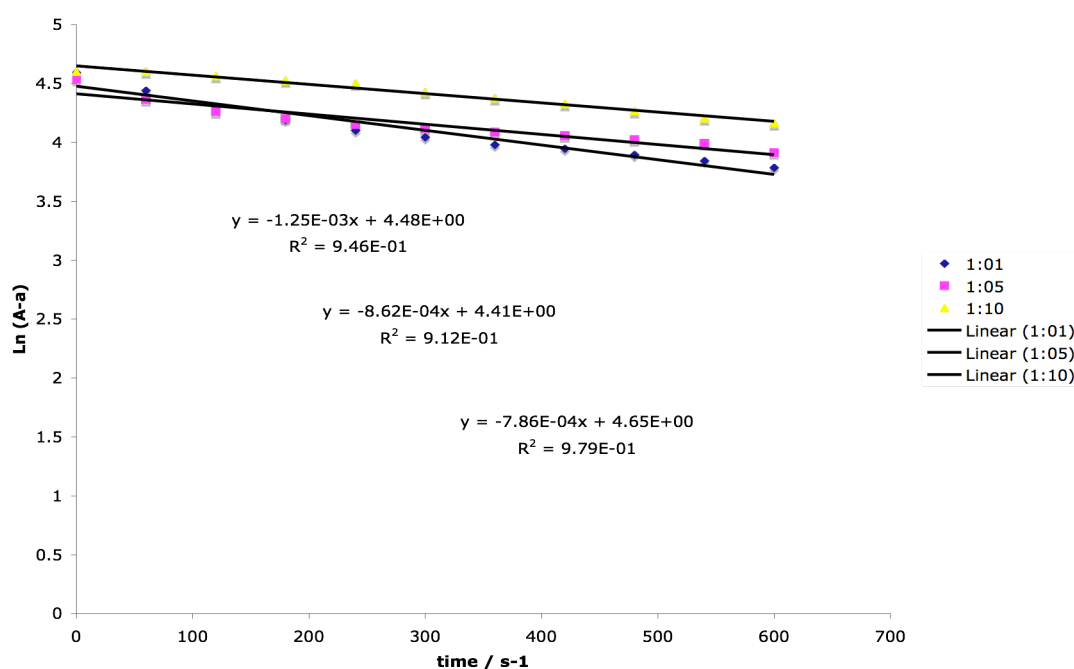


Figure 5.16: The first-order kinetic rate plot first 10 minutes for the migratory-insertion reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ at 40°C at varying molar ratios.

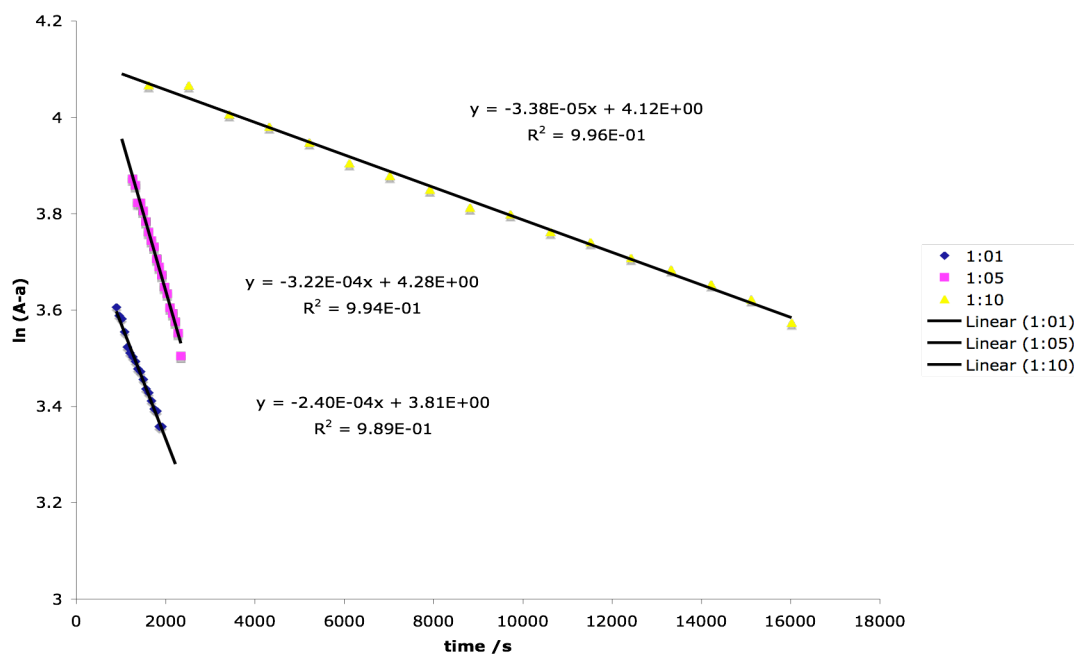


Figure 5.17: The first-order kinetic rate plot after 10 minutes for the migratory-insertion reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ at 40°C at varying molar ratios.

Table 5.3: Rate constants ($\times 10^{-4} \text{ s}^{-1}$) for the migratory-insertion reaction between $\text{CpMo(CO)}_3\text{Me}$ and phosphine ligand, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (with % conversion to the product in brackets) at different molar ratios at 40 °C

Molar Ratio	Rate constant for first 5 minutes (% conversion)	% R²	Rate constant for first 10 minutes (% conversion)	% R²	Rate constant after 10 minutes (% conversion)	% R²
1:1	15.1 (45)	97	12.5 (55)	95	2.40 (77)	99
1:5	8.91 (42)	95	8.62 (44)	91	3.22 (60)	99
1:10	7.40 (16)	98	7.85 (35)	98	0.338 (82)	100

The table is divided into three sections, depicting the rate constants for the first 5 minutes (**Figure 5.15**), the first 10 minutes (**Figure 5.16**) and the reaction after 10 minutes (**Figure 5.17**). In the first 5 minutes of the reaction, the rate of reaction decreases as the molar ratio of metal complex to ligand increases. The reaction after 10 minutes also yielded rather interesting results. An attempt to answer the questions raised from these results follows. This effect is more readily seen when the data is tabulated as % conversion (**Table 5.4**)

The **Table 5.4** shows that the rate of conversion to the product decreased as the mole ratios increased. For example, a ~ 40 % conversion was completed in 5 minutes for the 1:1 mole ratio, in 10 minutes for the 1:5 mole ratio and in ~30 minutes for the 1:10 mole ratio.

Table 5.4: The % reactant conversion to product for the different mole ratios for the migratory-insertion reaction between $\text{CpMo(CO)}_3\text{Me}$ and phosphine ligand, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ after various time intervals (40 °C)

Time / min	% conversion		
	1:01	1:05	1:10
0	0	0	0
2	14.12	14.95	0
4	38.38	30.02	9.64
5	41.80	32.12	15.76
10	54.74	43.49	35.34
27	67.99	50.48	41.22

It was observed from optical microscopy studies (see **below**) that only when the ligand and the metal complex was placed in contact with each other, at a temperature *above 40 °C*, that a melt occurs, and this facilitated the migratory-insertion reaction. Thus, in order for the reaction to take place the reactants have to come into contact at a temperature at which a melt is formed. It is to be noted that the reaction rate is slower between 5 – 10 minutes then between 0 – 5 minutes. The rate is also slower after 10 minutes. This implies some inhibiting reaction. Possible factors that could lead to the unusual kinetic data detected at 40 °C is as follows:

- 1) The melt was less viscous at higher liquid molar ratios
- 2) The diluent, KBr played a role in the reaction that was affected by the amount of ligand present in the reaction.

- 3) The product that formed precipitated from the reaction differently. Note:
At the higher temperature the above issues are not significant as shown by
the kinetic data and optical microscopy studies.

In supported of the above proposals the following was noted:

- (i) DSC profiles were recorded for the 1:1 and 1:10 mole ratio and showed that the melt commenced at $T < 60\text{ }^{\circ}\text{C}$ and was *complete below* $60\text{ }^{\circ}\text{C}$. Hence, the formation of a melt is not a rate limiting step in the reaction at higher temperatures.
- (ii) The issue of the diluent effect was explored and while it does play a role in the reaction (see later) thus issue would not explain the data seen.
- (iii) A precipitate was found to form as the reaction progressed as determined by optical microscopy. The DSC profiles at $T < 60\text{ }^{\circ}\text{C}$ in **Figure 5.18** could relate to this precipitate. It thus appears that the precipitate formation is more significant when the ligand concentration increases.

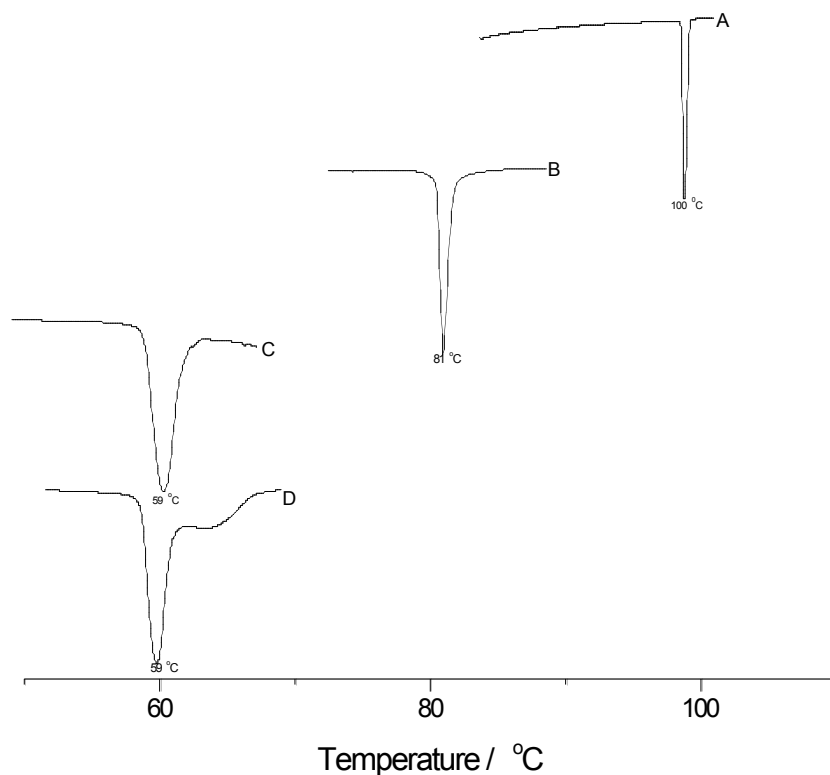


Figure 5.18: DSC plots where A: Mo complex, B: ligand, C: 1:1 mixture and D: 1:10 mixture.

5.3.4 Investigation of the migratory-insertion reaction between $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ and L ($\text{R} = \text{H}, \text{COMe}$; $\text{L} = \text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ and PPh_3 using optical photomicroscopy

In order to rationalize the kinetic data and determine a possible mechanism for the reaction an optical microscopy study was initiated. The data for the reaction of $(\text{CpCOMe})\text{Mo}(\text{CO})_3\text{Me} + \text{L}$ is used as an example to reveal the observations made in this study. It was found that when the two components were placed *in contact* with each other, a melt occurred (see **Figure 5.19**). This melt occurred far

below the either of the two components individual melting points i.e. a eutectic melt had formed (see **Table 5.5**).

Table 5.5: The melting of L and the eutectic melt temperature for (CpCOMe)Mo(CO)₃Me (m.p. 82 - 85 °C) + L

L	Melt temperature / °C	Melting point / °C
PPh ₃	42	79 - 81
P(<i>p</i> -FC ₆ H ₄) ₃	47.5	80 - 81
P(<i>p</i> -OMeC ₆ H ₄) ₃	48	120 - 124
P(<i>p</i> -MeC ₆ H ₄) ₃	56	145 - 148

Figure 5.19 shows that a melt *only* occurs when the two components touch, and this facilitates the migratory-insertion reaction to take place. This eutectic melt was observed in other migratory-insertion reactants and their optical microscopic photographs can be found in the **Appendix A3**.

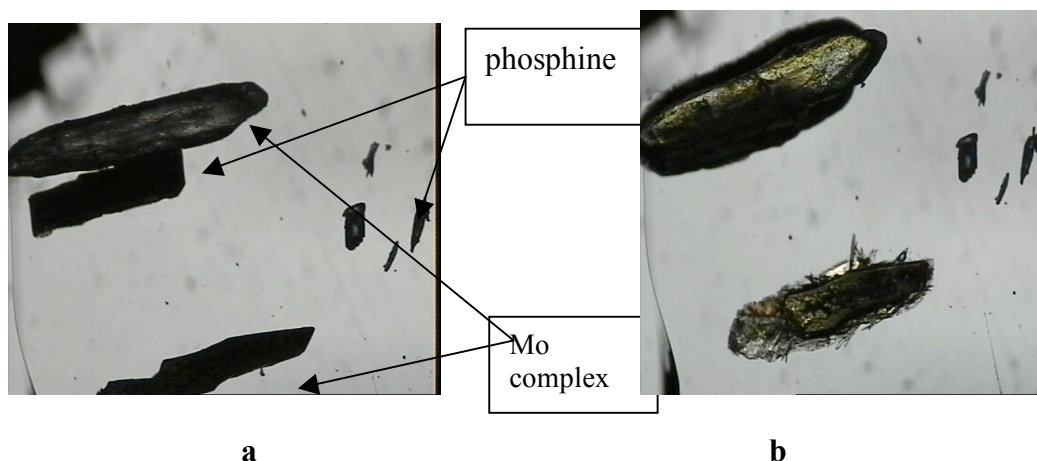


Figure 5.19: (a) Pictures taken of the phosphine ligand in contact with the Mo complex, as well as some the Mo complex and ligand well separated from each other (room temperature) (b), picture taken at 47.5 °C; the phosphine has melted into the Mo complex and the phosphine and Mo complex which do not touch are still solid.

The progression of the reaction resulted in a consumption of reactants and crystallisation of new material out of the melt. NMR analysis confirmed that the insertion product was formed in the crystalline material. A similar study by Manzini, discussed in **Chapter 2**, also showed a melt (upon contact) below the reactants' melting points and the crystallisation of the product from the melt.³² This will be further discussed below.

This study established that the migratory-insertion reaction that appeared to occur *via* a solid-solid reaction to the naked eye, was actually taking place *via a melt phase*. It rationalized the complexities observed in the kinetic study of the migratory-insertion reaction.

5.3.5. Investigation of the effect of ligand on the migratory-insertion reaction between (CpR)Mo(CO)₃Me (R = H, Me, COH, COMe) and phosphine ligands, L (L = P(*p*-OMeC₆H₄)₃, P(*p*-FC₆H₄)₃, P(*p*-MeC₆H₄)₃, PPh₃)

The phosphine ligand holds a prominent position in organometallic chemistry.¹⁹ In this study we have used different phosphine ligands to study the effects of the phosphine ligand on the migratory-insertion reaction. There are two factors to be considered when evaluating the effect of phosphines on a reaction. These are steric and electronic effects and they are controlled by changes in the nature of the substituents on the phosphorus atom.¹⁹ The two effects do not act independently of each other. Many years ago Tolman realized that steric and electronic parameters could not be viewed in isolation.²¹ A parameter, *Z*, was introduced to

determine the combined effects (steric and electronic) of a ligand by the use of an equation²¹:

$$Z = a\theta + b\nu + c \dots\dots\dots 5.2$$

where, θ and ν are the steric and electronic parameters, respectively, and, a , b and c are regression coefficients. The equation used implied that the effects were additive. The evaluation of Z is then determined by an appropriate choice of θ and ν terms. Tolman introduced measurements to quantify ligand effects with θ being determined from a so-called cone angle and ν from IR spectroscopy.²¹

In particular Tolman evaluated the size of a ligand by means of a cone angle, θ , in units of degrees, ($^{\circ}$)²¹ (See **Figure 5.20**). Electronic effects, on the other hand, are associated with the electron donating or attracting capacity of a ligand.³⁴ The electronic parameter, ν , which will be explained later, can be electron donating (downward arrow in **Figure 5.20**) or electron withdrawing (upward arrow in **Figure 5.20**)³⁴

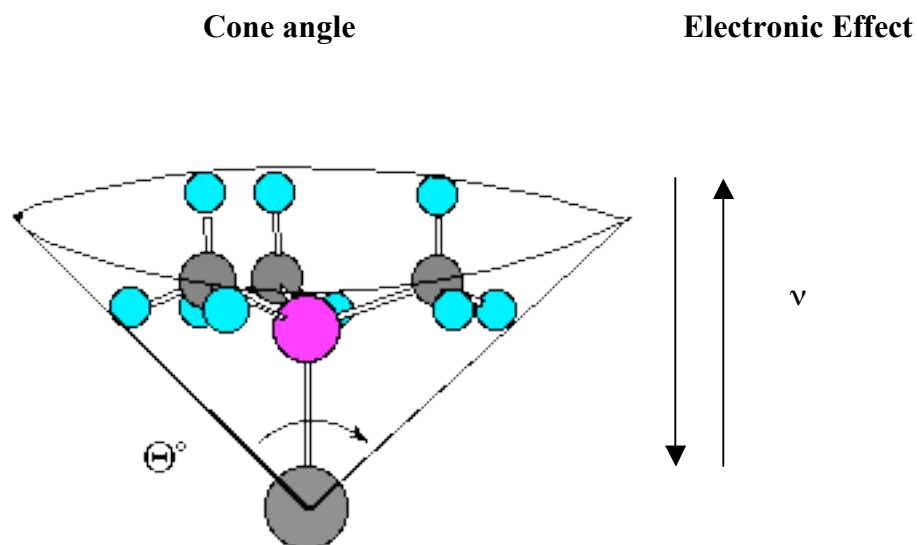


Figure 5.20: A representation of the definition of steric and electronic effects³⁵

Another method used to quantify a steric effect is by measurement of a solid angle.^{20,22} Mathematically the solid angle, Ω , at a point O of a surface can be defined as:

$$\Omega = \int_s \frac{\mathbf{r} \cdot d\mathbf{S}}{r^3} \quad 5.3$$

where $\mathbf{r}$ is the position vector of an element of the surface with respect to O and r is the magnitude of $\mathbf{r}$.²⁰ There are three important factors that the integrand covers: the size of the element of surface, its inclination to the line joining the element to O, and the distance from O.²⁰ In common terms the ‘solid angle can be viewed as the surface area of that part of a solid projected onto the surface of a sphere’.²² Unlike the Tolman cone angle, the solid angle is additive, meaning, that the solid angle of a ligand, can be dissected into the solid angles of individual substituents that make up that ligand.^{20,22} A summary of differences between the Tolman cone angle and the solid angle are displayed in **Chapter 2**.

In this specific study a range of *para*-substituted aryl phosphines have been used. The solid angles and the Tolman cone angles for the phosphine ligands are all identical and hence the steric influence of the ligands may be ignored.²¹

Thus, only the electronic effects are expected to influence the rate of this migratory-insertion reaction. The electronic effects are defined by the electronic parameter, ν (see earlier equation). Tolman used the frequency of the A_1 carbonyl mode of $Ni(CO)_3L$ in CH_2Cl_2 to evaluate ν and to create a table of electronic parameters for various phosphine ligands.²¹ Tolman stated that he could have used any other carbonyl complex, but $Ni(CO)_3L$ formed rather quickly when $Ni(CO)_4$ and L (1:1 mole ratio) were mixed together at room temperature, and the A_1 band could be measured with an accuracy of $\pm 0.3\text{ cm}^{-1}$ independent of the choice of L . This $\nu(CO)$ value was originally determined for the Ni system, but the value obtained is in principle transferable to any metal and to any metal complex.³⁶ For example, Anton and Crabtree obtained a related equation for bidentate phosphine ligands ($L-L$), in *cis*- $[Mo(CO)_4L-L]$ complexes^{36,37}:

$$\nu_{CO_{Ni}} = 0.593 \nu_{CO_{Mo}} + 871, \dots\dots\dots 5.4$$

that is related to the original Tolman data.

Tolman also introduced an equation that could be used to calculate the electronic parameter for other ligands that had not been measured experimentally. A

substituent contribution, χ_i , can be added according to **equation 5.5**, to estimate the electronic parameter for any PR_3 ligands that has not been measured.²¹

$$\text{For } \text{PX}_1\text{X}_2\text{X}_3 \quad \nu = 2056.1 + \sum_{i=1}^3 \chi_i \dots \dots \dots 5.5$$

The electronic parameters for the phosphine ligands used in this study were taken from Tolman's review²¹ (**Table 5.6**). Tolman also found that the electronic factor correlated with the pKa of the phosphonium ions which is also included in the **Table 5.6**.³⁶ The $\nu(\text{CO})$ value measured is determined by both the σ -donor ability and the π -acceptor strength of tertiary phosphines.³⁶

Table 5.6: The electronic parameter²¹ of some phosphine ligands and the corresponding pKa values³¹

Phosphine ligand	Electronic parameter (ν) / cm^{-1}	pKa
$\text{P}(p\text{-OMeC}_6\text{H}_4)_3$	2066.1	4.59
$\text{P}(p\text{-MeC}_6\text{H}_4)_3$	2066.7	3.84
PPh_3	2068.9	2.73
$\text{P}(p\text{-FC}_6\text{H}_4)_3$	2071.3	1.97

A DRIFTS experiment was used to study the four phosphines, $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, and PPh_3 that were used in the migratory-insertion reaction with $\text{CpMo}(\text{CO})_3\text{Me}$. These phosphines all have the same Tolman cone angle of 145° and solid angle of 129° meaning that the steric effect of the ligands can be neglected.²¹ Relative to PPh_3 the electron donating ligands are $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$ and $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, while $\text{P}(p\text{-FC}_6\text{H}_4)_3$ is electron withdrawing.³⁸

The reactions were all studied at 40 °C with a 1:10 metal complex : ligand ratio. These correlations were chosen since the reaction with PPh₃ revealed that when this temperature and metal complex : ligand ratio was used the reaction was well behaved but that the reaction appeared to be influenced by the melt phase. Thus working at this temperature allowed the possibility of establishing whether the melt phase could impact on the expected order of the reactivity of the reaction.

The combined results for the four ligands undergoing the migratory-insertion reaction with CpMo(CO)₃Me (1:10; 40 °C) are shown in **Figure 5.21**. The rates of the reactions were assumed to be first order, and the corresponding first-order rate plots are depicted in **Figure 5.22**. **Table 5.7** summarizes the results obtained from this plot.

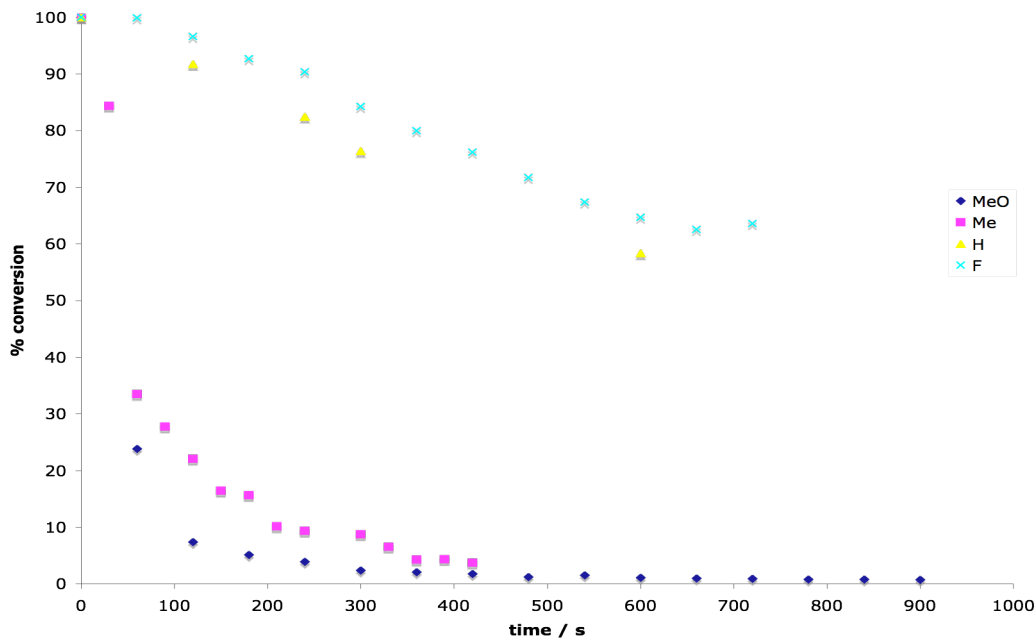


Figure 5.21: The conversion plot for the migratory-insertion reaction between CpMo(CO)₃Me and L (L = P(*p*-OMeC₆H₄)₃, P(*p*-FC₆H₄)₃, P(*p*-MeC₆H₄)₃, PPh₃) in a 1:10 molar ratio at 40 °C.

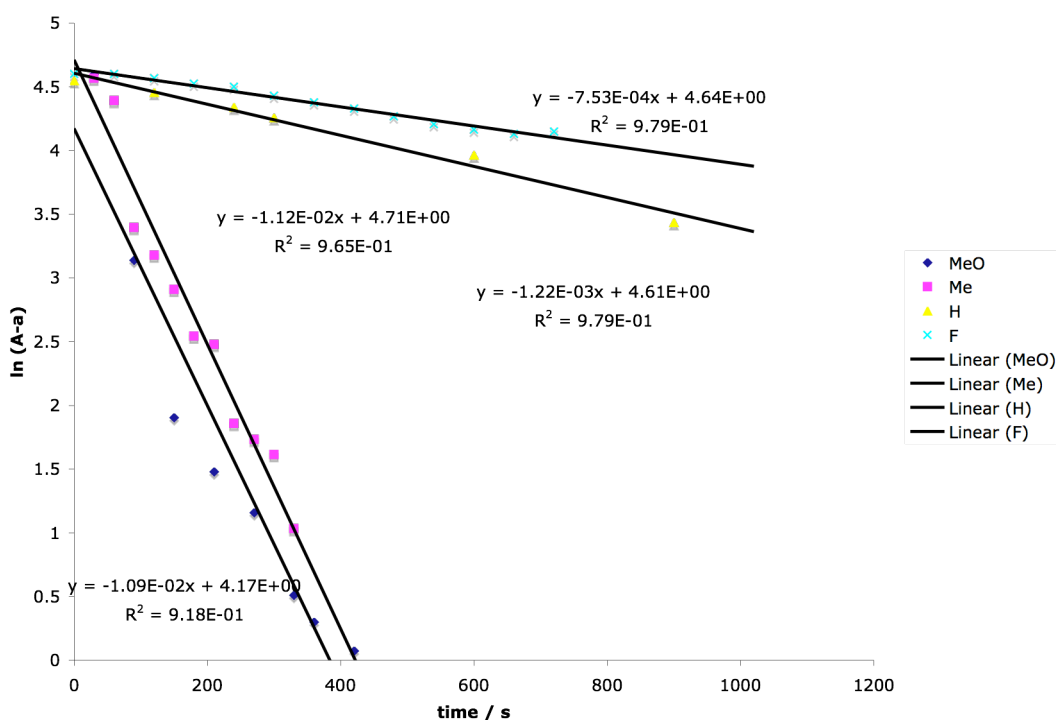


Figure 5.22: The first-order rate plot for the migratory-insertion reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and L ($\text{L} = \text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, PPh_3) in a 1:10 molar ratio at 40 °C.

Table 5.7: Rate constants for the migratory-insertion reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and different phosphine ligand, L , ($\text{L} = \text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, PPh_3) at 40 °C and molar ratio of 1:10

Ligand	Rate constant (s^{-1})	% R^2
$\text{P}(p\text{-MeC}_6\text{H}_4)_3$	11.2×10^{-3}	97
$\text{P}(p\text{-MeOC}_6\text{H}_4)_3$	10.9×10^{-3}	92
PPh_3	1.22×10^{-3}	98
$\text{P}(p\text{-FC}_6\text{H}_4)_3$	0.75×10^{-3}	98

The data in **Table 5.7** shows that the rate decreases in the following manner: $\text{P}(p\text{-$

$\text{MeC}_6\text{H}_4)_3 > \text{P}(p\text{-OMeC}_6\text{H}_4)_3 \gg \text{PPh}_3 > \text{P}(p\text{-FC}_6\text{H}_4)_3$ for the reactions occurring at 40 °C and with a 1:10 mole ratio for the migratory-insertion reaction. This sequence relates to the electron donating/withdrawing effect associated with the *para*-substituent and the effect can be quantified by the use of the Tolman electronic parameters (**Table 5.6**). This correlation is shown in **Figure 5.23**.

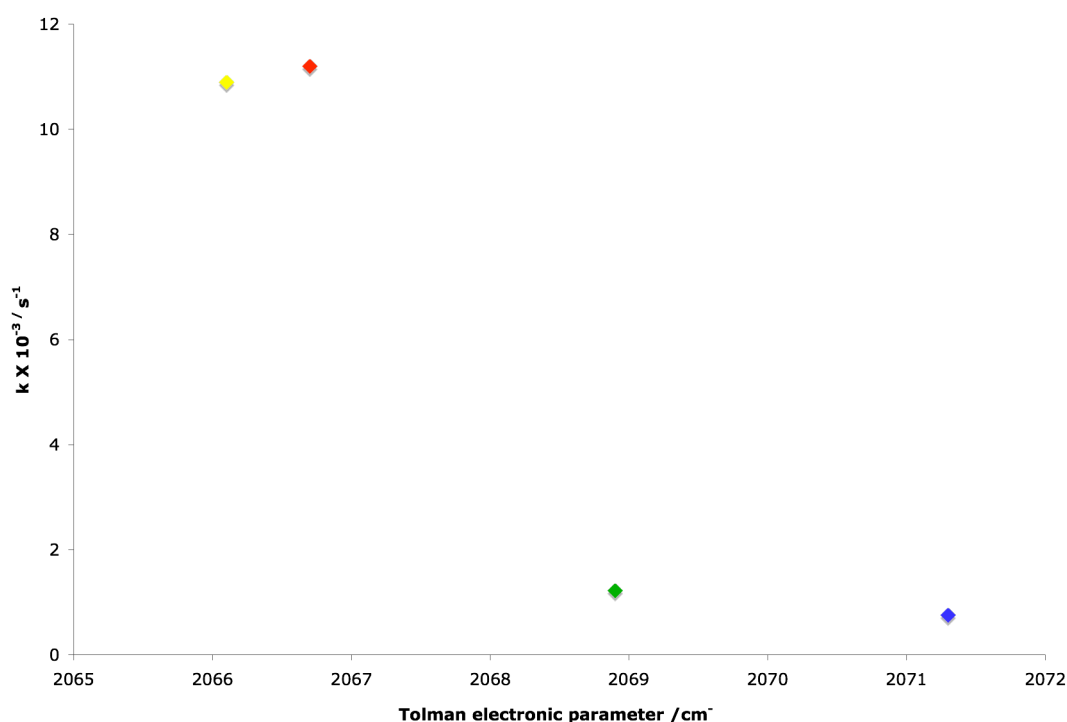


Figure 5.23: The rate constant, k ($\times 10^{-3}$) for the migratory-insertion reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and L ($\text{L} = \text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, PPh_3 , $\text{P}(p\text{-FC}_6\text{H}_4)_3$) against the Tolman electronic parameter for L

From the data it can be seen that as the electronic donation from PR_3 to the Mo increases the rate of the migratory-insertion decreases. Again, it must be stressed that this data was observed in the melt reaction. The question then is: how does the data compare with reactions performed in their solvent phase?

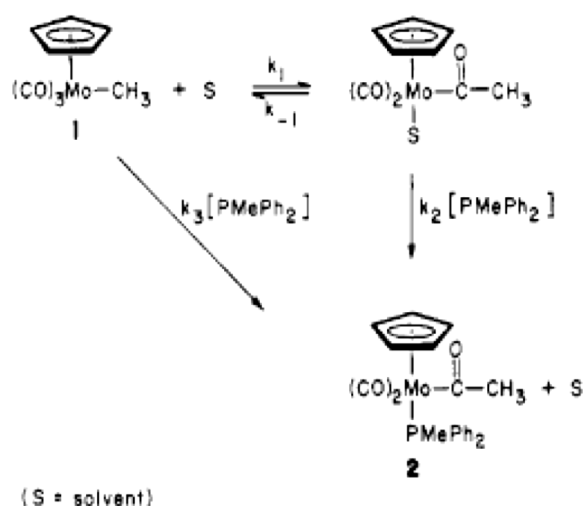
Comparative solution studies:

Solution studies on the insertion reactions of organometallic complexes have been performed over the decades.³⁹⁻⁴¹ Butler *et al.* found that the rate of reaction of $\text{CpMo(CO)}_3\text{Me}$ with PPh_3 is a linear function of the phosphine concentration in benzene, but is independent of the phosphine in THF.⁴⁰ In these and related studies a solvent effect on the reaction was observed and it was later suggested that the solvent was a catalyst for the reaction.^{40,41} Indeed Atwood proposed that the formation of a 16 electron intermediate in a pre-equilibrium mechanism would allow for solvent binding.⁴² **Table 5.8** shows the relative rate data for the migratory-insertion reaction of $\text{CpMo(CO)}_3\text{Me}$ in different solvents.⁴²

Table 5.8: Solvent effect on methyl migration reaction of $\text{CpMo(CO)}_3\text{Me}$ ⁴²

Solvent	Relative rate
toluene	1
THF	10
nitromethane	70
DMF	8000

In a later study, Wax and Bergman found the rate constants for reactions of $\text{CpMo(CO)}_3\text{Me}$ with PPh_2Me in various THF solvents, (the methyl-substituted tetrahydrofuran donor solvents used had high nucleophilicity but varied in steric ability) as indicated in **Table 5.9** (k values as shown in the reaction scheme).⁴¹



Scheme 5.2: The reaction scheme of the solvent coordinated migratory-insertion reaction of $\text{CpMo}(\text{CO})_3\text{Me}$ with PMePh_2 ⁴¹

The effect of α -substituted methyl groups on the THF on the k_1 value was explained by the steric hindrance to the direct co-ordination of THF to molybdenum in the transition state in the migratory-insertion reaction, indicating the effect of the solvent on the reaction rate (see **Table 5.9**).⁴¹

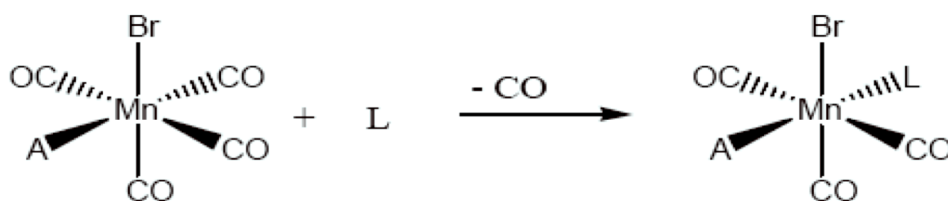
Table 5.9: Rate constants for the reaction of $\text{CpMo}(\text{CO})_3\text{Me}$ with PPh_2Me at 59.8 - 60.0 °C⁴¹

solvent	$k_1 (\times 10^4) / \text{s}^{-1}$	$k_1/k_2 / \text{M}$	$k_3 (\times 10^4) / \text{M}^{-1}\text{s}^{-1}$
THF	7.78 ± 0.07	0.0104 ± 0.0004	1.73 ± 0.08
3-MeTHF	6.46 ± 0.05	0.00821 ± 0.00045	1.86 ± 0.08
2-MeTHF	1.48 ± 0.05		1.95 ± 0.12
2,5-Me ₂ THF	0.23 ± 0.03		1.67 ± 0.07

Surprisingly our literature search has not indicated any definitive studies on the effect of electronic effects associated with the use of different incoming ligands

on the above migratory-insertion reaction. However, a comparison of the data in **Table 5.9** for PPh_2Me reveals that the reaction in a solvent was much slower when compared to the similar reaction e.g. with $\text{P}(p\text{-FC}_6\text{H}_4)_3$ when performed in a solvent-free process. From **Table 5.2** the rate constants for the migratory-insertion reactions at 60°C for 1:1 and 1:10 mole ratios of $\text{CpMo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ were 20.3×10^{-4} and $25.2 \times 10^{-4} \text{ s}^{-1}$, respectively. This increased rate is expected to relate to a concentration effect.

Some other reactions also have relevance to our study. Manzini has carried out a related DRIFTS solvent-free study.³² In this instance the kinetics of the substitution reaction of $\text{Mn}(\text{CO})_4(\text{A})\text{Br}$ (where A is a CO or phosphine ligand) and L ($\text{L} = \text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, PPh_3) was studied as depicted in **Scheme 5.3**.³²



Scheme 5.3: The solvent-free substitution of CO, A can be CO or phosphine, by solid a phosphine on $\text{Mn}(\text{CO})_4(\text{A})\text{Br}$ ³²

Manzini found that the rate of the reaction sequence for substitution reactions on Mn complexes were in decreasing order: $\text{P}(p\text{-MeOC}_6\text{H}_4)_3 > \text{P}(p\text{-MeC}_6\text{H}_4)_3 > \text{PPh}_3 > \text{P}(p\text{-ClC}_6\text{H}_4)_3 > \text{P}(p\text{-FC}_6\text{H}_4)_3$, i.e. the reaction rate was in the order: electron-donating ligand > electron-withdrawing ligand.³² The sequence of the electron donating/withdrawing group is thus the same for both the substitution and

migratory-insertion reactions in a solvent-free reaction

Romeo *et al.* reported a kinetic study of the displacement of 5-aminoquinoline (referred to as 5-AQ) from the platinum complex, *cis*-[PtPh₂(CO)(5-AQ)], by a number of phosphines. The reaction rate obtained was as follows (adapted for the phosphines used in this study): P(*p*-MeOC₆H₄)₃ > P(*p*-MeC₆H₄)₃ > PPh₃ > P(*p*-ClC₆H₄)₃.¹⁹ This study, although performed in a solvent, compared well to our results, showing that once again the greater the electron donating ability of the phosphine ligand, the faster the reaction.¹⁹

It thus appears that for both substitution and migratory-insertion reactions, whether carried out in solvent or in the melt that certain conclusions can be drawn:

- 1) Reaction rates are determined by the basicity of the incoming ligand.
- 2) In the melt, concentrations of reactants are higher and hence reactions proceed more rapidly.
- 3) The melt phase does not modify the course of the reaction when compared to reactions performed in solvents
- 4) When the temperature of the reaction is close to the melt formation temperature, issues of solubility / precipitation do occur but may not be dominant.

5.4.6 Investigation of the effect of the substituent, R, on the Cp ring, on the migratory-insertion reaction between (CpR)Mo(CO)₃Me, (R = H, Me, COH, COMe) and phosphine ligand, L (L = P(*p*-FC₆H₄)₃)

The previous study (Section 5.4.3) focused on the influence of the incoming ligand on the rate of the migratory-insertion reaction and was discussed in terms of the effect of the electronic properties of the ligands (all the Tolman cone angles and the solid angles were equal for all the *para*-substituted phosphine ligands). In this section the role of the substituent, R on the Cp ring in the complexes (CpR)Mo(CO)₃Me (R = H, Me, CHO, COMe)) has been investigated. The substituents, R, were chosen to cover a range of steric and electronic values.

According to studies by White *et al.*, the cone angle (θ) and average solid angle (Ω_{av}) for the Cp ring in substituted Cp metal complex are greater than determined for the unsubstituted Cp metal complex i.e. R = H (see Table 5.10).²⁰ Thus it can be expected that steric effects are greater when a substituent is attached to the Cp ring is an atom or group larger than an H atom. Table 5.10 indicates two different methods used to measure cone angles of Cp ring substituents. These are, θ_1 , which is measured with the metal as the apex of the cone, and θ_2 , which is measured with the ring centroid as the apex.^{20,43} This is indicated in Figure 5.24.

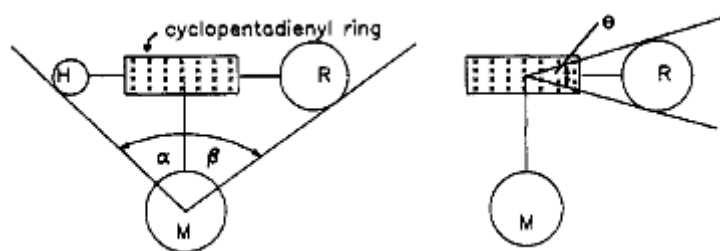


Figure 5.24: The measurement of the Cp ring cone angle (a) with metal as apex (θ_1) and (b) with ring centroid as apex (θ_2)⁴³

When the R group is Me or COMe the cone angles differ by only 1° for θ_1 , while for θ_2 a larger difference exists (1.4 times). No difference in values was observed for the solid angles (see **Table 5.10**).

A steric value for COH was not given in the literature, but the program STERIC⁴⁴ was used to calculate it, using organometallic complexes (containing the metal-CpCOH fragment) found in the Cambridge Structural Database.⁴⁵ The complex, *Xawzaw*, which was a bis(formyl)ferrocene complex elucidated by Braga *et al.*, was used for the study.⁴⁶ This structure had COH substituents on each Cp ring. STERIC calculated the Tolman cone angle θ_1 , (and solid angle), to be 140°, using the Fe atom as the origin, and θ_2 (and solid angle) of 40°, using the Cp-centroid as the origin. The results were in accordance with the rest of the data given in **Table 5.10**. The conflicting data could be attributed to STERIC, as it was not designed to measure the angle about a ring, and it requires a bond to the metal. In this case, delocalized bonds attach to the metal. In this case the Cp-centroid was represented by a dummy atom.

Table 5.10 also lists various measurements for the electronic factors obtained from the literature.⁴⁷

Table 5.10: The cone angles and solid angles for $C_5H_4R^{20}$ and electronic factors for CH_2R^{47}

R	θ_1 (°)	θ_2 (°)	Ω_{av} (°)	F	σ_I	σ_R
H	128	55	131	0.03	0	-
Me	141	64	144	0.01	-0.05	-0.13
COH	140*	40*	140*	0.33	-	0.23
COMe	142	47	144	0.33	0.27	0.16

Note * calculated using STERIC (see above)

In addition, to the steric effect, the R group also has the ability to be electron donating or electron withdrawing. The Me group is weakly electron donating, while both COH and COMe groups are strongly electron withdrawing.³⁴ The various methods used to quantify the electronic effect include: F (combination of inductive and resonance effects), σ_I (electronic effect dominated by inductive effects) and σ_R (electronic effect dominated by resonance effects).⁴⁷

A DRIFTS study was carried out on the migratory-insertion reaction of $(CpR)Mo(CO)_3Me$ ($R = H, Me, CHO, COMe$) with $P(p-FC_6H_4)_3$ to ascertain the effect of the R group on the rate of the reaction. The conversion graphs for the insertion reactions are depicted in **Figure 5.25**. The rate data for $CpMo(CO)_3Me$ with $P(p-FC_6H_4)_3$ was only used until 60 % conversion due to the obvious change in rate indicated by the conversion graph (**Figure 5.25**). The reactions were

assumed to be first-order and the rate plots are displayed in **Figure 5.26**. The rate plots correlate with first-order behaviour and rate constants are given in **Table 5.11**. A surprisingly small effect on k was noted for the four different substituents used ($H > Me > COH > COMe$). If electronic effects are assumed to be important the electron-withdrawing group slow down the reaction.

A similar DRIFTS kinetic study was carried out using other phosphine ligands, namely $P(p\text{-OMeC}_6\text{H}_4)_3$, $P(p\text{-MeC}_6\text{H}_4)_3$ and PPh_3 , with the substituted-Cp metal complexes (see **Appendix A4** for rate plots) and a summary of these results are presented in **Table 5.11**. The migratory-insertion reaction when $P(p\text{-FC}_6\text{H}_4)_3$ and PPh_3 were used showed similar rate constants with all Mo complexes. Both $P(p\text{-MeC}_6\text{H}_4)_3$ and $P(p\text{-MeOC}_6\text{H}_4)_3$ showed marked differences in rate constants with the various Mo complexes.

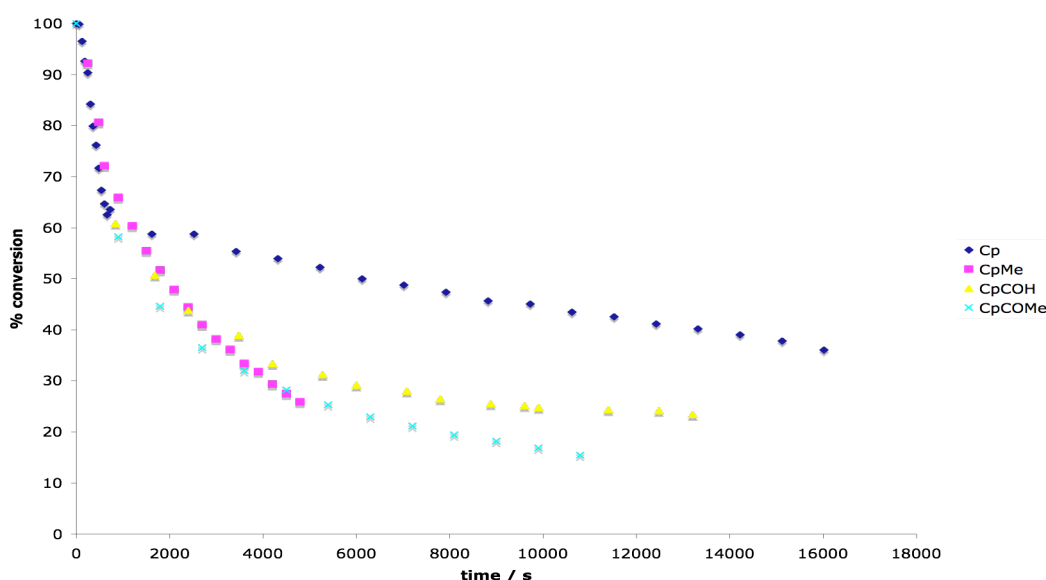


Figure 5.25: The conversion graph for the migratory-insertion reaction between $(CpR)Mo(CO)_3Me$ ($R = H, Me, CHO, COMe$) and $P(p\text{-FC}_6\text{H}_4)_3$ in a 1:10 molar ratio at 40 °C.

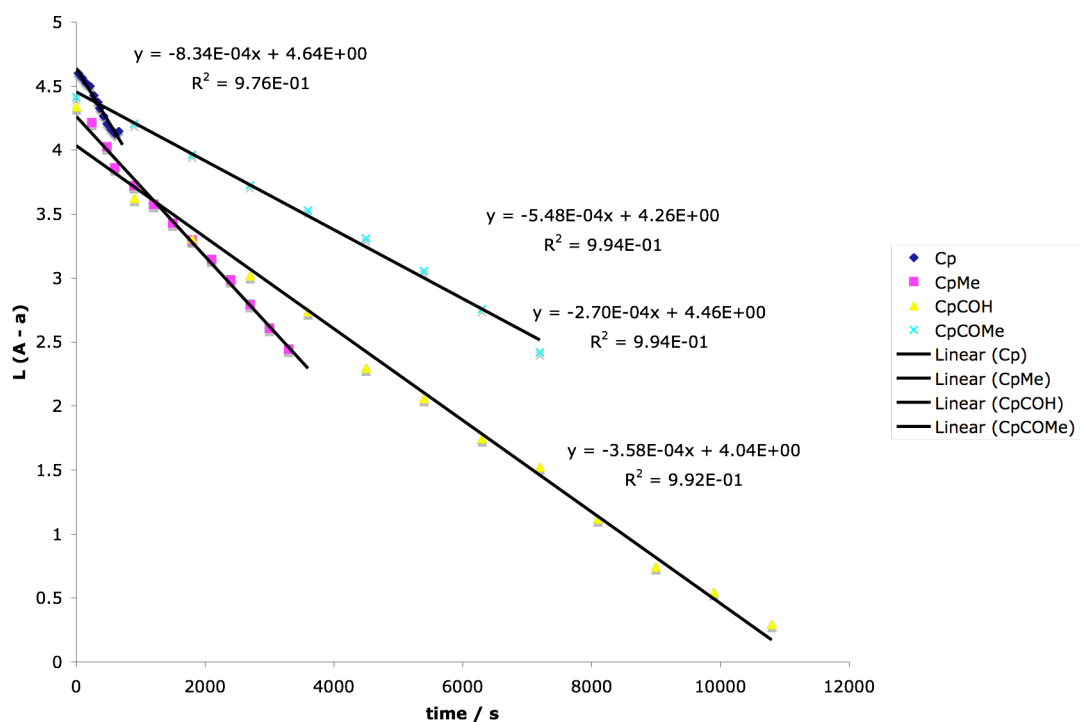


Figure 5.26: The rate plots for the migratory-insertion reaction between (CpR)Mo(CO)₃Me (R = H, Me, CHO, COMe) and P(*p*-FC₆H₄)₃ in a 1:10 molar ratio at 40 °C.

Table 5.11: The rate constants for the migratory-insertion reaction of (CpR)Mo(CO)₃Me (R = H, Me, CHO, COMe) with ligand, L (L = P(*p*-OMeC₆H₄)₃, P(*p*-FC₆H₄)₃, P(*p*-MeC₆H₄)₃, PPh₃), at 40 °C with a 1:10 molar ratio

$\begin{matrix} \text{R} \\ \text{L} \end{matrix}$	H / k x10 ⁻³	Me/ k x10 ⁻³	COH/ k x10 ⁻³	COMe/ k x10 ⁻³
P(<i>p</i> -MeC ₆ H ₄) ₃	11.2 (97)	3.76 (93)	0.158 (99)	0.289 (99)
P(<i>p</i> -OMeC ₆ H ₄) ₃	10.9 (92)	2.24 (98)	0.069 (99)	0.314 (98)
PPh ₃	1.22 (98)	0.224 (99)	0.358 (99)	0.319 (99)
P(<i>p</i> -FC ₆ H ₄) ₃	0.753 (98)	0.518 (100)	0.358 (99)	0.248 (100)

The many results are discussed below according to the impact of the same cyclopentadienyl substituent group for the range of PR_3 ligands.

It is clear from this data that no simple explanation can be given for the rate constant data. The following points are to be noted.

- 1) In general, for a fixed phosphine the reaction with $\text{R} = \text{H}$ are fastest and typically reaction with $\text{R} = \text{Me}$ are faster than for $\text{R} = \text{COH}$ and COMe . Thus, small electron donating groups give faster reaction rates with size being more important than donation ability.
- 2) The reaction rates for a fixed phosphine and $\text{R} = \text{COMe}$ or COH show variable reaction rates with electron donating phosphines giving faster reactions for $\text{R} = \text{COMe}$ than for $\text{R} = \text{CHO}$. The reverse occurs for relatively stronger electron withdrawing phosphines.
- 3) For a fixed R group reactions with $\text{R} = \text{H} > \text{R} = \text{Me}$ (as discussed earlier). For COH and COMe the rates show tighter clustering, but with no clear trends. This would suggest that the contribution of steric and electronic effects are not independent variables

An attempt has been made to show these trends graphically in both 2D and 3D plots. For example **Figure 5.27** shows the plot of rate constant against the Tolman electronic parameter for the phosphine ligands. The data indicates a greater separation of rate constant for the electron donating phosphine ligands, since these rate constants varied greatly as with the different CpR-Mo complexes (see the distant points in **Figure 5.27** for $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$ and $\text{P}(p\text{-MeC}_6\text{H}_4)_3$) as

opposed to the little variation of rate constants for the electron-withdrawing ligand (see the close points in **Figure 5.27** for $P(p\text{-FC}_6\text{H}_4)_3$).

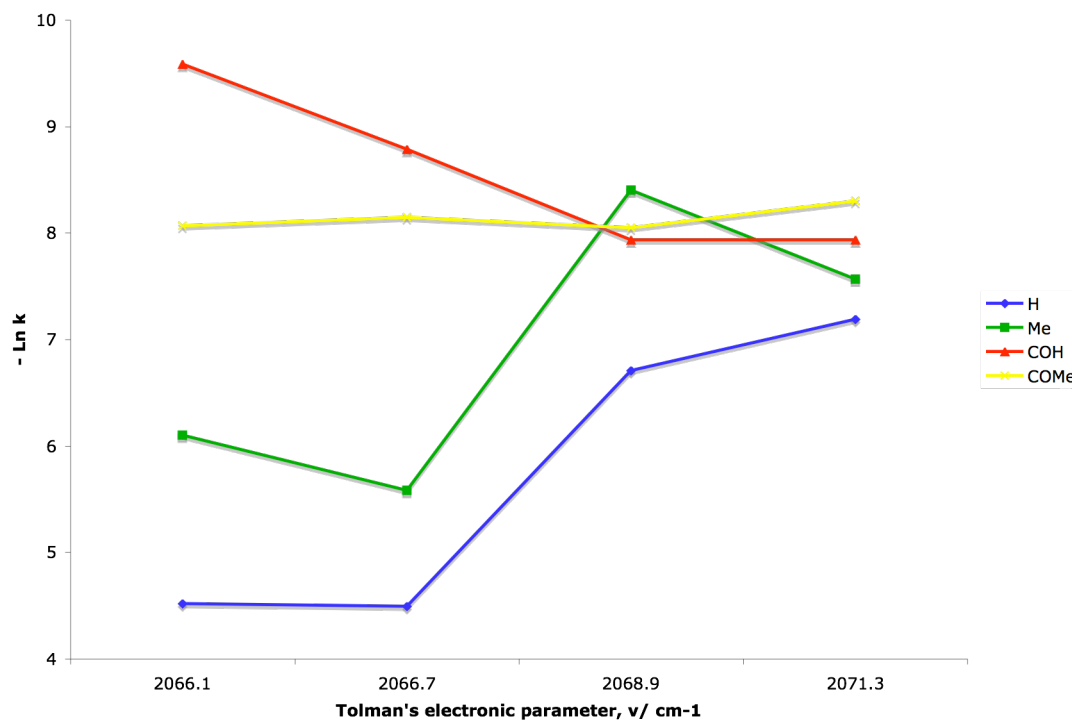


Figure 5.27: Graph of the rate constant for the reaction between $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$, ($\text{R} = \text{H}, \text{Me}, \text{COH}, \text{COMe}$) and L , against the electronic factor of L : $(P(p\text{-OMeC}_6\text{H}_4)_3 : 2066.1, (P(p\text{-MeC}_6\text{H}_4) : 2066.7, \text{PPh}_3 : 2068.9, P(p\text{-FC}_6\text{H}_4)_3 : 2071.3)$

A 2D plot of pK_a of the phosphine against the rate was plotted (**Figure 5.28**).

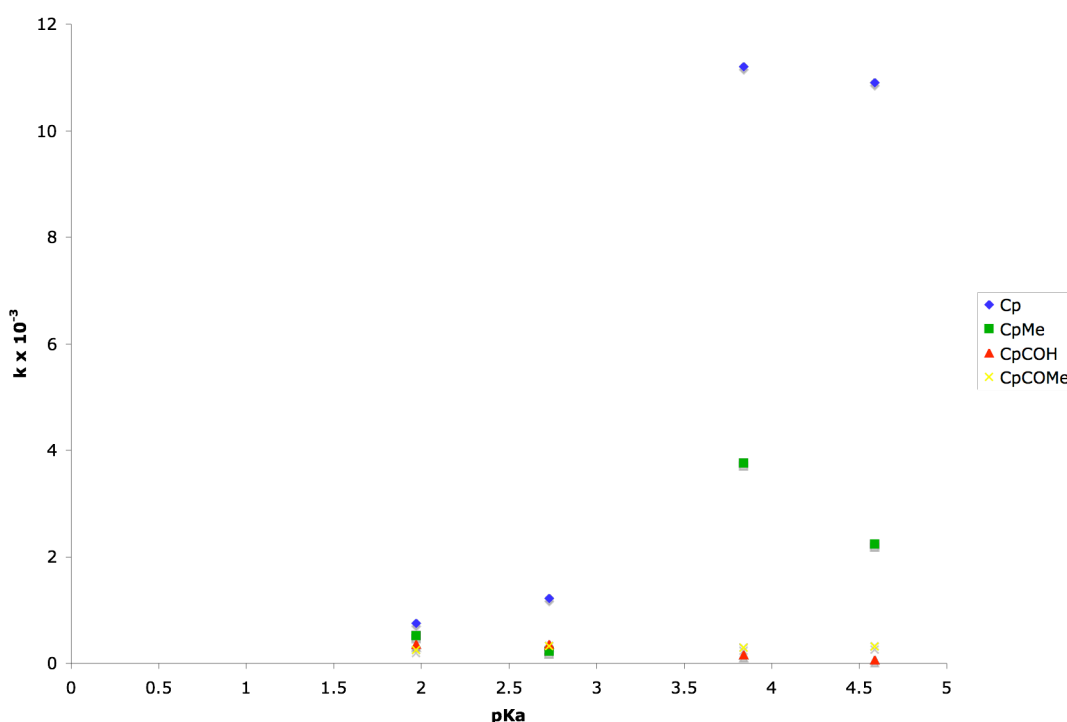


Figure 5.28: Graph of $k \times 10^{-3}$ (rate constant for insertion reaction) against the pK_a of phosphines (1.79 - $P(p\text{-FC}_6\text{H}_4)_3$, 2.73 - PPh_3 , 3.84 - $P(p\text{-MeC}_6\text{H}_4)_3$, 4.59 - $P(p\text{-OMeC}_6\text{H}_4)_3$)

Relatively higher rates of reaction are observed for the reactions between more basic phosphine ligands ($P(p\text{-MeC}_6\text{H}_4)_3$ and $P(p\text{-OMeC}_6\text{H}_4)_3$) and the unsubstituted and methyl-substituted Cp metal complexes. Also these particular phosphine ligands are electron withdrawing. The aforementioned metal complexes, have only H or Me attached to the Cp rings, which as stated before, have little steric hindrance (owing to the relative size of the substituents). The Me group only has a weak electron donating ability, while H has no relative effect. The electron donating ligand ($P(p\text{-FC}_6\text{H}_4)_3$) and the reference ligand (PPh_3), show very low reaction rates.

Reactions with the COH- and COMe-substituted Cp metal complexes show very little change in rate, and the reactions are also independent of the basicity or the electron withdrawing / donating ability of the phosphine ligand.

Henderson *et al.*, used the Taft equation, $\log k$ against σ^* (σ^* represents the Taft parameter), to indicate if there were steric effects, resonance effects or changes in hybridization when any deviation from a straight line was observed.⁴⁸ This plot (found in **Appendix A5**) was observed to be similar to the plot of k versus the Tolman electronic parameter above (**Figure 5.26**), thus indicating the existence of steric effects.

The plot of the Tolman cone angle for the ring substituent, R and the $\nu(\text{CO})$ wavenumber for $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ (R = H, Me, COH, COMe) showed a direct correlation between them (see **Figure 5.29**). Tolman had used the $\nu(\text{CO})$ peak to estimate the Tolman electronic parameter (see above), thus this plot indicates the relationship between the electronic property of the Mo complex with the Tolman cone angle of the R group. **Figure 5.30** shows the plot of $\nu(\text{CO})$ against the rate of the migratory-insertion reaction.

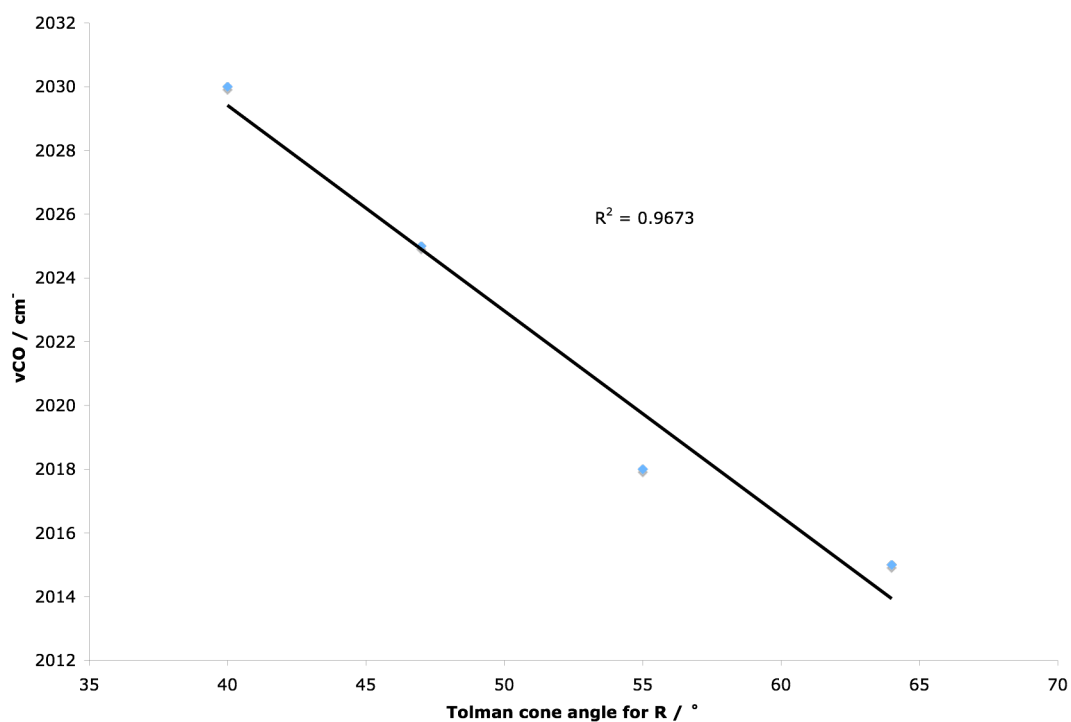


Figure 5.29: Graph of $\nu(\text{CO})$ of $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R} = \text{H}, \text{Me}, \text{COH}, \text{COMe}$) against the Tolman cone angle of R

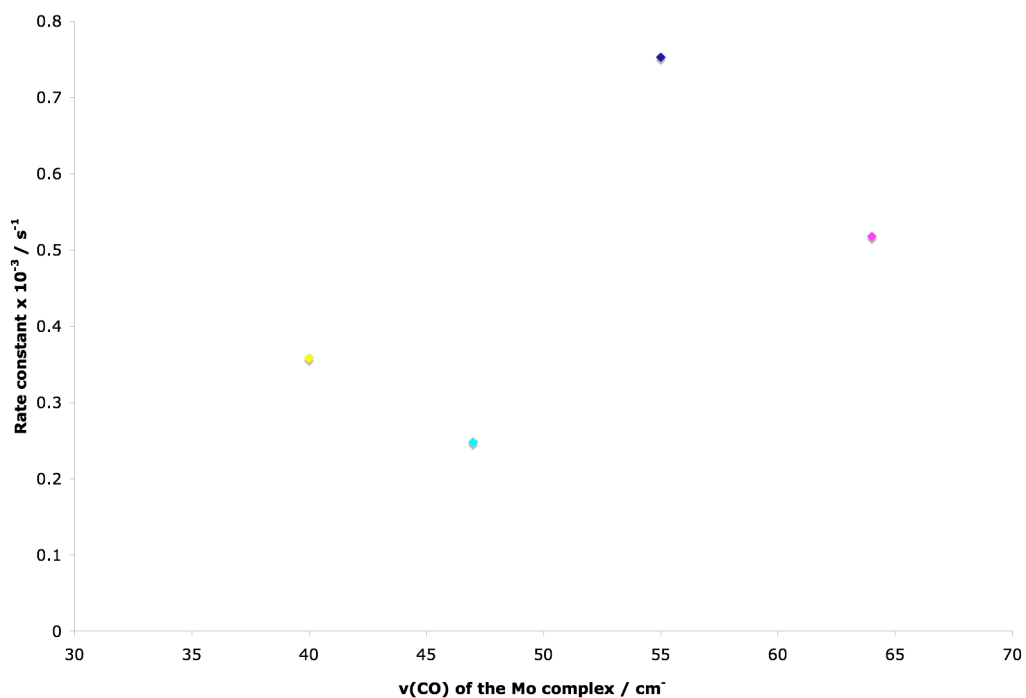


Figure 5.30: Graph of the of $\nu(\text{CO})$ of $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R} = \text{H}, \text{Me}, \text{COH}, \text{COMe}$) against the rate of the migratory-insertion reaction with $\text{P}(p\text{-FC}_6\text{H}_4)_3$.

A set of 3 dimensional graphs depicting both the steric and electronic effects on the rate of the migratory-insertion reaction of the $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R} = \text{H}, \text{Me}, \text{COH}, \text{COMe}$) and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ has also been attempted. **Figure 5.31** shows the 3D plot of activity versus Tolman cone angle versus the electronic effect for the Cp ring (for $\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$). 3D plots for other L can be found in **Appendix A6**.

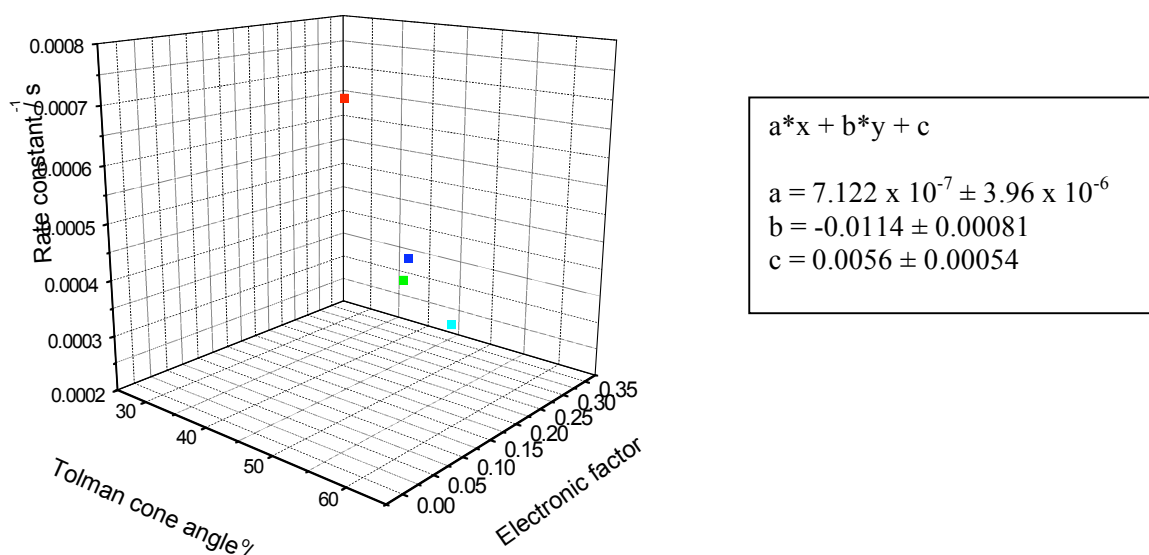


Figure 5.31: A 3D plot of the steric (Tolman cone angle) and electronic (F) effects of the R group on the rate of the migratory-insertion of $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R} = \text{H}, \text{Me}, \text{COH}, \text{COMe}$) and $\text{P}(p\text{-FC}_6\text{H}_4)_3$

Figure 5.31 shows that the rate of the reaction decreases as both the steric and electronic effects increase. Although, $\text{R} = \text{Me}$ and COMe have similar cone angles (see **Table 5.10**), the reaction decreases further owing to the increase in electronic effect from Me to COMe . This indicates that both electronic and steric effects of the R group are controlling the rate of the migratory-insertion reaction.

Using the correlation of the $\nu(\text{CO})$ to the electronic property of the Mo complex, another 3D plot was plotted to indicate the relationship between the electronic and steric properties of the Mo complex and the rate of the migratory-insertion reaction (see **Figure 5.32**). It is noted that the rate increased as the electronic and steric properties decreased.

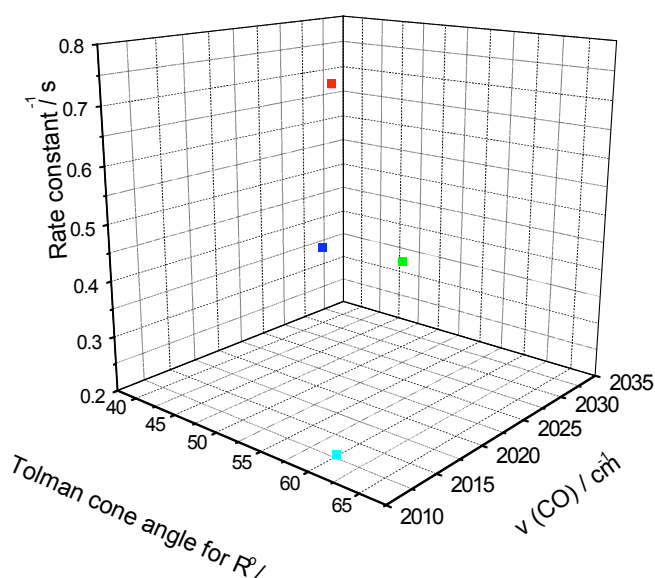


Figure 5.32: 3D plot of the Tolman cone angle of R versus the $\nu(\text{CO})$ of $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R} = \text{H}$, Me , COMe) and the rate of the migratory-insertion reaction of $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$

5.3.7 The correlation of rates with the melting points of reactants

The migratory-insertion reaction depends on a melt being formed. The melt formation is determined by the melting points of the ligands and the

(CpR)Mo(CO)₃Me complex. **Table 5.12** gives the melting points of the metal complexes and the various ligands used in the study. A plot of the rate of the reaction (of (CpR)Mo(CO)₃Me (R = H, Me, CHO, COMe) with ligand, L (L P(*p*-OMeC₆H₄)₃, P(*p*-FC₆H₄)₃, P(*p*-MeC₆H₄)₃, PPh₃), at 40 °C in a 1:10 molar ratio) against the melting point of the phosphine ligands was generated (**Figure 5.33**)

Interestingly, the order of the melting points decreases in the following order: P(*p*-MeC₆H₄)₃ > P(*p*-OMeC₆H₄)₃ > P(*p*-FC₆H₄)₃ > PPh₃, which is similar to the sequence observed for the migratory-insertion reaction of L with (CpMe)Mo(CO)₃Me.

Table 5.12: The melting points of the Mo complexes (starting material and some insertion products) and the various phosphine ligands

Metal complex	mp of metal complex / °C	Ligand	mp of ligand/ °C
CpMo(CO) ₃ Me	100	P(<i>p</i> -MeOC ₆ H ₄) ₃	120
(CpMe)Mo(CO) ₃ Me	50-51	P(<i>p</i> -MeC ₆ H ₄) ₃	145
(CpCHO)Mo(CO) ₃ Me	106-110	P(<i>p</i> -FC ₆ H ₄) ₃	80
(CpCOMe)Mo(CO) ₃ Me	82-85	PPh ₃	78
CpMo(CO) ₂ [P(<i>p</i> -MeOC ₆ H ₄) ₃]COMe	173-175		
(CpMe)Mo(CO) ₂ [P(<i>p</i> -MeOC ₆ H ₄) ₃]COMe	153-155		
(CpMe)Mo(CO) ₂ [PPh ₃]COMe	125-127		
CpMo(CO) ₂ [P(<i>p</i> -FC ₆ H ₄) ₃]COMe	143-145		

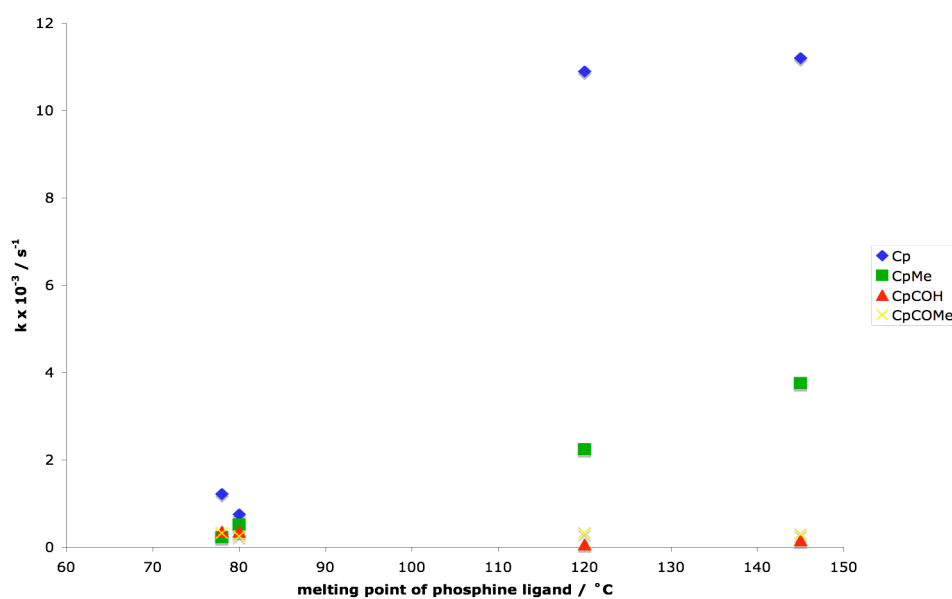


Figure 5.33: The graph of the rate constant against the melting point of the phosphine ligand

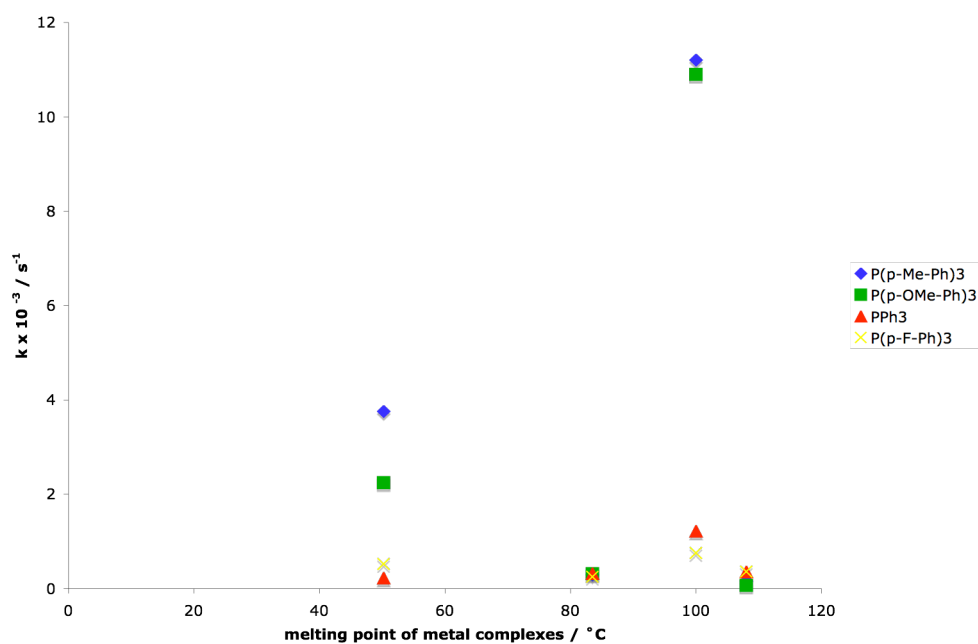


Figure 5.34: The graph of the rate constant against the melting point of the Mo complex, (CpR)Mo(CO)₃Me (R = H, Me, CHO, COMe).

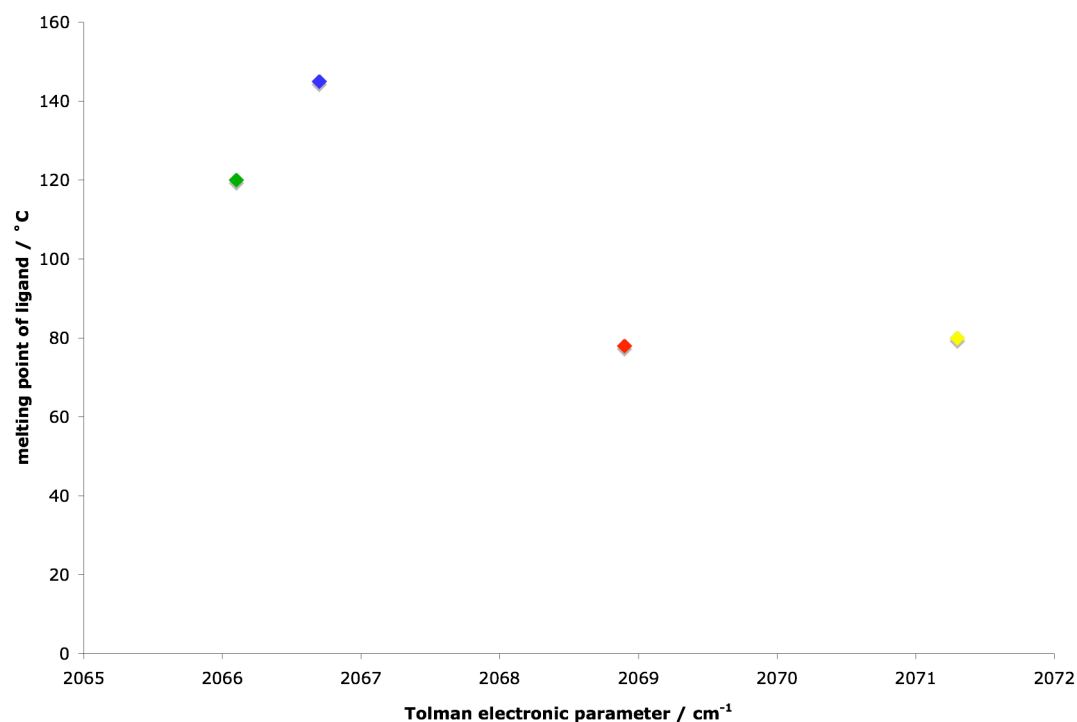


Figure 5.35: Graph of the melting point of phosphine ligand against the respective Tolman electronic parameter.

The following points are indicated from the above graphs:

- 1) Only the methyl-substituted Cp metal complex, which has the lowest melting point of the metal complexes used, showed an increased rate of reaction as the melting point of the ligand increased. Since it has the lower melting point of the two reactants, it melts first to facilitate the reaction.
- 2) Both the COH- and COMe-substituted Cp metal complexes show no dependence on the melting point of the ligand. Also it is important to note that these are relatively the slowest reaction rates.

- 3) The rate of the reaction increases for the unsubstituted Cp metal complex with ligands having melting points higher than 80 °C.
- 4) All metal complexes showed low reaction rates with the two lowest melting phosphines, PPh₃ and P(*p*-FC₆H₄)₃.

Thus, according to the DRIFTS study there appears to be no correlation of the melting point of the phosphine ligand and the rate of the migratory-insertion reaction.

5.3.8 Proposed mechanism for the migratory-insertion reaction:

An electron donating substituent on the phenyl group on the phosphine donates electron density to the phosphorous atom. This then interacts with the electrophilic site, namely the metal atom in the metal complex. Thus when the two reactants “touch” this interaction can occur, facilitated by the melt process. After interaction occurs the bond between the Mo and alkyl group weakens, allowing the alkyl migration to the -CO group to take place, followed by attachment of the ligand to the electron deficient metal. Therefore, the rate of migratory-insertion reaction would be faster when the ligand is more nucleophilic.

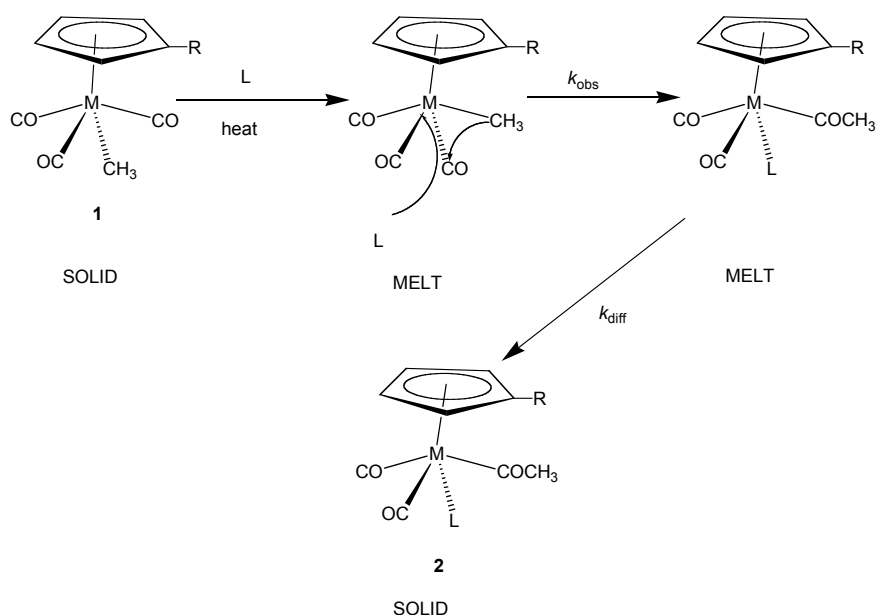
Since an electron withdrawing substituent on the phenyl group, withdraws electron density away from the ring centre, it makes the phosphorus electron

deficient. Thus, it interacts with the nucleophilic sites on the metal complex. This interaction leads to the melt process and to the weakening of the Mo-alkyl bond.

In addition, the interaction is slow when it involves an electron withdrawing substituent, such as $R = \text{COMe}$, on the Cp ring and the reaction is relatively faster if $R = \text{Me}$. If R is electron donating it adds electron density to the Cp ring. This strengthens the Cp-Mo bond and permanently weakens the Mo-Me and Mo-CO bonds. When the phosphine interacts with the metal complex, the already weak bond between Mo-alkyl breaks, allowing for a faster rate of alkyl migration. Similarly, if R is electron withdrawing, the Cp ring is electron deficient, weakening the Cp-Mo bond. When the phosphine interacts with the metal complex, the rate of alkyl migration is very slow.

Steric effects associated with R also can be important. The size of R i.e. the cone angle associated with the ring substituent may control the access to the reaction site on the metal. It has been observed that a larger group, like $R = \text{COMe}$ and CHO , have slower reaction rates when compared to $R = \text{H}$ and Me , which have faster reaction rates.

Another important issue is the occurrence of the melt that can only occur when the Mo complex and the phosphine ligand “touch”. The occurrence of the melt is imperative for the migratory-insertion reaction to take place. The insertion product solidifies out of the melt, which is depicted in the reaction mechanism (**Scheme 5.4**).



Scheme 5.4: Proposed mechanism for the migratory-insertion reaction of $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ and $\text{L} = \text{phosphine}$.

5.3.9 Investigation of the effect of the diluent in the DRIFTS analysis for the migratory-insertion reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and phosphine ligand, $\text{P}(p\text{-FC}_6\text{H}_4)_3$

A reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (1:1, 50 °C) was used to evaluate the effect of diluents on the reaction. At 50 °C, the reactants are in the melt and thus the solid diluent can act to modify the interaction between the reactants in the melt phase. The summarized data are shown in **Table 5.13**. An example of a rate plot can be found in **Appendix A7**.

Table 5.13: Reaction between $\text{CpMo}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (1:1, 50 °C)

Diluent	$k \times 10^{-4} / \text{s}^{-1}$
K_2SO_4	0.821
Na_2SO_4	1.63
Al_2O_3	2.29
KCl	2.67
NaCl	3.14
CaSO_4	3.46
CaO	3.66
KI	5.01
Sucrose	5.21
KBr	6.36
Silica	10.5
MgO	11.7

The data obtained show a dependence of the rate of the reaction on the type of diluent used. MgO and silica gave the fastest rates ($1.17 \times 10^{-3} \text{ s}^{-1}$ and $1.05 \times 10^{-3} \text{ s}^{-1}$, respectively).

A similar study of diluents on the CO substitution reaction of $\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{Br}$ with PPh_3 (1:19 mol ratio) at 70 °C resulted in the following sequence of data (in decreasing order): $\text{SiO}_2 > \text{Sucrose} > \text{Al}_2\text{O}_3 > \text{TiO}_2 > \text{NaNO}_3 > \text{Na}_2\text{CO}_3 > \text{NaC}_2\text{H}_3\text{O}_2 > \text{Na}_2\text{SO}_4 > \text{NaNO}_2 > \text{KBr}$.³² The data showed that when silica (which is weakly acidic), was used as the diluent, the reaction had the fastest rate. However in our study SiO_2 (weakly acidic) and MgO (basic) gave the fastest reactions suggesting that acidity / basicity properties were not important in the reactions.

The slowest rate was recorded when K_2SO_4 and Na_2SO_4 were used as diluents. Next, alumina, a network solid, gave a slower reaction rate than the Group 1 chlorides (KCl and NaCl). It can be seen that the Group 1 chlorides reacted faster than Group 1 sulphates, and that Na salts gave faster rates than K salts for both groups of salts. In the oxide group, $\text{MgO} > \text{CaO}$. A common feature is that the rate of the reaction decreases as the element in the periodic table increases in atomic mass down a group.

Irrespective as the reason for these effects, the data in **Table 5.13** shows that the diluent has an influence on the rate of the reaction. This provides a way of controlling the reaction rate. The following conclusions can be drawn from **Table 5.13**.

- 1) Acidity / basicity of diluent does not play a role in the rate.
- 2) Interactions, such as hydrogen-bonding and van der Waal's forces between the diluent and the reactants and product are significant. The high rate constant observed the reaction with sucrose as the diluent, attests to this statement.

5.4 Conclusions

A successful study of the migratory-insertion reaction between $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R} = \text{H}, \text{Me}, \text{CHO}, \text{COMe}$) with ligand, L ($\text{L} = \text{P}(p\text{-OMeC}_6\text{H}_4)_3, \text{P}(p\text{-FC}_6\text{H}_4)_3,$

$P(p\text{-MeC}_6\text{H}_4)_3$, PPh_3) was done by DRIFTS. The migratory-insertion reactions studied were influenced by the temperature of the reaction and molar ratio of the reactants. Problematic data were explained by optical microscopy studies that revealed that the migratory-insertion reaction under study was a melt phase reaction. A eutectic melt formed for all reactions between $\text{CpMo(CO)}_3\text{Me}$ and the phosphines at $T > 40\text{ }^\circ\text{C}$. For reactions that occurred at $T = 40\text{ }^\circ\text{C}$, complexities in the reactions were noted.

Additionally, the type of ligand and the substituent attached to the Cp-ring controlled the rate of the migratory-insertion both sterically and electronically. Considering a fixed phosphine ligand, the reactions with small electron donating groups, like $R = \text{H}$ displayed faster reaction rates with size being more important than donation ability. Electron donating phosphines gave faster reaction rates for $R = \text{COMe}$ than for $R = \text{COH}$, while the reverse was true for strong electron withdrawing phosphines. Additionally, for fixed R groups the reaction rate was faster for $R = \text{H}$ (smaller in size and electron donation) than $R = \text{Me}$, while $R = \text{COH}$ and COMe showed no clear trends.

Thus, the combination of both steric and electronic effects of both the phosphine ligand and the ring substituent, R controlled the rate of the migratory-insertion reaction.

It was also found that different diluents used in the DRIFTS study affected the rate of the reaction, namely K_2SO_4 gave the slowest rate constant, while MgO

gave the fastest rate constant, both used in separate reactions between $\text{CpMo(CO)}_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$.

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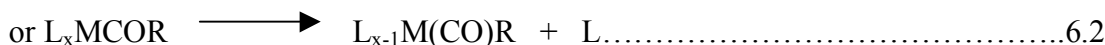
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CHAPTER 6: THE USE OF DRIFTS TO STUDY THE SOLVENT-FREE DECARBONYLATION REACTION OF Mo COMPLEXES

6.1 Introduction

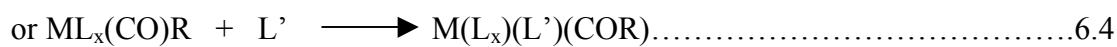
Decarbonylation is termed the reverse of a migratory-insertion reaction.¹ It involves the conversion of a metal-acyl complex to a metal-alkyl complex as shown below:



Manske who was investigating the synthesis of morphine first reported this type of reaction in the literature in 1931.² The importance of the reaction is that it provides a method for shortening a carbon-containing moiety by one carbon atom. In the decarbonylation reaction the metal oxidation state and the coordination number to not change. The reaction is known for many metals and can also involve removal of entities other than CO in a metal complex e.g. CO_3^{2-} and H_2O .¹

The starting metal acyl complex can be synthesized either from a metal and an acyl complex or by a migratory-insertion reaction of CO into a metal-alkyl complex as described in **Chapter 5**, for e.g.

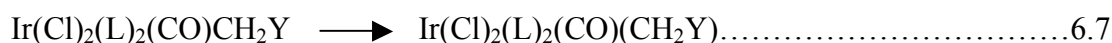




The latter reaction suggests that the mechanism for the decarbonylation reaction could involve the reverse of the CO insertion / alkyl migration reaction. The decarbonylation reaction tends to be a facile process and in many reports it is apparent that the product formed was produced accidentally while investigating the migratory-insertion reaction³⁻⁶,



Note that the decarbonylation reaction can produce a different product to the starting complex, that underwent the migratory-insertion reaction if $\text{L} \neq \text{CO}$. Kubota studied the decarbonylation of a range of Ir(III) complexes, which underwent the following reaction⁷:



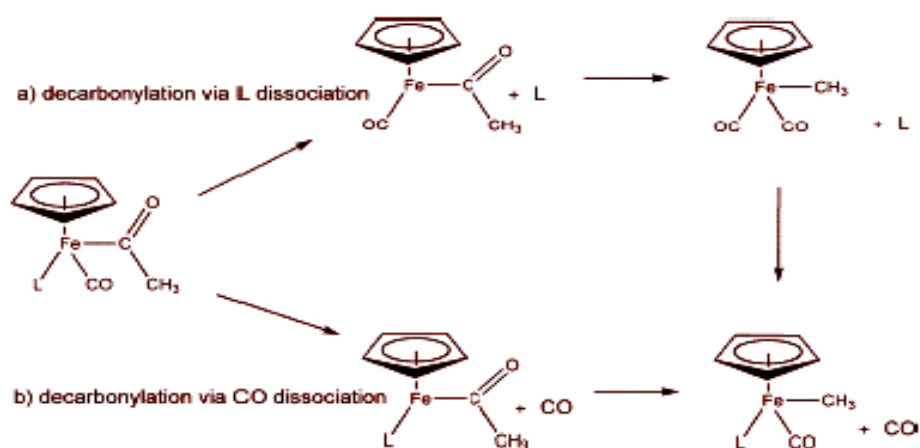
where $\text{Y} = \text{C}_6\text{H}_6, p\text{-CH}_3\text{OC}_6\text{H}_4, p\text{-CH}_3\text{C}_6\text{H}_4, p\text{-O}_2\text{NC}_6\text{H}_4, \text{C}_6\text{F}_5$ and the decarbonylation took place in the temperature range 30 – 40 °C in various solvents, like benzene.⁷ An important observation was the finding that electron withdrawing groups slowed the process, while electron-donating groups promoted the reaction since the rate decreased in the following manner according to Y: $\text{C}_6\text{H}_6 > p\text{-CH}_3\text{OC}_6\text{H}_4 > p\text{-CH}_3\text{C}_6\text{H}_4 > p\text{-O}_2\text{NC}_6\text{H}_4 \gg \text{C}_6\text{F}_5$.⁷

Yih and Lin have investigated the decarbonylation reaction of $[\text{Et}_4\text{N}][\text{Mo}(\text{CO})_5(\text{PPh}_2\text{CS}_2)]$.⁸ This compound was dissolved in CH_3CN . The solution was stirred at room temperature and the reaction monitored by IR spectra. After stirring the IR spectrum indicated that the starting material was completely consumed to give the decarbonylated product, $[\text{Et}_4\text{N}][\text{Mo}(\text{CO})_4(\text{PPh}_2\text{CS}_2)]$ as shown in the equation below⁸:



The authors studied the reaction in different solvents and found that reaction were more rapid in CH_3CN than in CH_2Cl_2 , and hence that the donor ability of the solvent was important.⁸

In a recent study Llewellyn *et al.* showed that the complex $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{IMes})(\text{CO})(\text{COMe})]$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) decarbonylated over time in solvent at room temperature, but that the related complex $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{PPh}_3)(\text{CO})(\text{COMe})]$ was stable with respect to decarbonylation at temperatures of up to about 100 °C.⁹ Two generalized mechanisms for the reaction are shown below (**Scheme 6.1**) for $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{L})(\text{CO})(\text{COMe})]$.⁹



Scheme 6.1: The two mechanisms proposed for the decarbonylation reaction⁹

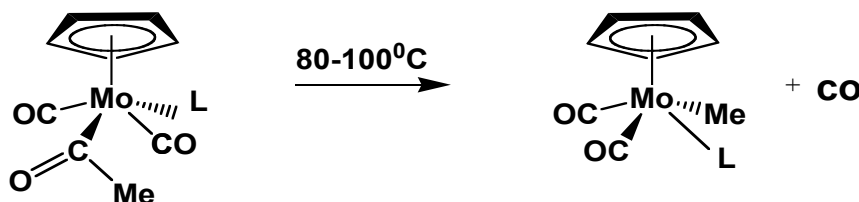
The mechanism that was consistent with their investigations of the compound $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{PPh}_3)(\text{CO})(\text{COMe})]$ was that the thermal decarbonylation process ($\sim 98\text{ }^\circ\text{C}$) occurred *via* the dissociation of PPh_3 to give $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{Me})]$.⁹

In all earlier studies the decarbonylation reaction has been studied in a solvent.

In **Chapter 5**, the migratory-insertion reaction between $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R} = \text{H}, \text{Me}, \text{COH}, \text{COMe}$) and L ($\text{L} = \text{P}(p\text{-OMeC}_6\text{H}_4)_3, \text{P}(p\text{-FC}_6\text{H}_4)_3, \text{P}(p\text{-MeC}_6\text{H}_4)_3, \text{PPh}_3$) was studied under solvent-free conditions using the DRIFTS technique. It was noted that in some of the reactions performed at high temperature and after long reaction times that some decarbonylation of the acyl complex had occurred at the higher temperatures ($60\text{ }^\circ\text{C}$). It was this that made it easier to study this reaction by DRIFTS at high temperatures.

The aim of this study was to perform the solvent-free decarbonylation reaction of $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{R} = \text{H}, \text{Me}, \text{CHO}, \text{COMe}$ and $\text{L} = \text{PPh}_3, \text{P}(p\text{-OMeC}_6\text{H}_4)_3,$

$P(p\text{-FC}_6\text{H}_4)_3$ and $P(p\text{-MeC}_6\text{H}_4)_3$) (**Scheme 6.2**) using DRIFTS. The reactions were monitored by varying reaction conditions, such as the reaction temperature and the nature of the ring substituent, R and the inserted ligand, L.



Scheme 6.2: The decarbonylation reaction of $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{R} = \text{H}, \text{Me}, \text{CHO}, \text{COMe}$ and $\text{L} = \text{PPh}_3, \text{P}(p\text{-OMeC}_6\text{H}_4)_3, \text{P}(p\text{-FC}_6\text{H}_4)_3, \text{P}(p\text{-MeC}_6\text{H}_4)_3$)

6.2 Experimental

6.2.1 DRIFTS study of the decarbonylation reaction

$(\text{CpR})\text{Mo}(\text{CO})_3\text{CH}_3$ ($\text{R} = \text{H}, \text{Me}, \text{CHO}, \text{COMe}$), hereafter referred to as the Mo complex, was synthesized as discussed in **Chapter 3**. The solid phosphines were obtained from Sigma-Aldrich and Strem Chemicals.

6.2.1.1 Sample Preparation for DRIFTS analysis

The Mo complex (0.01 - 0.02 g) was mixed in KBr (1.0 g) to produce a 1 - 2 % starting material in KBr and, this material acted as a reference material. Similarly,

the solid phosphine (0.01 g - 0.4 g) was mixed with 1 - 2 g KBr to produce 1 - 20 % ligand in KBr.

The components were ground together separately in air using a mortar and pestle for ≈ 10 minutes to achieve a particle size in the range of 60 – 80 μm .

6.2.2.2 Steps in the Analysis process

The same procedure as described in **Chapter 5** was used to generate the starting material for the decarbonylation reaction. These steps are described here for completeness.

1. Equal amounts (≈ 5 mg) of finely ground KBr and ligand/KBr sample were mixed together in a vial using a micro spatula.
2. A background spectrum was recorded.
3. Equal amounts of a ligand/KBr sample were quickly mixed with the starting material/KBr sample.
4. The mixture was placed in the DRIFTS cell.
5. The mixed sample was heated to 50 $^{\circ}\text{C}$ to generate the product $\text{CpMo}(\text{CO})_2(\text{L})\text{COMe}$.
6. Once the migratory-insertion reaction was complete (observed by the disappearance of the 2020 cm^{-1} absorption peak), the sample in the cell was heated to the required temperature.

7. IR spectra were then recorded as a function of time at pre-set time intervals.

6.2.2 Investigation of the effect of temperature on the decarbonylation reaction of $\text{CpMo(CO)}_2(\text{L})\text{COMe}$, (L= $\text{P}(p\text{-FC}_6\text{H}_4)_3$ and $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$)

A mixture of 1 – 2 % powdered $\text{CpMo(CO)}_3\text{Me/KBr}$ and 1 – 20 % powdered $\text{P}(p\text{-FC}_6\text{H}_4)_3/\text{KBr}$ or $\text{P}(p\text{-OMeC}_6\text{H}_4)_3/\text{KBr}$, were mixed together in a 1:1 molar ratio. The mixture was then placed in the DRIFTS cell and temperatures of 50 °C for migratory-insertion to take place. Once the insertion Mo complex was produced, the temperature was elevated to the required temperature range of 80 - 100 °C and the IR spectra recorded at pre-set time intervals.

6.2.3 Investigation of the effect of ligand (L) and ring substituent, (R) on the decarbonylation reaction of $(\text{CpR})\text{Mo(CO)}_2(\text{L})\text{COMe}$ (R= H, Me, CHO, COMe) and L = $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, PPh_3

A mixture of 1 – 2 % powdered $\text{CpMo(CO)}_3\text{Me/KBr}$ and 1 – 20 % powdered L/KBr, (L = $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, PPh_3), were mixed together in a 1:10 molar ratio. The mixture was then placed in the DRIFTS cell at a temperature of 50 °C for migratory-insertion reaction to take place. Once the insertion Mo complex was produced, the temperature was elevated to the required temperature range of 80 - 100 °C and the IR spectra recorded at pre-set time intervals.

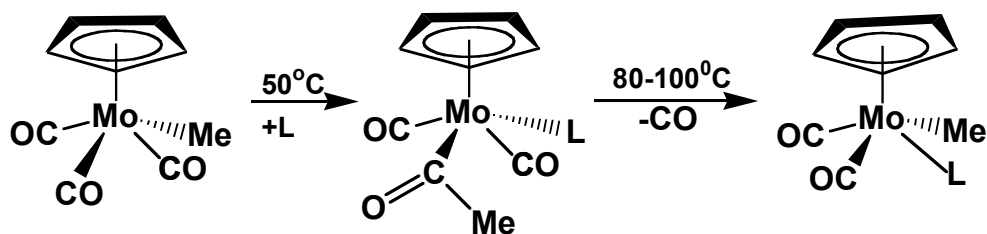
6.2.4 Use of photomicroscopy to study the decarbonylation reaction of $\text{CpMo(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ crystals.

Photomicroscopy was used to monitor the decarbonylation reaction. A digital camera, attached to an optical microscope was used to photograph the progression of the reaction as discussed in **Chapter 5**. Yellow needle-like crystals of $\text{CpMo(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ were placed into the heating block (on the optical stage) and positioned correctly to obtain favorable pictures. The heating block was closed and a flow of N_2 was introduced. The temperature of the block was set to 120 °C and the reaction was monitored by recording the progression of the reaction by digital photography. The apparatus used in the study was designed by Bogadi *et al.*¹⁰ and is shown **Figure 5.2** in **Chapter 5**.

6.3 Results and Discussion

6.3.1 DRIFTS study of the decarbonylation reaction

The reactants used for the decarbonylation reaction were synthesized by the migratory-insertion reactions described in **Chapter 5**. The insertion compounds that were generated *in situ* were all *trans* complexes. Thereafter, the decarbonylation reaction was investigated at an elevated temperature (**Scheme 6.3**).



Scheme 6.3: A general reaction scheme in which $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ underwent migratory-insertion, at 50 °C, to form $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$, ($\text{R} = \text{H}, \text{Me}, \text{COH}$ and COMe ; $\text{L} = \text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, PPh_3), and then decarbonylation, (80 - 100 °C) to form $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{Me}$.

The migratory-insertion was monitored by following the disappearance of the $\sim 2020 \text{ cm}^{-1}$ peak and the appearance of the $\sim 1600 \text{ cm}^{-1}$ peak (see **Figure 6.1**). The temperature of the IR cell was then elevated (80 - 100 °C) and the decarbonylation reaction was then monitored. The end of decarbonylation was signaled by the total disappearance of the carbonyl peak at $\sim 1600 \text{ cm}^{-1}$ (see **Figure 6.1**)

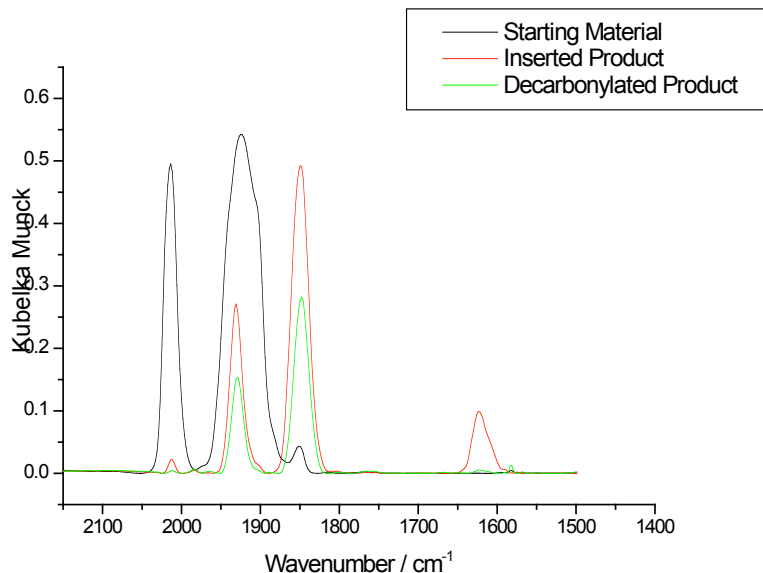


Figure 6.1: Spectra showing the starting material, $(\text{CpMe})\text{Mo}(\text{CO})_3\text{Me}$, the insertion product, $(\text{CpMe})\text{Mo}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ and finally the decarbonylated product, $(\text{CpMe})\text{Mo}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{Me}$.

The decarbonylation progress was easily monitored by DRIFTS, and a typical set of spectra is shown in **Figure 6.2**. In this instance the data was obtained for the reaction of $(\text{CpMe})\text{Mo}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ to form $(\text{CpMe})\text{Mo}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{Me}$.

This data was used to plot a conversion graph as shown in **Figure 6.3**. This was done by following the gradual disappearance of the $\sim 1600\text{ cm}^{-1}$ peak.

It was assumed that the reaction was first order and the conversion graph was used to plot the rate plot $(\ln A - a)$ against time) as displayed in **Figure 6.4**. This plot suggested that the rate could be approximated as a first order reaction. The rate constant for the reaction is given in **Table 6.1**.

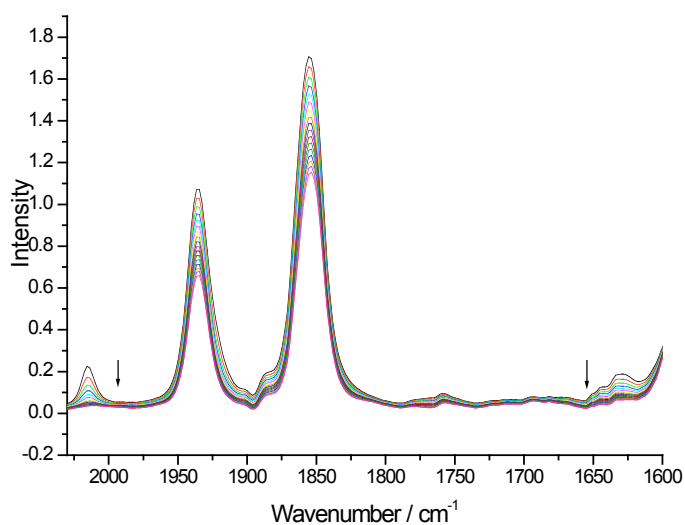


Figure 6.2: The DRIFTS spectra showing the decarbonylation of $\text{CpMo(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ to $\text{CpMo(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{Me}$ at 100 °C.

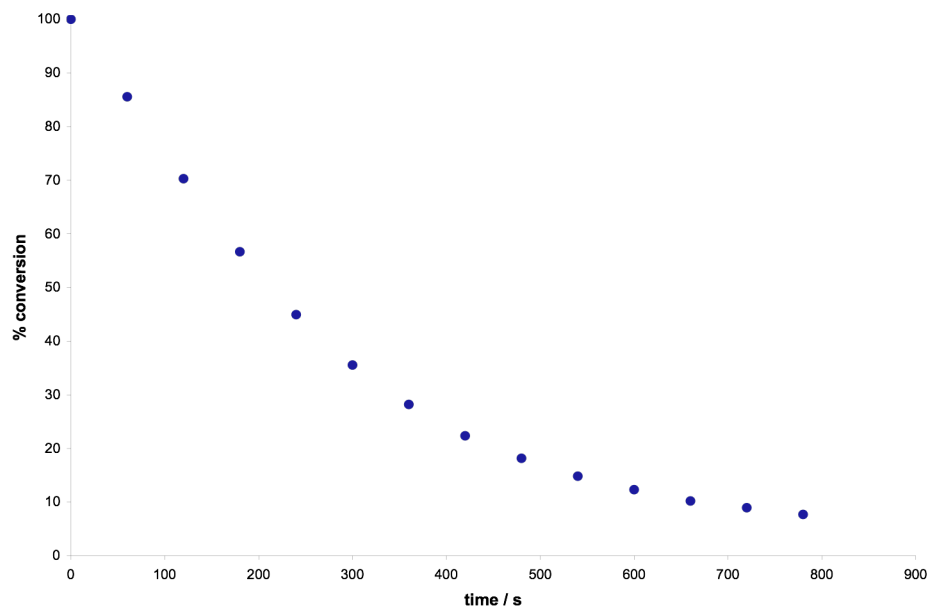


Figure 6.3: A typical conversion graph showing the % conversion of $(\text{CpMe})\text{Mo(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ to the decarbonylated product, $(\text{CpMe})\text{Mo(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{Me}$ at 100 °C.

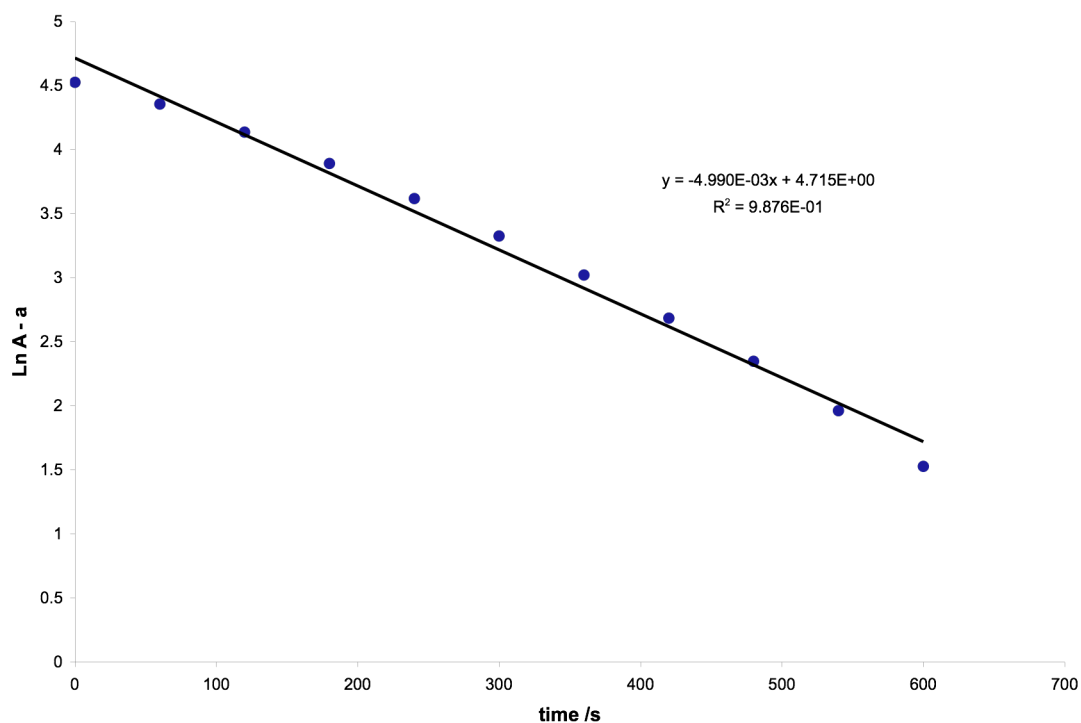


Figure 6.4: The rate plot of the decarbonylation of $(\text{CpMe})\text{Mo}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$.

6.3.2 Investigation of the effect of temperature on the decarbonylation of $\text{CpMo}(\text{CO})_2(\text{L})\text{COMe}$, ($\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$ and $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$)

Both an electron withdrawing, $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$, and an electron donating, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, phosphine ligand were chosen to investigate the effect of the reaction temperature on the decarbonylation reaction. The conversion plots are given in **Figures 6.6** and **6.8**. An attempt was made to plot the data as a first order reaction and the plots are shown in **Figure 6.7** and **Figure 6.9**. An attempt to obtain the activation energies from the Arrhenius plot (**Figure 6.10**) is given in **Table 6.1**.

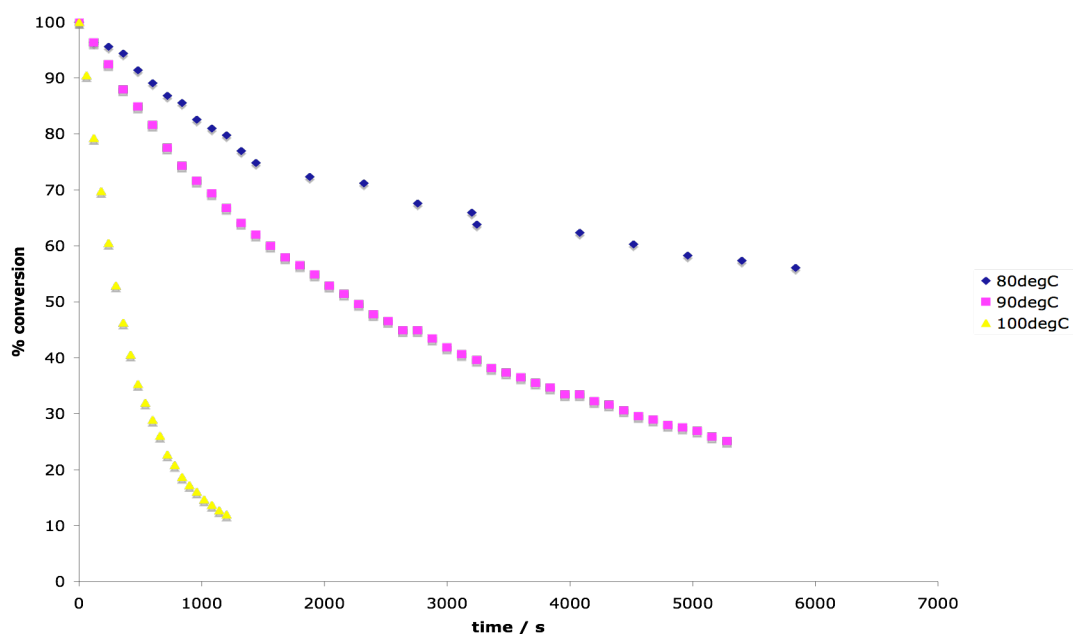


Figure 6.5: The conversion graph for the decarbonylation of $\text{CpMo(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COME}$ at varying temperatures.

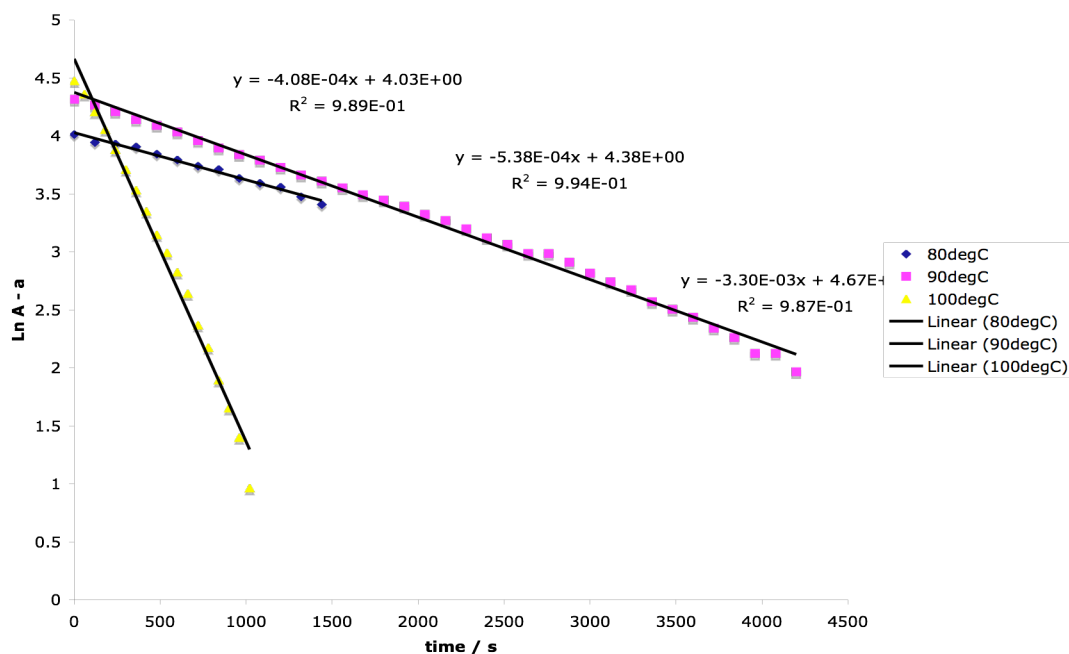


Figure 6.6: The first-order rate plots for the decarbonylation of $\text{CpMo(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COME}$ at varying temperatures.

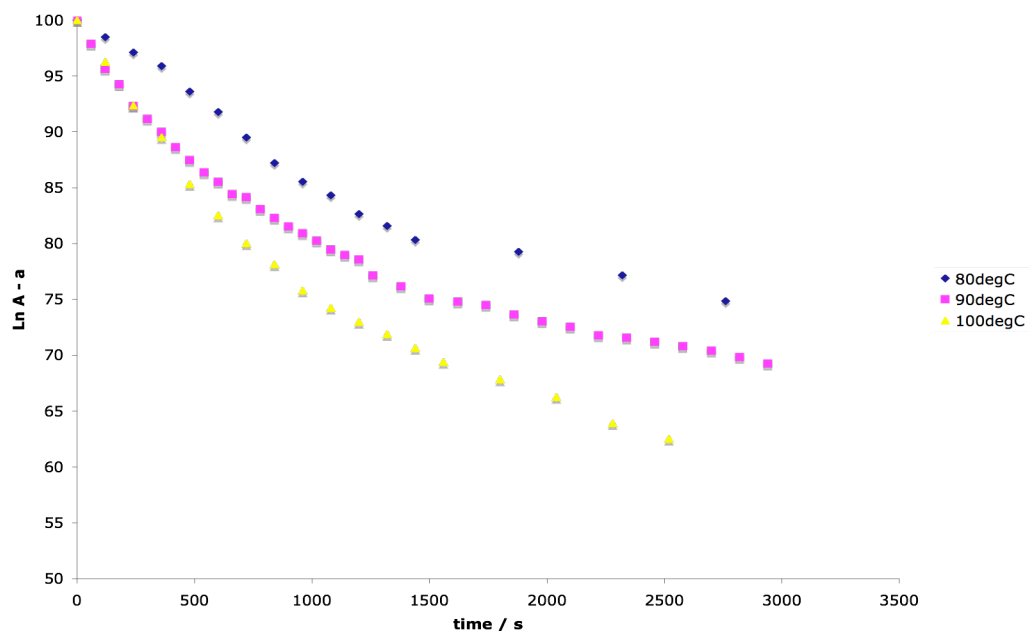


Figure 6.7: The conversion graphs for the decarbonylation of $\text{CpMo(CO)}_2[\text{P}(p\text{-MeOC}_6\text{H}_4)_3]\text{COMe}$ at varying temperatures.

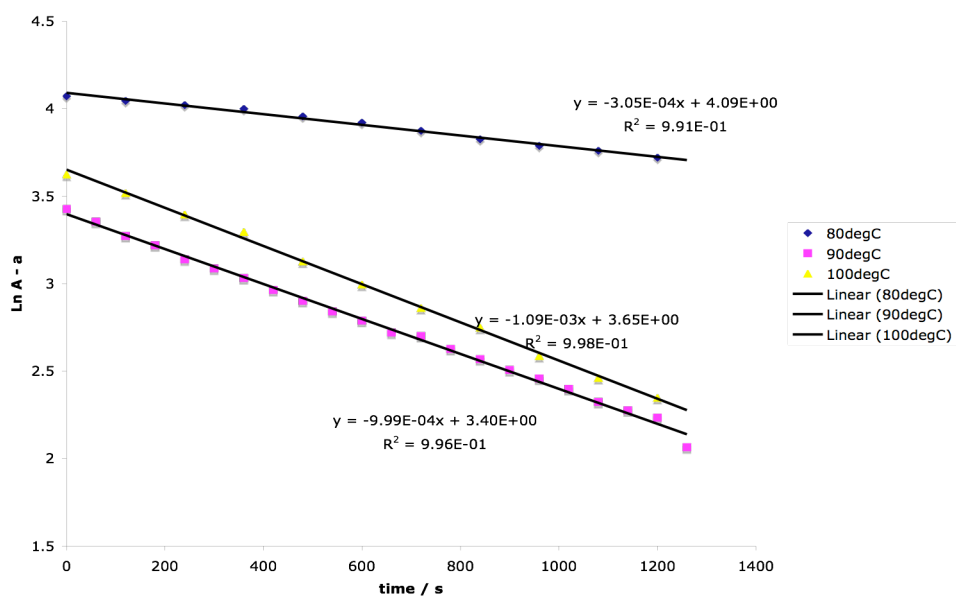


Figure 6.8: The first-order rate plots for the decarbonylation of $\text{CpMo(CO)}_2[\text{P}(p\text{-MeOC}_6\text{H}_4)_3]\text{COMe}$ at varying temperatures.

Table 6.1: Rate constants for the decarbonylation of $\text{CpMo(CO)}_2(\text{L})\text{COMe}$ ($\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$ and $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$) at varying temperatures.

Temp/ °C	$k[\text{P}(p\text{-FC}_6\text{H}_4)_3]/\text{s}^{-1}$	$k[\text{P}(p\text{-MeOC}_6\text{H}_4)_3]/\text{s}^{-1}$
80	4.08×10^{-4}	1.87×10^{-4}
90	5.28×10^{-4}	9.93×10^{-4}
100	33.0×10^{-4}	10.3×10^{-4}

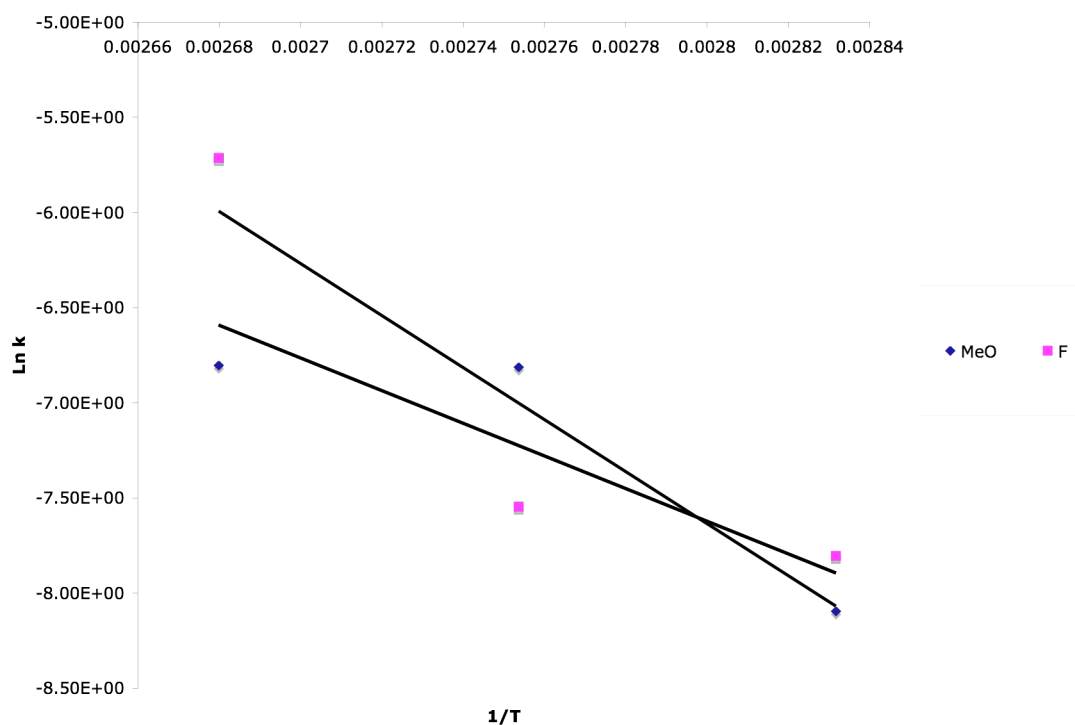


Figure 6.9: The activation energy plots for the decarbonylation reactions of $\text{CpMo(CO)}_2(\text{L})\text{COMe}$ ($\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$ and $\text{P}(p\text{-OMeC}_6\text{H}_4)_3$)

Comment on the study

The decarbonylation reaction observed in this study occurred in the absence of solvent. Both ligands, showed that as the temperature increased the rate of the decarbonylation reaction also increased.

- (1) At 80 °C ($L = P(p\text{-FC}_6\text{H}_4)_3$) the rate data appears to follow two pathways as indicated by the change in the rate profile at ~1500 s (**Figure 6.5**). For times < 1000 s a reasonable fit to a first order reaction plot for all temperatures is to be noted (**Figure 6.6**) but the activation energy plot (**Figure 6.9**) is poor.
- (2) The rate of the decarbonylation reaction when $L = P(p\text{-OMeC}_6\text{H}_4)_3$ is much slower than when $L = P(p\text{-FC}_6\text{H}_4)_3$. The rate data are also poor, especially at 80 °C (see **Figure 6.6**).
- (3) The activation energies for the decarbonylation reaction of $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($R = \text{H}$; $L = P(p\text{-OMeC}_6\text{H}_4)_3$ (electron-donating ligand), $P(p\text{-FC}_6\text{H}_4)_3$ (electron-withdrawing ligand)) are 67 and 114 kJmol^{-1} respectively.

In summary, while the reaction does occur at $T > 80\text{ }^\circ\text{C}$, the data appear to be complicated. At $T > 100\text{ }^\circ\text{C}$ better quality rate data are obtained, but this single set of data prevents measurement of activation energy parameters. An explanation for the poor quality data will be given below.

6.3.3 Investigation of the effect of ligand on the decarbonylation reaction of (CpR)Mo(CO)₂(L)COMe (R = H; L = P(*p*-OMeC₆H₄)₃, P(*p*-FC₆H₄)₃, P(*p*-MeC₆H₄)₃, PPh₃)

From the above study it was apparent that a reaction temperature of 100 °C gave rate data could be used for comparative purposes. Additional *para*-substituted phosphines were then studied to enlarge the database. The steric effect was kept constant while the electronic effects were varied. This is shown in **Table 6.2** where the Tolman electronic parameter is displayed.¹¹

Table 6.2: The Tolman electronic parameters¹¹ and the electron donating / withdrawing ability¹² of phosphine ligands used in this decarbonylation study

Phosphine ligand	Tolman Electronic parameter (ν) ¹¹ / cm ⁻¹	Electron donating / withdrawing ¹²
P(<i>p</i> -OMeC ₆ H ₄) ₃	2066.1	donating
P(<i>p</i> -MeC ₆ H ₄) ₃	2066.7	donating
PPh ₃	2068.9	reference ligand
P(<i>p</i> -FC ₆ H ₄) ₃	2071.3	withdrawing

The conversion graphs for the decarbonylation reactions of (CpR)Mo(CO)₂(L)COMe (R = H, and L = P(*p*-OMeC₆H₄)₃, P(*p*-MeC₆H₄)₃, PPh₃ and P(*p*-FC₆H₄)₃ at 100 °C are all shown in **Figure 6.10** and the corresponding rate plots are shown in **Figure 6.11**. A summary of the rate constants is also displayed in **Table 6.3**.

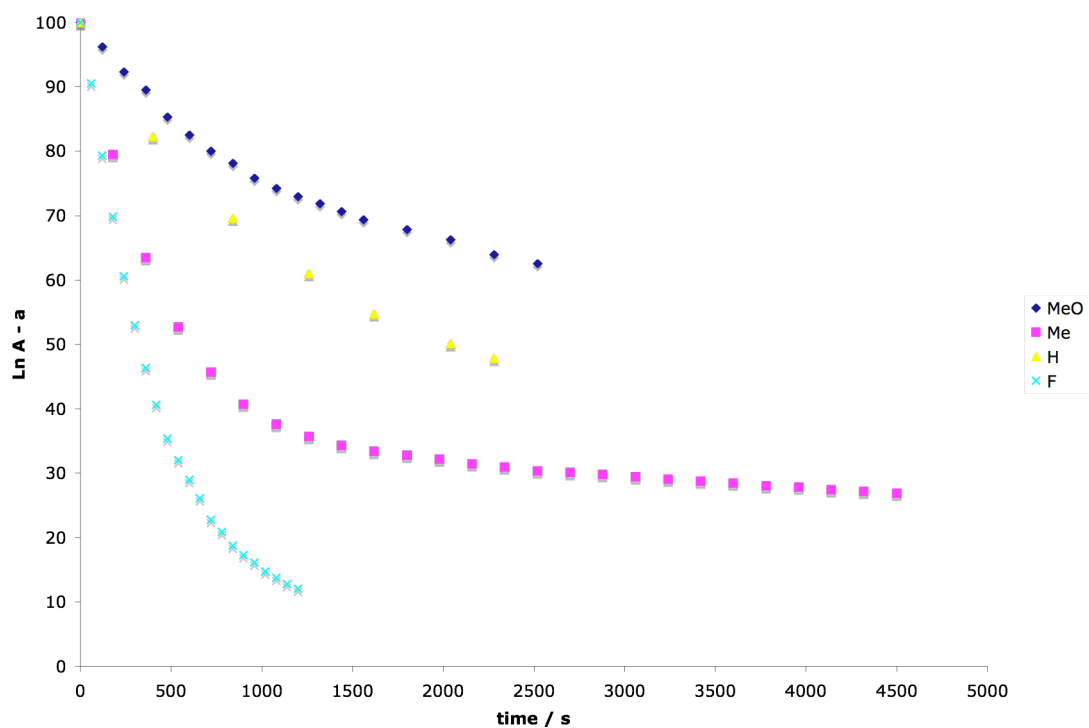


Figure 6.10: The conversion graphs for the decarbonylation of $\text{CpMo}(\text{CO})_2[\text{P}(p\text{-XC}_6\text{H}_4)_3]\text{COMe}$, where $\text{X} = \text{MeO}, \text{Me}, \text{H}$ and F at $100\text{ }^\circ\text{C}$.

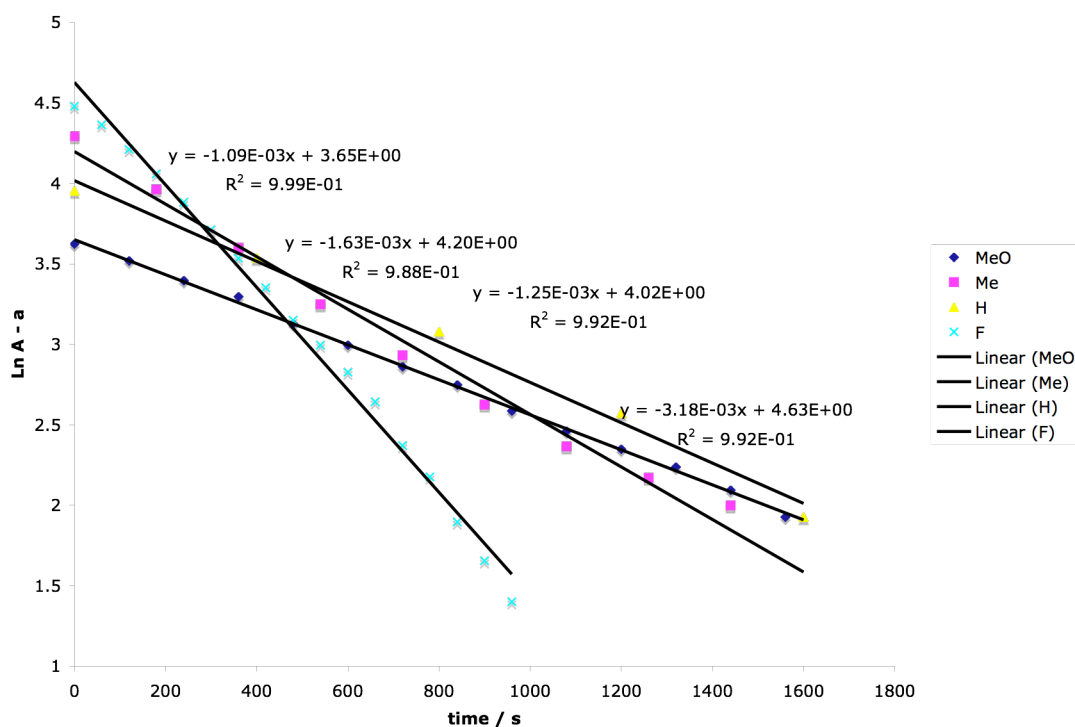


Figure 6.11: The first-order rate plots for the decarbonylation of $\text{CpMo(CO)}_2[\text{P}(p\text{-XC}_6\text{H}_4)_3]\text{COMe}$, where $\text{X} = \text{MeO}, \text{Me}, \text{H}$ and F , at $100\text{ }^\circ\text{C}$.

Table 6.3: Rate constants for the decarbonylation of $\text{CpMo(CO)}_2(\text{L})\text{COMe}$ ($\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3, \text{P}(p\text{-OMeC}_6\text{H}_4)_3, \text{P}(p\text{-MeC}_6\text{H}_4)_3$ and PPh_3) at $100\text{ }^\circ\text{C}$

Ligand	Rate constant (s^{-1})	% R^2
$\text{P}(p\text{-MeOC}_6\text{H}_4)_3$	1.09×10^{-3}	100
$\text{P}(p\text{-MeC}_6\text{H}_4)_3$	1.65×10^{-3}	99
PPh_3	1.25×10^{-3}	99
$\text{P}(p\text{-FC}_6\text{H}_4)_3$	3.18×10^{-3}	99

Table 6.3 reveals the following trend in the rate of decarbonylation with respect to the phosphine: $P(p\text{-FC}_6\text{H}_4)_3 > P(p\text{-MeC}_6\text{H}_4)_3 > PPh_3 > P(p\text{-MeOC}_6\text{H}_4)_3$. This trend is similar to the trend of increasing electronic effect (see **Table 6.2**). Thus, it is observed that as the Tolman electronic parameter of the phosphine increases the rate of the decarbonylation reaction also increases, viz. electron-withdrawing ligand > electron-donating ligand (**Table 6.3**). This was contrary to the findings of Kubota *et al.*⁷ found that the electron withdrawing groups slow down the reaction. It is important to note that these trends are opposite to that found for the migratory-insertion reactions discussed in **Chapter 5**.

Llewellyn *et al.* proposed that the decarbonylation of acyl compounds of the form $[Fe(\eta\text{-C}_5\text{H}_5)(L)(CO)(COMe)]$ ($L = PPh_3$ and $IMes = 1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{imidazol-2-ylidene}$) might proceed via one of two routes (see **Scheme 6.3**).⁹

1. The reaction may occur *via* dissociation of L, so that after the reverse migratory insertion reaction, the compounds $[(\eta\text{-C}_5\text{H}_5)Fe(CO)_2(Me)]$, and free L are formed.⁹ Displacement of CO by L would then lead to the observed product of decarbonylation, $[(\eta\text{-C}_5\text{H}_5)Fe(L)(CO)(Me)]$.⁹
2. Alternatively, this may occur by loss of CO, followed by a reverse migratory insertion reaction of the acyl CO.⁹ This represents the exact reverse of the CO migratory insertion reaction.⁹

Theoretical studies were performed on the above reaction pathways.⁹ The activation

energy for the formation of $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{COMe})] + \text{L}$ from $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{L})(\text{CO})(\text{COMe})]$, was calculated as 86 kJmol^{-1} for $\text{L} = \text{PH}_3$. Their finding compared well with a study by Cao *et al.*, on a PH_3 -induced migratory insertion in $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{Me})]$, (*i.e.* the reverse process), who reported a rate-determining step of 74 kJmol^{-1} using a the Gaussian 94 program.⁹ For the complex $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{PH}_3)(\text{CO})(\text{COMe})]$ the energies for the two different dissociation processes vary significantly.

The activation energy barrier to decarbonylation *via* tertiary phosphine dissociation is 84 kJmol^{-1} and is much higher than that due to decarbonylation *via* CO dissociation, 170 kJmol^{-1} .⁹ This suggests that decarbonylation *via* phosphine dissociation is favoured in $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{PH}_3)(\text{CO})(\text{COMe})]$ and indeed this has been shown experimentally to occur for $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{PPh}_3)(\text{CO})(\text{COMe})]$.⁹

Thus, the nature of the phosphine ligand plays an important role in the decarbonylation process.

Our studies have indicated that the acyl complex, containing a phosphine ligand that has a high Tolman electronic parameter *i.e.* highly electron-withdrawing, undergoes a faster decarbonylation reaction. It indicates that the greater the electron withdrawing power on the phosphine, the easier for the phosphine to dissociate from the metal complex as the first step in the proposed mechanism dictates (see **Figure 6.1**).

6.3.4 Investigation of the effect of R group on the decarbonylation reaction of $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{R} = \text{H}, \text{Me}, \text{CHO}, \text{COMe}$ and $\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$)

According to observations on the migratory-insertion reactions (**Chapter 5**), the R group plays a role and affects the rate of the reaction. The effect of the ring substituent on the decarbonylation reaction was studied at 100 °C by varying the R groups in the complex $(\text{CpR})\text{Mo}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ ($\text{R} = \text{H}, \text{Me}, \text{CHO}, \text{COMe}$). The results are shown in conversion graphs and rate plots that are displayed in **Figure 6.12** and **Figure 6.13**, respectively. The summary of these results is shown in **Table 6.4**.

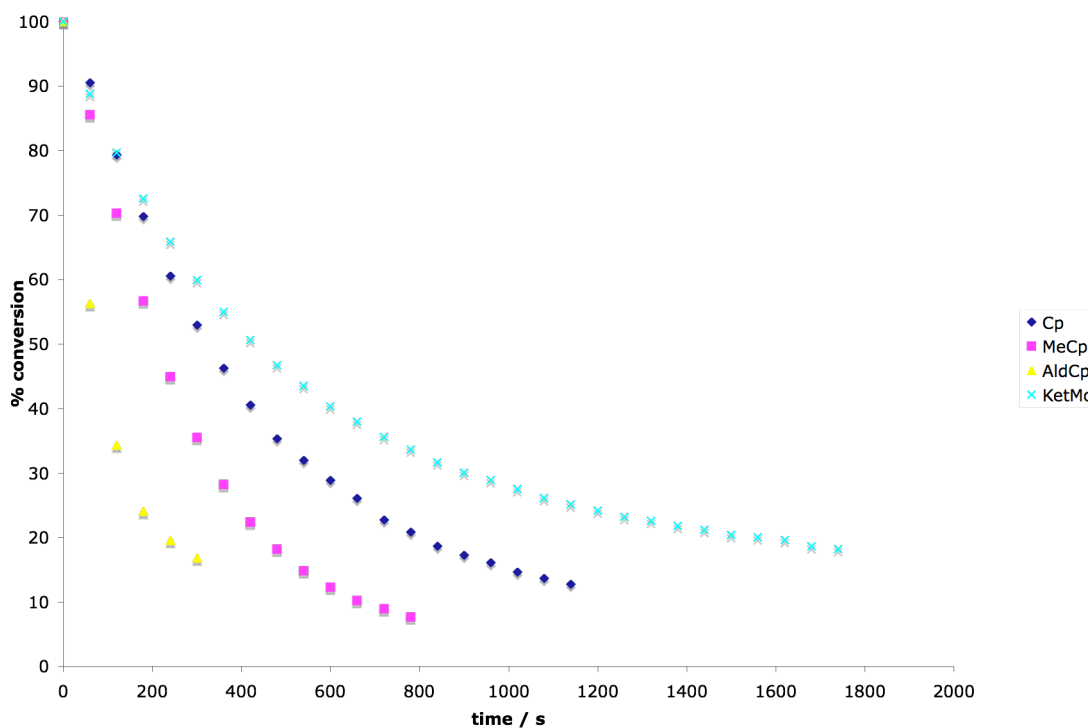


Figure 6.12. The conversion graphs for the decarbonylation reactions of $(\text{CpR})\text{Mo}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$, where $\text{R} = \text{H}, \text{Me}, \text{COH}$ and COMe , at 100 °C.

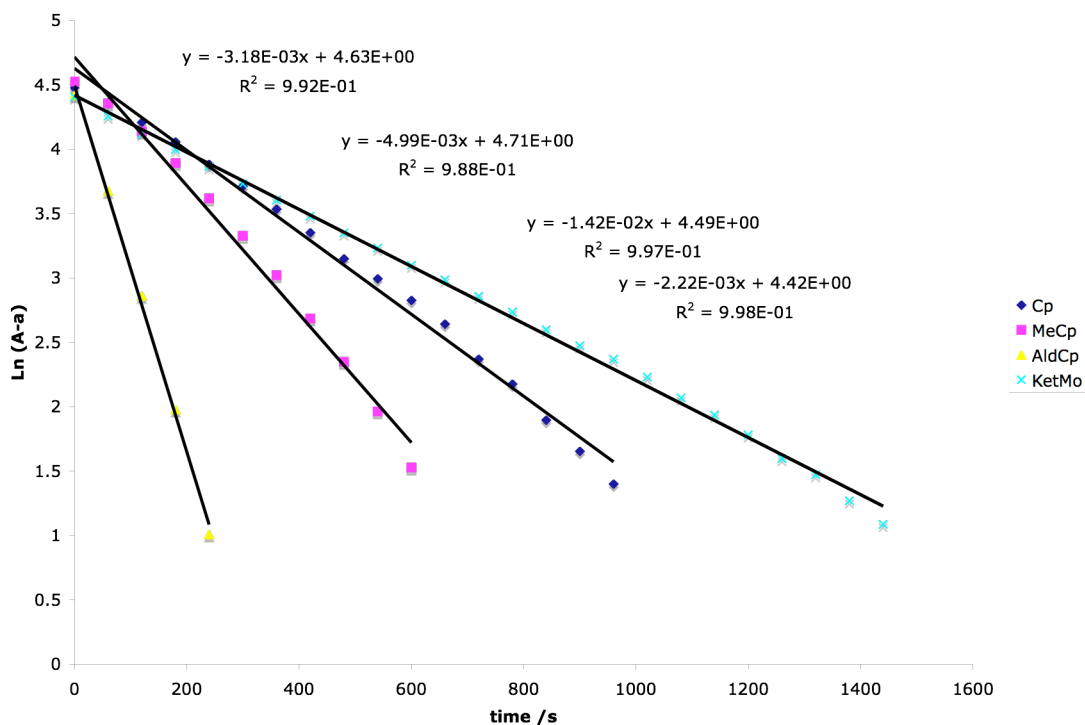


Figure 6.13. The first order plots for the decarbonylation reactions of $(CpR)Mo(CO)_2[P(p-FC_6H_4)_3]COMe$, where $R = H, Me, COH$ and $COMe$, at $100\text{ }^\circ C$.

Table 6.4 Rate constants for the decarbonylation of $(CpR)Mo(CO)_2[P(p-FC_6H_4)_3]COMe$ ($R = H, Me, COH, COMe$) at $100\text{ }^\circ C$

R	Rate constant (s^{-1})	% R^2
H	3.18×10^{-3}	99
Me	4.99×10^{-3}	99
COH	14.2×10^{-3}	100
COMe	2.22×10^{-3}	100

The trend of decreasing rate of the decarbonylation reaction with respect to the R

group, extracted from **Table 6.4**, is as follows: COH > Me > H > COMe. In this reaction both the steric and electronic factors vary as the range of R group is varied. The steric (cone, θ_1 and θ_2 , and solid angles, Ω_{av} ¹³) and electronic effects¹⁴ (F (σ_I (inductive) + σ_R (resonance))) of these R groups are displayed in **Table 6.5**.

Table 6.5: The cone angles and solid angles for C₅H₄R¹³ and electronic factors for CH₂R¹⁴

R	θ_1 (°)	θ_2 (°)	Ω_{av} (°)	F	σ_I	σ_R
H	128	55	131	0.03	0	-
Me	141	64	144	0.01	-0.05	-0.13
COH	140*	40*	140*	0.33	-	0.23
COMe	142	47	144	0.33	0.27	0.16

*calculated using STERIC (see **Chapter 5**)

The decrease in the rate of the decarbonylation reaction is related to the decrease of the cone angles, θ_1 and θ_2 , and solid angles, Ω_{av} , of the R group (see **Table 6.5**). Graphs showing the relation of the Tolman cone angle, θ_2 , and $\nu(\text{C}=\text{O})$ and the rate constant for the decarbonylation reaction, are displayed in **Figure 6.15** and **Figure 6.16**, respectively. Note that the $\nu(\text{C}=\text{O})$ can be associated with the electronic property of the Mo complex, as discussed in **Chapter 5**. For this decarbonylation reaction there is no correlation with $\nu(\text{C}=\text{O})$ and the rate of the reaction. There is, however, a correlation with the electronic parameter defined by the combination of the resonance and inductive effects of the R group, F, and the rate of decarbonylation i.e. as F decreases the rate increases. There is no clear trend associated with the other

electronic parameters and the rate constants. Thus, it was observed that the steric and electronic effects affect the rate of the decarbonylation reaction.

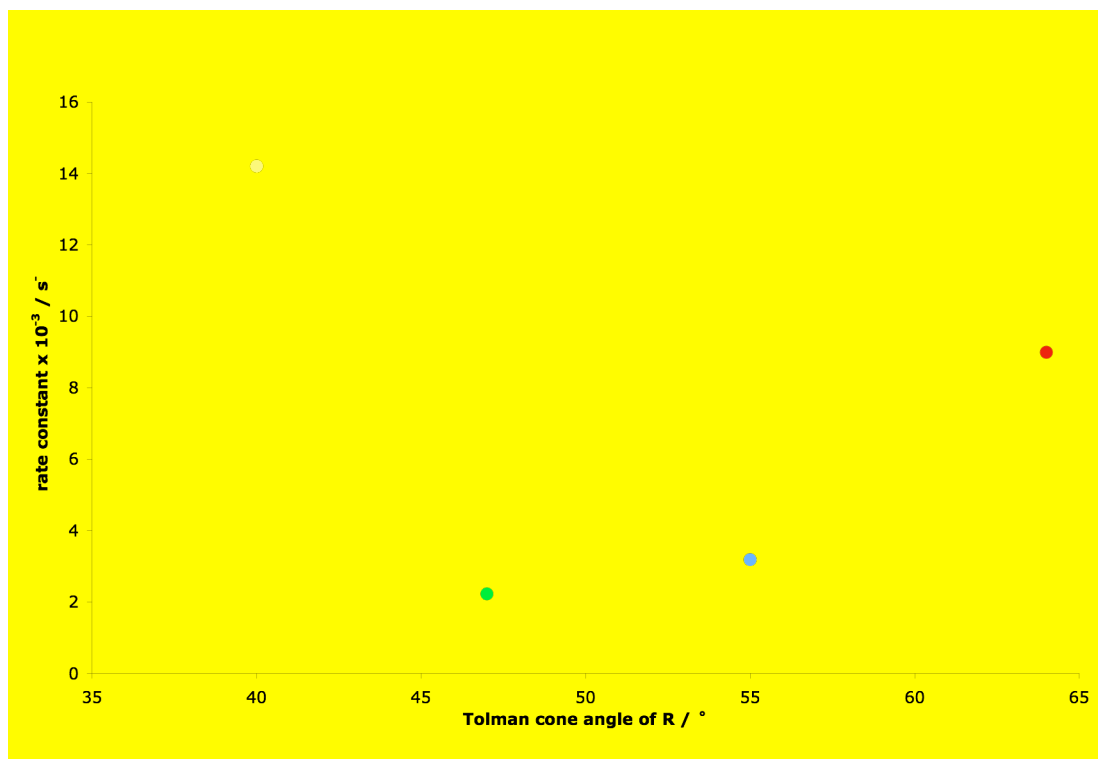


Figure 6.14 The graph of the rate constants for the decarbonylation of $(\text{CpR})\text{Mo}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ ($\text{R} = \text{H}$, Me , COH , COMe) against the Tolman cone angle of R

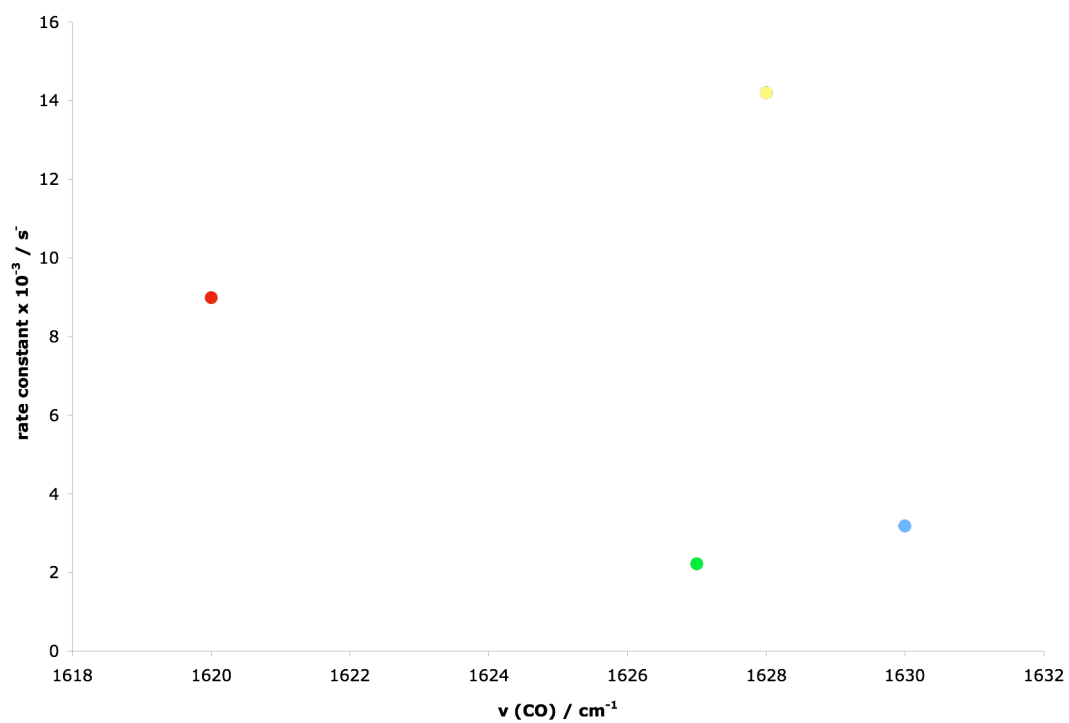


Figure 6.15 Graph of the rate constant for the decarbonylation of $(\text{CpR})\text{Mo}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ ($\text{R} = \text{H}, \text{Me}, \text{COH}, \text{COMe}$) against $\nu(\text{C}=\text{O})$ of $(\text{CpR})\text{Mo}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$

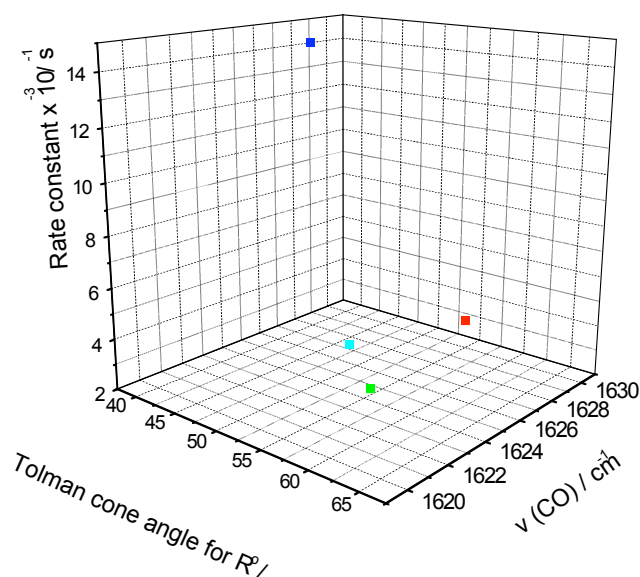


Figure 6.16: 3D plot showing the relationship of the rate constant, for the decarbonylation reaction of $(\text{CpR})\text{Mo}(\text{CO})_2(\text{P}(p\text{-FC}_6\text{H}_4)_3)\text{COMe}$ ($\text{R} = \text{H}$, Me , COH , COMe), with the steric (Tolman cone angle) and electronic ($\nu(\text{CO})$) effects.

The study was extended to a study of other phosphines in which the ring substituent, R was varied. The effect of the rate of decarbonylation for all *trans* complexes was also done (see **Appendix A7** for the rate plots). A summarized table showing the decarbonylation reactions of $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{R} = \text{H}$, Me , COH , COMe and $\text{L} = \text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, PPh_3 and $\text{P}(p\text{-FC}_6\text{H}_4)_3$) is shown in **Table 6.6**.

Table 6.6. The rate constants ($\times 10^{-3} \text{ s}^{-1}$) for the decarbonylation reactions of $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{R} = \text{H}, \text{Me}, \text{COH}, \text{COMe}$ and $\text{L} = \text{P}(p\text{-OMeC}_6\text{H}_4)_3, \text{P}(p\text{-MeC}_6\text{H}_4)_3, \text{PPh}_3$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$)

R \ L	H	Me	COH	COMe
$\text{P}(p\text{-MeC}_6\text{H}_4)_3$	1.65	3.24	0.502	3.85
$\text{P}(p\text{-MeOC}_6\text{H}_4)_3$	1.09	2.93	4.63	8.81
PPh_3	1.25	2.21	4.07	4.06
$\text{P}(p\text{-FC}_6\text{H}_4)_3$	3.18	4.99	14.2	2.22

The following conclusions can be drawn from the above table:

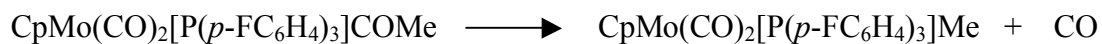
- 1) For the electron-donating, $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$ ligand, the trend of increasing rate of decarbonylation is similar to the decrease in steric effect of the R group (θ_1 and θ_2), the decrease of electronic effect defined by the decrease of $\nu(\text{CO})$.
- 2) For the electron-withdrawing, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ ligand, the trend of increasing rate of decarbonylation is similar to the increase in steric effect of the R group and the decrease the electronic effect (relative to F).
- 3) For the electron-donating, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ ligand, the trend of increasing rate of decarbonylation is similar to the decrease in steric effect of the R group (θ_1 and θ_2), the increase of electronic effect defined by F and σ_R and the decrease of $\nu(\text{CO})$.
- 4) When considering the unsubstituted Cp complex ($\text{R} = \text{H}$), the rate decreases as the Tolman electronic parameter of the phosphine decreases i.e. as the phosphine changes from electron-withdrawing to electron-donating,

- 5) The same conclusion can be drawn for the weakly donating Me-substituted Cp complex, if the reaction with $L = PPh_3$ is ignored.
- 6) No correlations can be extracted from reactions involving the strongly withdrawing R groups, -COH and -COMe and the various phosphines.

Both the steric and electronic effects of both the R group and the phosphine ligand, thus affect the rate of the decarbonylation reaction.

6.3.5 Use of photomicroscopy to study the decarbonylation reaction of $CpMo(CO)_2[P(p-FC_6H_4)_3]COMe$ crystals

As mentioned in the early part of this chapter the solvent-free reaction was found to be complex, especially at the lower temperature. The aim of this study was to observe the decarbonylation reaction under a microscope to assess whether the reaction occurred in the solid state or in the melt phase. A model reaction was chosen for the study:



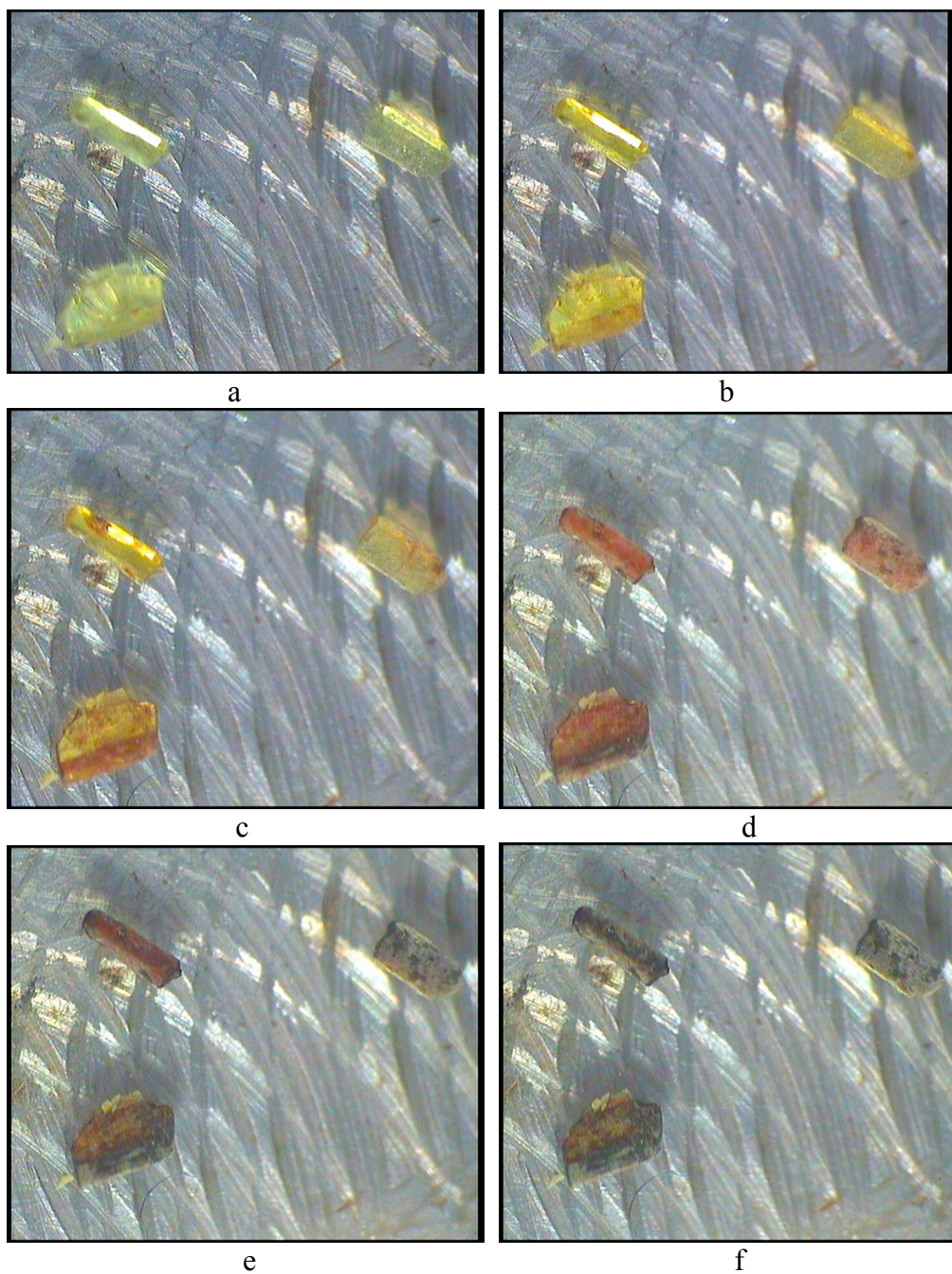


Figure 6.17: Decarbonylation of $\text{CpMo}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ at 100 °C, a = 0 time, b = after 2 hr, c = after 3 hr, d = after 6hr, e = after 7.5 hr, f = after 8.5 hr.

Single crystals of $\text{CpMo(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ were used for this study (**Figure 6.17a**). The crystal were placed on the heating device and rapidly heated ($10\text{ }^\circ\text{C/min}$) to $100\text{ }^\circ\text{C}$. The reaction was then monitored at the temperatures for 8.5 hours. During the course of the reaction no melt phase was observed. Changes in the crystal colour were observed as early as the first hour of heating at $100\text{ }^\circ\text{C}$. The photograph after 2 hr showed that the yellow crystal had begun to develop a slight orange tinge on one side of the crystal (**Figure 6.17b**). After 3 hr, a distinct orange colour covered half of the crystal (**Figure 6.17c**). The orange colour depicts the conversion of the decarbonylated product as observed from previous experiments. The orange colour turned dark brown by the 6th hour (**Figure 6.17d**). The crystal then progressively turned black (**Figure 6.17e**). After 8.5 h, a white colour appeared at the surface of the crystal, probably owing to the presence of the phosphine ligand (**Figure 6.17f**).

The reaction was stopped after 8 hr 30 min. The crystal was removed from the heating block and analysed by $^1\text{H-NMR}$ spectroscopy. The analysis revealed 77 % conversion of $\text{CpMo(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ ($5.00\text{ }\{4\text{H}\}$ Cp-Mo, $2.63\text{ }\{3\text{H}\}$ Me-CO ppm) to $\text{CpMo(CO)}_2[\text{P}(\text{FC}_6\text{H}_4)_3]\text{Me}$ ($4.63\text{ }\{4\text{H}\}$ Cp-Mo, $4.01\text{ }\{3\text{H}\}$ Me ppm).

6.4 Conclusions

The kinetics of the decarbonylation reaction of Mo complexes of the type, $(\text{CpR})\text{Mo(CO)}_2(\text{L})\text{COMe}$ (where $\text{R} = \text{H, Me, CHO, COMe}$) and $\text{L} = \text{P}(p\text{-}$

OMeC₆H₄)₃, P(*p*-FC₆H₄)₃, P(*p*-MeC₆H₄)₃, PPh₃) were successfully studied using the DRIFTS technique. The dependence of the decarbonylation reaction on the reaction temperature was observed.

The effect of the ligand, L on the rate of the decarbonylation reaction was as follows: P(*p*-FC₆H₄)₃ > P(*p*-MeC₆H₄)₃ > PPh₃ > P(*p*-MeOC₆H₄)₃ i.e. electron-withdrawing ligand > electron donating ligand. This was opposite to the findings of the migratory-insertion reaction, which is the reverse of the decarbonylation reaction. It is assumed that the mechanism of the decarbonylation reaction entailed the dissociation of the phosphine, thus the dependence of the rate of the reaction on the phosphine. An electron-withdrawing ligand dissociates easier from the metal than an electron-donating ligand. This explains why the reaction is promoted by electron-withdrawing ligands.

The overall effect of the Cp ring substituent, R on the reaction rate is as follows: COH > COMe > Me > H. This trend correlates with the decrease in steric effect (θ_1 and θ_2), the increase of electronic effect (as defined by F and σ_R) yet a decrease of electronic effect (as defined by ν (CO); see **Figure 6.16**).

An optical microscopy study of a model decarbonylation reaction of CpMo(CO)₂[P(*p*-FC₆H₄)₃]COMe revealed that these reactions occurred in the solid

state and not in the melt. The kinetics of the decarbonylation reaction, thus differed from that of the migratory-insertion reaction.

6.5 References

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CHAPTER 7: THE STUDY OF THE MIGRATORY- INSERTION AND DECARBONYLATION REACTIONS OF TUNGSTEN COMPLEXES

7.1 Introduction

The study of the kinetics of the solvent-free migratory-insertion reaction between solid $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R} = \text{H}, \text{Me}, \text{CHO}, \text{COMe}$) and solid phosphines (L), and the subsequent decarbonylation reaction of $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ using DRIFTS was shown to be successful (see **Chapter 5**). Although the migratory-insertion reactions appeared to occur in the solid state, in actual fact, the reactions occurred via a melt phase that took place *below the melting points of both reactants*, i.e. the reaction occurred in a eutectic melt.¹ In contrast, the decarbonylation reaction was observed to occur in a solid-solid reaction. To extend this study and evaluate the generality of the approach, a similar set of reactions was performed with the related W complexes. Literature reports have indicated that migratory-insertion reactions of W complexes in solution occur more slowly than with Mo complexes and it is anticipated that similar findings would occur with solvent-free reactions.² A DRIFTS study of $\text{CpW}(\text{CO})_3\text{Me}$ with a range of solid phosphines in the absence of solvents was then undertaken.

7.2 Experimental

The method followed for the DRIFTS analysis of the $\text{CpW}(\text{CO})_3\text{Me}$ complex was the same as the Mo complexes, described in **Section 5.2.1**.

7.2.1 Temperature study of the migratory-insertion and decarbonylation reactions

A mixture of 1 – 2 % powdered $\text{CpW}(\text{CO})_3\text{Me/KBr}$ and 1 – 20 % powdered $\text{P}(p\text{-FC}_6\text{H}_4)_3/\text{KBr}$ were mixed together in a 1:1 or 1:10 molar ratio. The mixture was then placed in the DRIFTS cell and the IR spectra recorded at temperatures of 40, 50 and 60 °C for pre-set time intervals.

The insertion W complexes were used in the decarbonylation reaction. The DRIFTS cell containing the insertion W complex was elevated to the required temperature (100 – 120 °C), and the IR spectra were recorded for pre-set time interval.

7.2.2 Mole ratio study of the migratory-insertion reaction

A mixture of 1 – 2 % powdered $\text{CpW}(\text{CO})_3\text{Me/KBr}$ and 1 – 20 % powdered $\text{P}(p\text{-F-Ph})_3/\text{KBr}$ were mixed together in specified molar ratios (1:1, 1:5 and 1:10). The mixture was then placed in the DRIFTS cell and the IR spectra recorded at temperatures of 40, 50 and 60 °C for pre-set time intervals.

7.2.3 Ligand effects of the migratory-insertion and decarbonylation reactions

A mixture of 1 – 2 % powdered $\text{CpW(CO)}_3\text{Me/KBr}$ and 1 – 20 % powdered L/KBr , ($\text{L} = \text{P}(p\text{-OMeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, PPh_3), were mixed together in a 1:10 molar ratio. Then the mixture was placed in the DRIFTS cell and the IR spectra recorded at 40 °C for pre-set time intervals.

Again for the decarbonylation reaction, the DRIFTS cell containing the insertion W complex was elevated to the required temperature (100 – 120 °C), and the IR spectra were recorded for a pre-set time interval.

7.2.4 Optical microscopy study of the migratory-insertion reaction

The experimental set-up for the optical microscopy study was similar to that described in **Chapter 5**. In summary it consisted of a glass heating-device with dome that could be placed under an optical microscope that was equipped with a digital camera.³ The reactants were placed on the glass surface, heated accordingly, and pictures of the progression of the reaction were taken.

7.3 Results and Discussion

7.3.1 Investigation of the migratory-insertion reactions of the $\text{CpW(CO)}_3\text{Me}$ complex using DRIFTS

The investigation of the migratory-insertion of the W complex using the DRIFTS technique was the same as that used for the Mo complexes in **Chapter 5**. Temperatures of 40 °C and above were chosen for the reaction since (i) little if any reaction occurred at temperatures below 40 °C (ii) this temperature was lower than the melting points of the piano-stool complexes and the ligands. Reactions were performed using a range of W complex: ligand molar ratios ranging from 1:1 to 1:10.

The reaction was monitored in the $\nu(\text{CO})$ and $\nu(\text{COR})$ region of the IR spectrum since the starting W complex had absorptions at 2016 and 1940 cm^{-1} , while the product had absorptions at ~ 1940 , ~ 1850 and ~ 1600 cm^{-1} .

Initially spectra were recorded on the pure reactant to ascertain the correct absorption peaks for the W complex. The W complex absorption peaks occur at 2016 cm^{-1} and 1940 cm^{-1} . The conversion to the insertion product was observed by the disappearance of the 2016 cm^{-1} absorption peak (one CO band) and the appearance of the ~ 1850 cm^{-1} and ~ 1600 cm^{-1} (R-C=O) absorption peaks. The band at ~ 1940 cm^{-1} remained a constant feature as it was associated with both reactant and product.

A typical example of the spectra of the starting material and the insertion product is shown for $\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$ in **Figure 7.1**. As can be seen the IR band at 1940 cm^{-1} could not be used for the analysis.

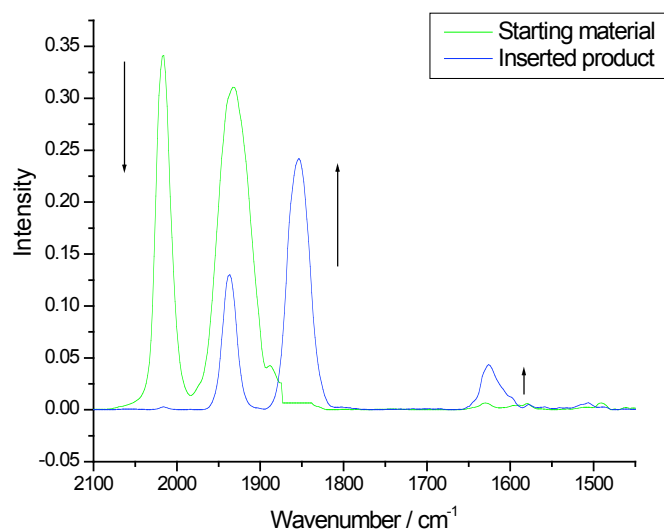


Figure 7.1: Spectra showing the starting material, $\text{CpW(CO)}_3\text{Me}$ and the insertion product, $\text{CpW(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ (1:10, 60 °C).

The reaction changes were thus easily monitored using DRIFTS and a typical set of spectra obtained during the course of a reaction for the migratory-insertion of $\text{CpW(CO)}_3\text{Me}$ with $\text{P}(p\text{-FC}_6\text{H}_4)_3$ to give $\text{CpW(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ is shown in **Figure 7.2**.

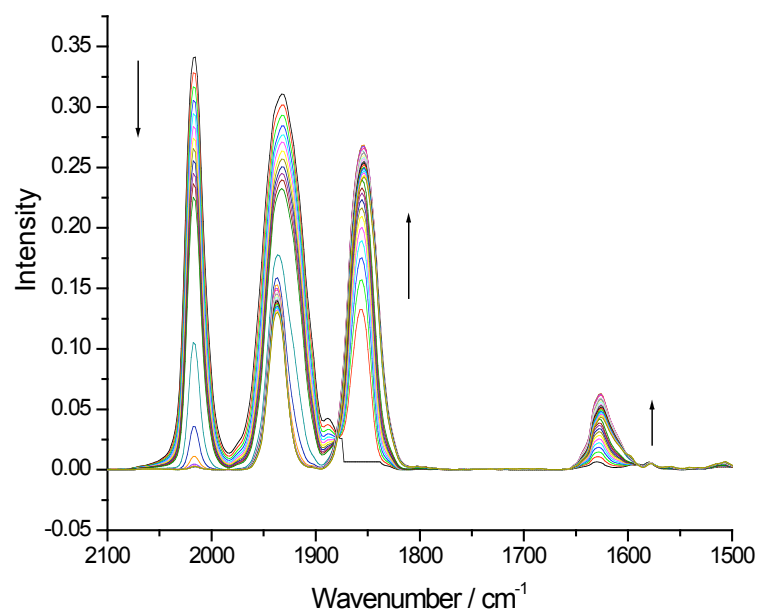


Figure 7.2: DRIFTS spectra showing the typical conversion of $\text{CpW(CO)}_3\text{Me}$ to $\text{CpW(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ (1:10, 60 °C).

This data was used to plot a conversion graph shown in **Figure 7.3**. This was done by following the gradual disappearance of the 2015 cm^{-1} absorption peak, as it changed from 100 % to 0 %, (> 5000 min) as the migratory-insertion progressed and the reactant converted to product.

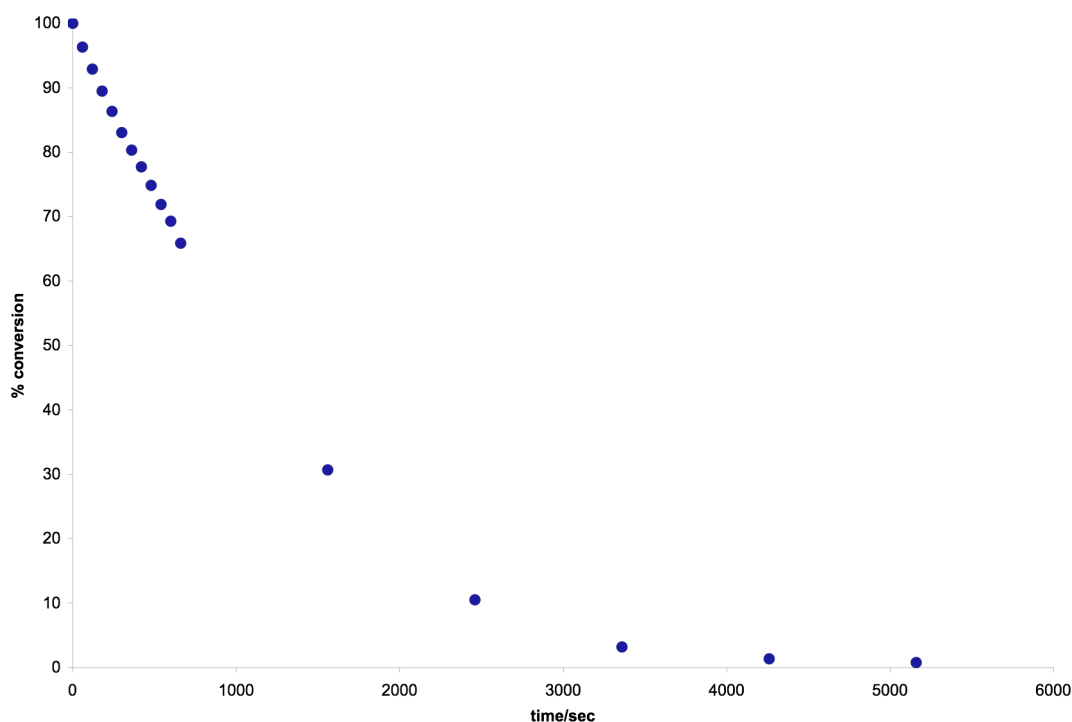


Figure 7.3: $\text{CpW}(\text{CO})_3\text{Me}$ conversion to $\text{CpW}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ (1:10, 60 °C)

The data were then re-plotted making the assumption that the rate of the reaction was first order. The above data was used to construct the rate plot ($\ln(A - a)$) against time, where 'A' represents the % reaction conversion at a specific time, and 'a' is the % unconverted reactant at the end of the reaction shown in **Figure 7.4**. As can be seen the rate data are consistent with first order kinetics. Further attempts to plot the data according to other rate law equations (e.g. second order) did not give a good fit to the data.

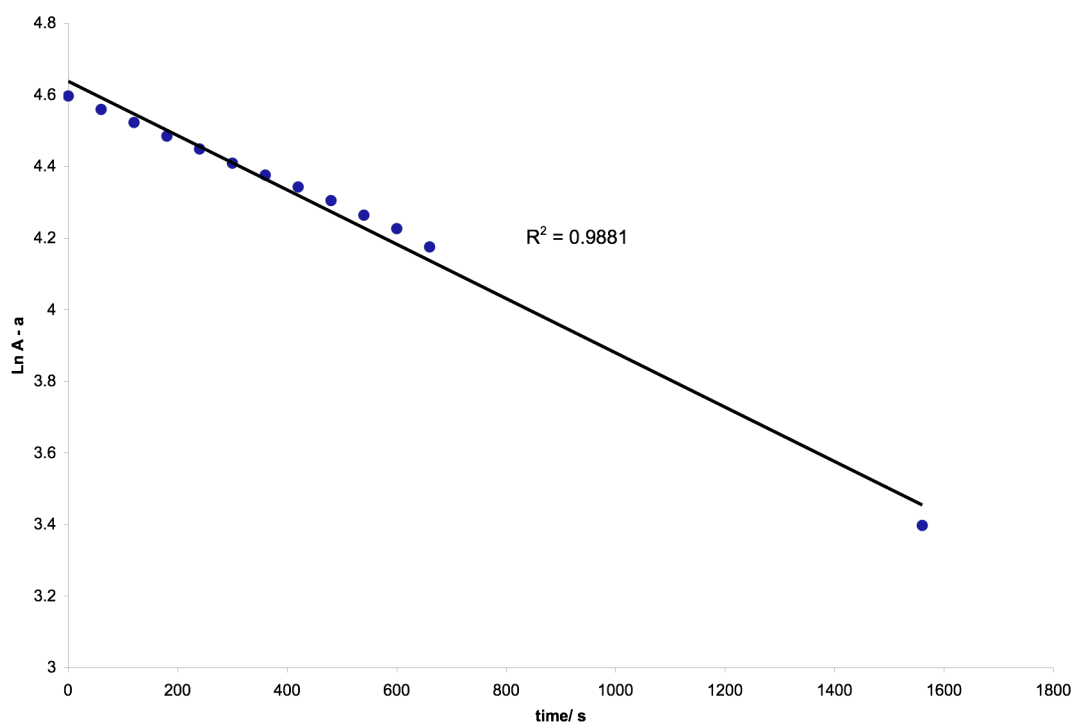


Figure 7.4: First order kinetic plot for the conversion of $\text{CpW}(\text{CO})_3\text{Me}$ to $\text{CpW}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ (1:10, 60 °C)

Similar data and plots were obtained for the other reactions monitored in this study and the actual data will be discussed in the sections below.

7.3.1.1 The effect of temperature on the migratory-insertion reaction of $\text{CpW}(\text{CO})_3\text{Me}$

The effect of temperature on the migratory-insertion reaction was investigated using $\text{CpW}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$. The study was undertaken in the temperature range of 40 - 60 °C. The % reaction conversion and the rate plot for the migratory-insertion reaction of the two reactants using a 1:1 mole ratio is found in **Figure 7.5** and **Figure 7.6**, respectively.

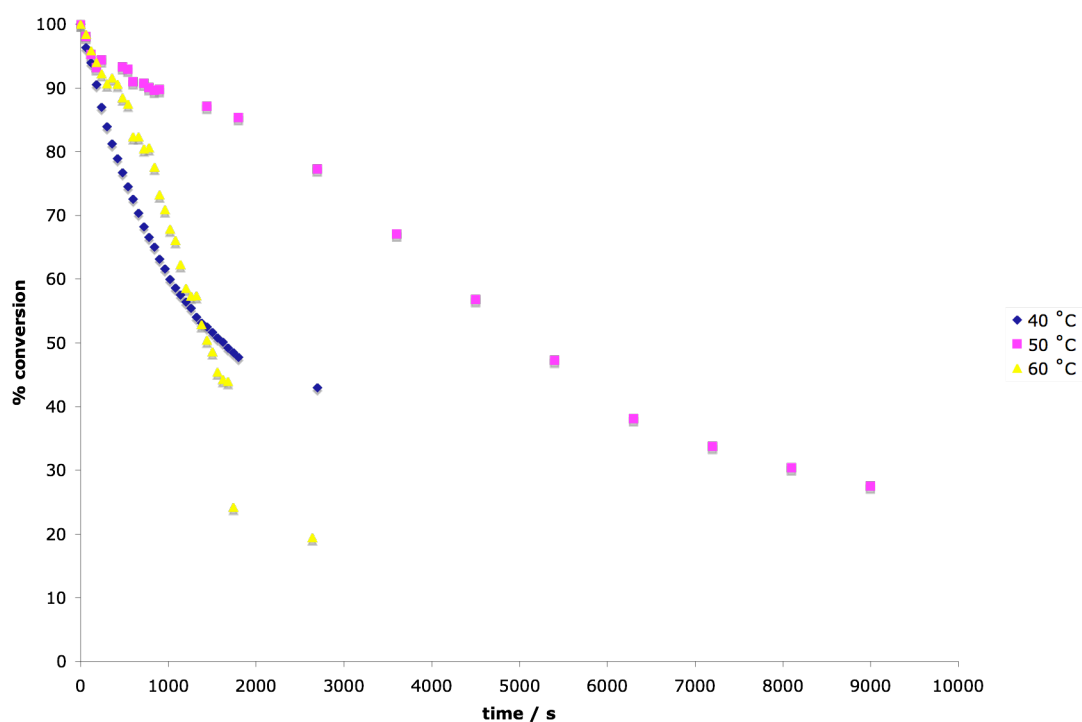


Figure 7.5: The conversion plot for migratory-insertion reaction between $\text{CpW}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (1:1) at varying temperatures

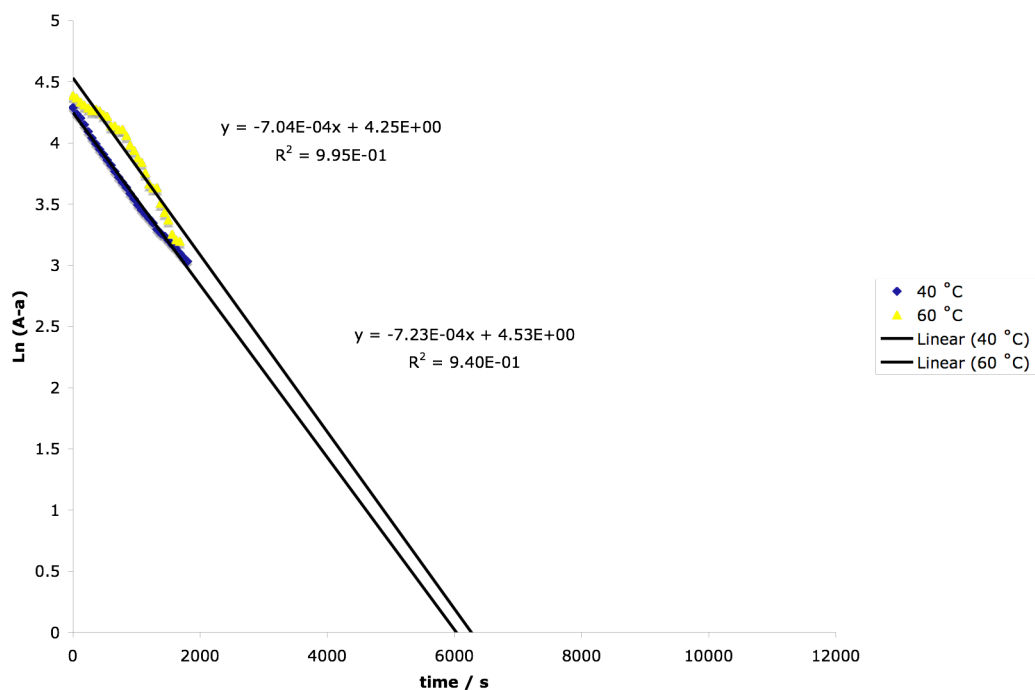


Figure 7.6: The rate plot for migratory-insertion reaction between $\text{CpW}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (1:1) at varying temperatures

In the rate plot shown in **Figure 7.6**, the 50 °C data was omitted owing to a poor fit in the initial part of the reaction as can be seen in the conversion plot in **Figure 7.5**. The rates of the reactions for the 1:1 mole ratio did not increase as expected as the temperature increased. Thus, similar reactions were performed under the same experimental conditions, but using a 1:10 mole ratio. The % reaction conversion and rate plots for these reactions are shown in **Figure 7.7** and **Figure 7.8**, respectively. The rate constants for the above reactions for both the 1:1 and 1:10 mole ratios are displayed in **Table 7.1**.

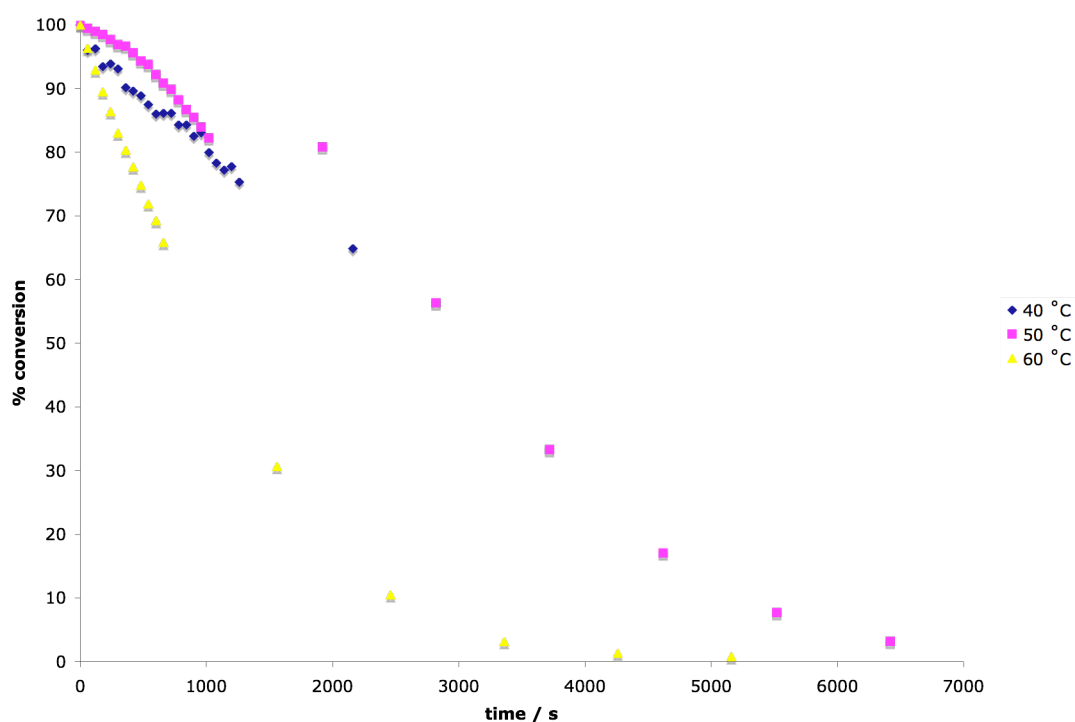


Figure 7.7: The conversion plot for migratory-insertion reaction between $\text{CpW}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (1:10) at varying temperatures

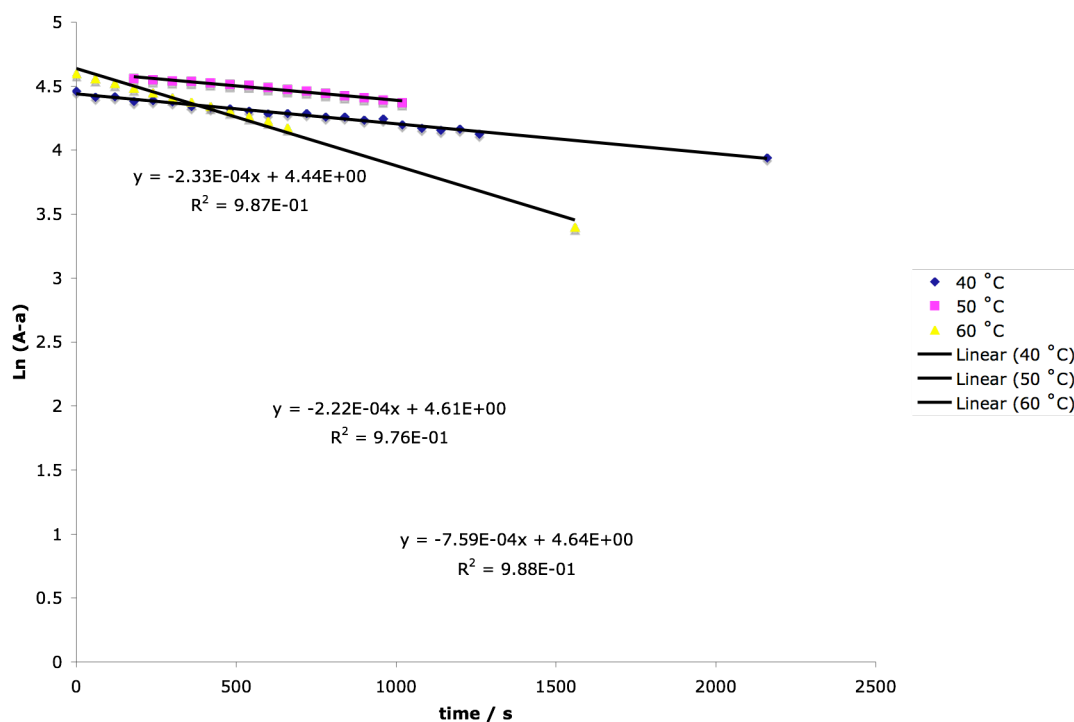


Figure 7.8: The rate plot for migratory-insertion reaction between $\text{CpW}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (1:10) at varying temperatures

Table 7.1: The rate constants for the migratory-insertion reaction of $\text{CpW}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (1:1 and 1:10 mole ratios) at varying temperatures.

Temperature / °C	$k \times 10^{-4} / \text{s}^{-1}$ (1:1)	% R^2	$k \times 10^{-4} / \text{s}^{-1}$ (1:10)	% R^2
40	7.04	100	2.33	99
50	1.11	87	2.22	98
60	7.23	94	7.59	99

The odd data was again reproduced for the 1:10 mole ratio reactions (see **Table 7.1**) i.e. the migratory-insertion reactions at 50 °C showed a lower rate constant than at 40 °C for both mole ratio reactions.

7.3.1.2 The effect of the mole on the migratory-insertion reaction of $\text{CpW}(\text{CO})_3\text{Me}$

From the above temperature study, the rates of the migratory-insertion reactions changed when different mole ratios were used. More information is shown in this section. The migratory-insertion reaction of $\text{CpW}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ was carried out at a temperature of $40\text{ }^\circ\text{C}$ using varying mole ratios of 1:1, 1:5 and 1:10. The % reaction conversion graph is displayed in **Figure 7.9**. The rate was fitted to a first-order rate plot as seen in **Figure 7.10**. The rate constants for these reactions are condensed into **Table 7.2**.

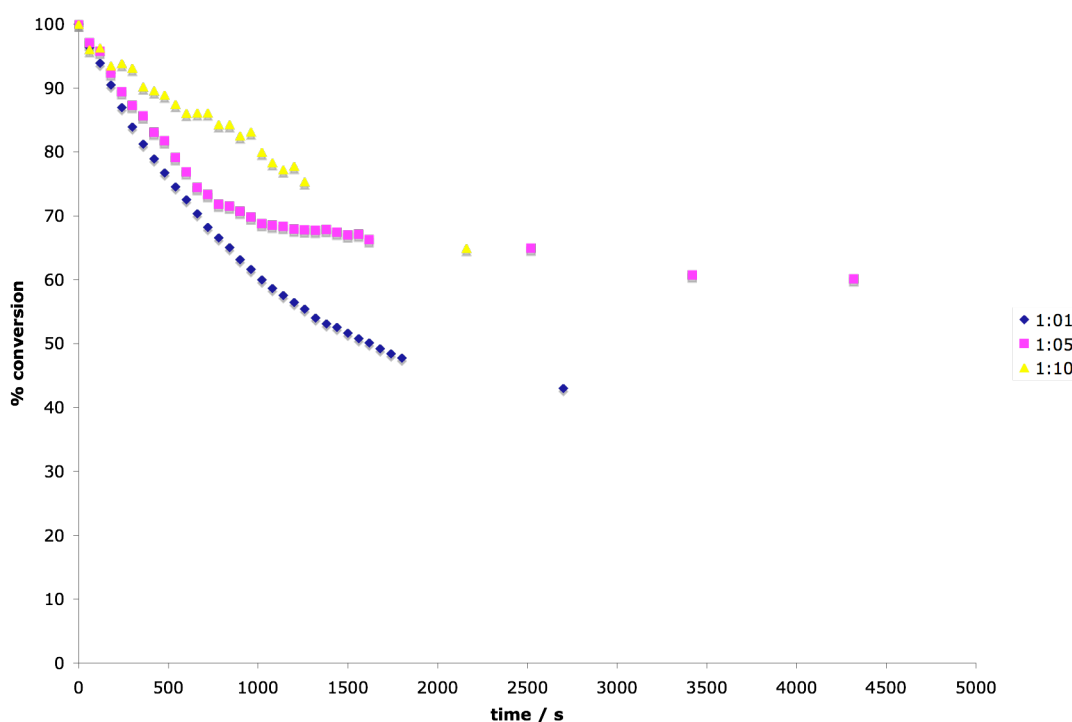


Figure 7.9: The conversion plot for migratory-insertion reaction between $\text{CpW}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ ($40\text{ }^\circ\text{C}$) at varying mole ratios.

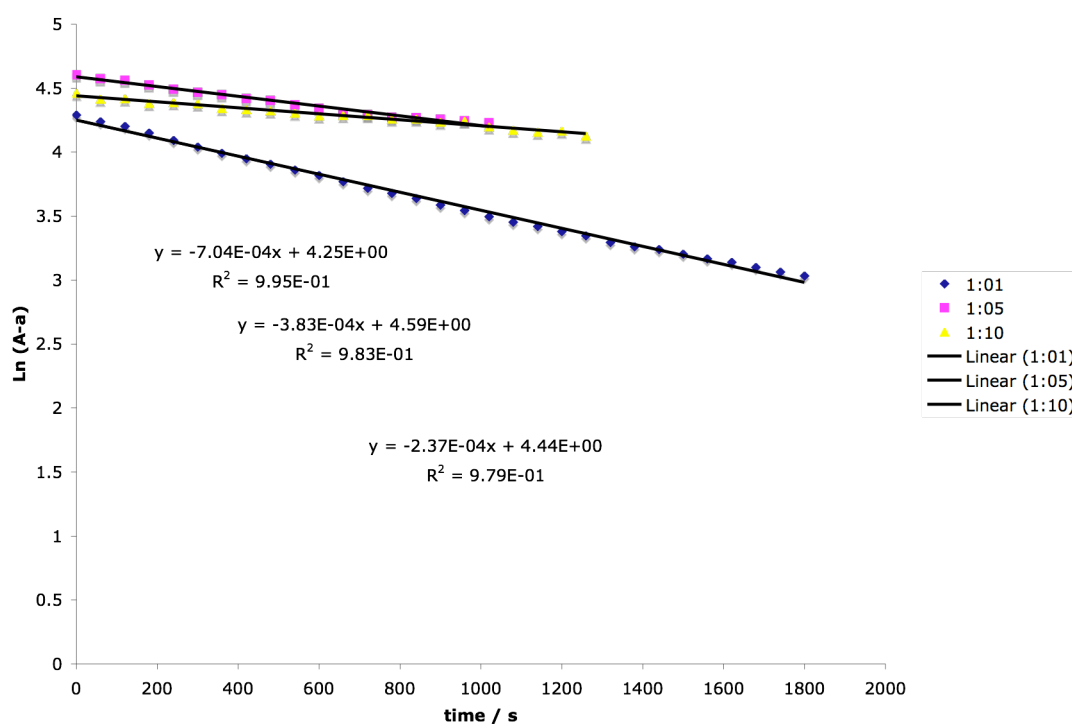


Figure 7.10: The conversion plot for migratory-insertion reaction between $\text{CpW}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (40 °C) at varying mole ratios

Table 7.2: The rate constants for the migratory-insertion reaction of $\text{CpW}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (40 °C) at varying mole ratios.

Mole ratio	$k \times 10^{-4}$	% R^2
1:1	7.04	100
1:5	3.83	98
1:10	2.37	98

Once again the data showed irregularities in that the rate of the migratory-insertion reaction decreased as the mole ratio increased at the constant temperature of 40 °C. The difference in the rates is explained in **Section 7.3.2**, where an optical microscopy study was used to explain the unusual results.

7.3.1.3 The ligand effect of the migratory-insertion reaction on $\text{CpW}(\text{CO})_3\text{Me}$

The effect of the ligand on the migratory-insertion reaction was studied at 60 °C using the following ligands: PPh_3 , $\text{P}(p\text{-FC}_6\text{H}_4)_3$, and $\text{P}(p\text{-MeC}_6\text{H}_4)_3$. The conversion graphs for the successful reactions are displayed in **Figure 7.11**. The rates of the reactions were fitted to first-order plots (**Figure 7.12**) and a summary of this data is shown in **Table 7.3**.

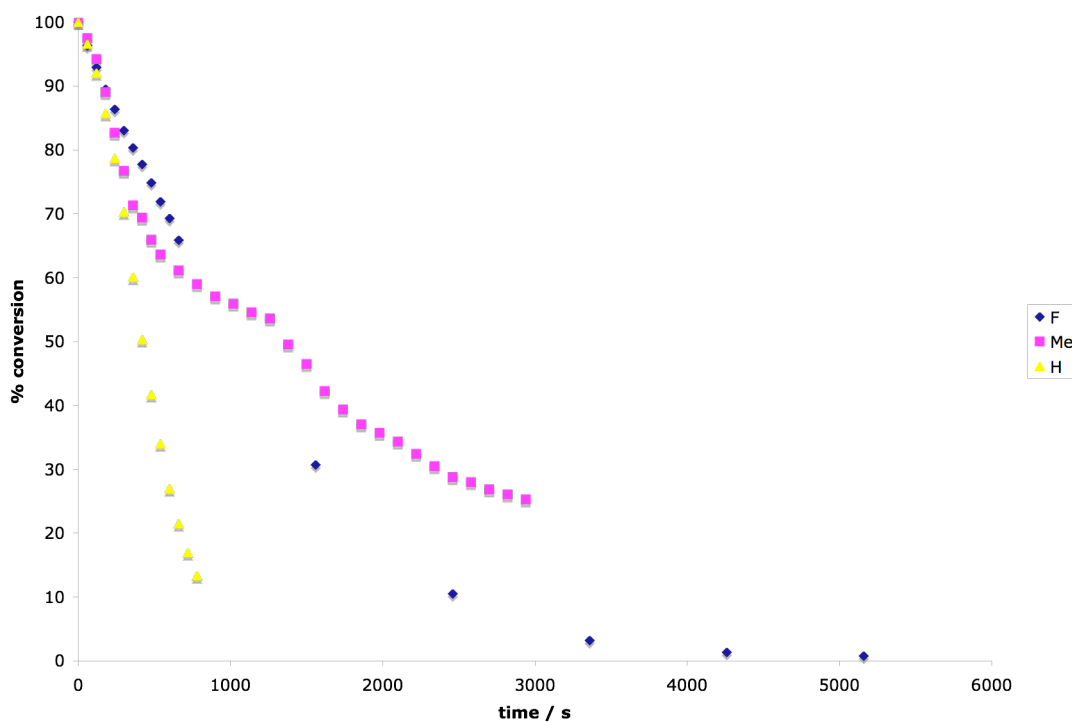


Figure 7.11: The conversion plot for migratory-insertion reaction between $\text{CpW}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-XC}_6\text{H}_4)_3$ ($\text{X} = \text{F}, \text{Me}, \text{H}$) at 60 °C at 1:10 mole ratio

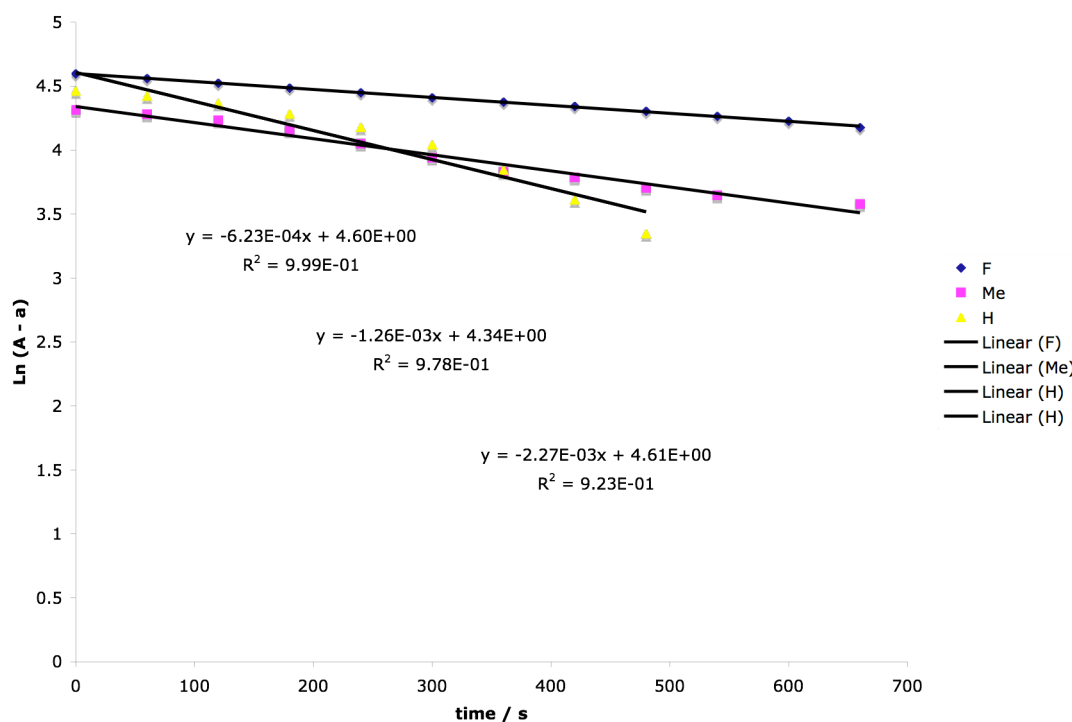


Figure 7.12: The rate plot for migratory-insertion reaction between $\text{CpW(CO)}_3\text{Me}$ and $\text{P}(p\text{-XC}_6\text{H}_4)_3$ ($\text{X} = \text{F}, \text{Me}, \text{H}$) at 60°C at 1:10 mole ratio

Table 7.3: The rate constants for the migratory-insertion reaction of $\text{CpW(CO)}_3\text{Me}$ and $\text{P}(p\text{-XC}_6\text{H}_4)_3$ ($\text{X} = \text{F}, \text{Me}, \text{H}$) at 60°C at 1:10 mole ratio

Ligand	$k \times 10^{-3}$	% R^2
PPh_3	2.27	92
$\text{P}(p\text{-MeC}_6\text{H}_4)_3$	1.26	98
$\text{P}(p\text{-FC}_6\text{H}_4)_3$	0.623	100

Table 7.3 indicates that the rate of the migratory-insertion reaction decreases in the following manner: $\text{PPh}_3 > \text{P}(p\text{-MeC}_6\text{H}_4)_3 > \text{P}(p\text{-FC}_6\text{H}_4)_3$. When the electronic properties of the phosphines are compared with the latter data there is no

correlation of the Tolman electronic parameter (see **Table 7.4**) with the trend in the rate constants. However, it is observed that the electron donating ligand has a faster rate constant than the electron withdrawing ligand. The migratory-insertion reaction of the similar Mo complex, investigated in **Chapter 5**, showed the same trend.

Table 7.4: The Tolman electronic parameters⁴ and the electron donating or withdrawing ability⁵ of phosphine ligands used in this migratory-insertion reaction study

Phosphine ligand	Tolman Electronic parameter (ν) ⁴ / cm ⁻¹	Electron donating / withdrawing ⁵
P(<i>p</i> -MeC ₆ H ₄) ₃	2066.7	donating
PPh ₃	2068.9	reference ligand
P(<i>p</i> -FC ₆ H ₄) ₃	2071.3	withdrawing

7.3.1.4 Optical microscopy of the migratory-insertion reaction

The migratory-insertion reaction was observed for the Mo complexes to take place in a melt (see **Chapter 5**). The following pictures (see **Figure 7.13**) show that this was also the case for the W complex undergoing migratory-insertion reaction with P(*p*-FC₆H₄)₃. The optical microscopy study clearly shows the crystallisation of product *in the low temperature reactions* (**Figure 7.13d**).¹ This is also indicated by the change in the kinetics with time at 40 °C (see above) that indicates a diffusion controlled reaction. The effect of diffusion was also noted

for the reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Me}$ with different amounts of $\text{P}(p\text{-FC}_6\text{H}_4)_3$ at low temperature. The unexpected lowering of reaction rate with increased ratio of $\text{P}(p\text{-FC}_6\text{H}_4)_3$ can be explained by the lowered ability to form a melt, resulting in the greater difficulty of the W complex to make intimate contact with the phosphine.

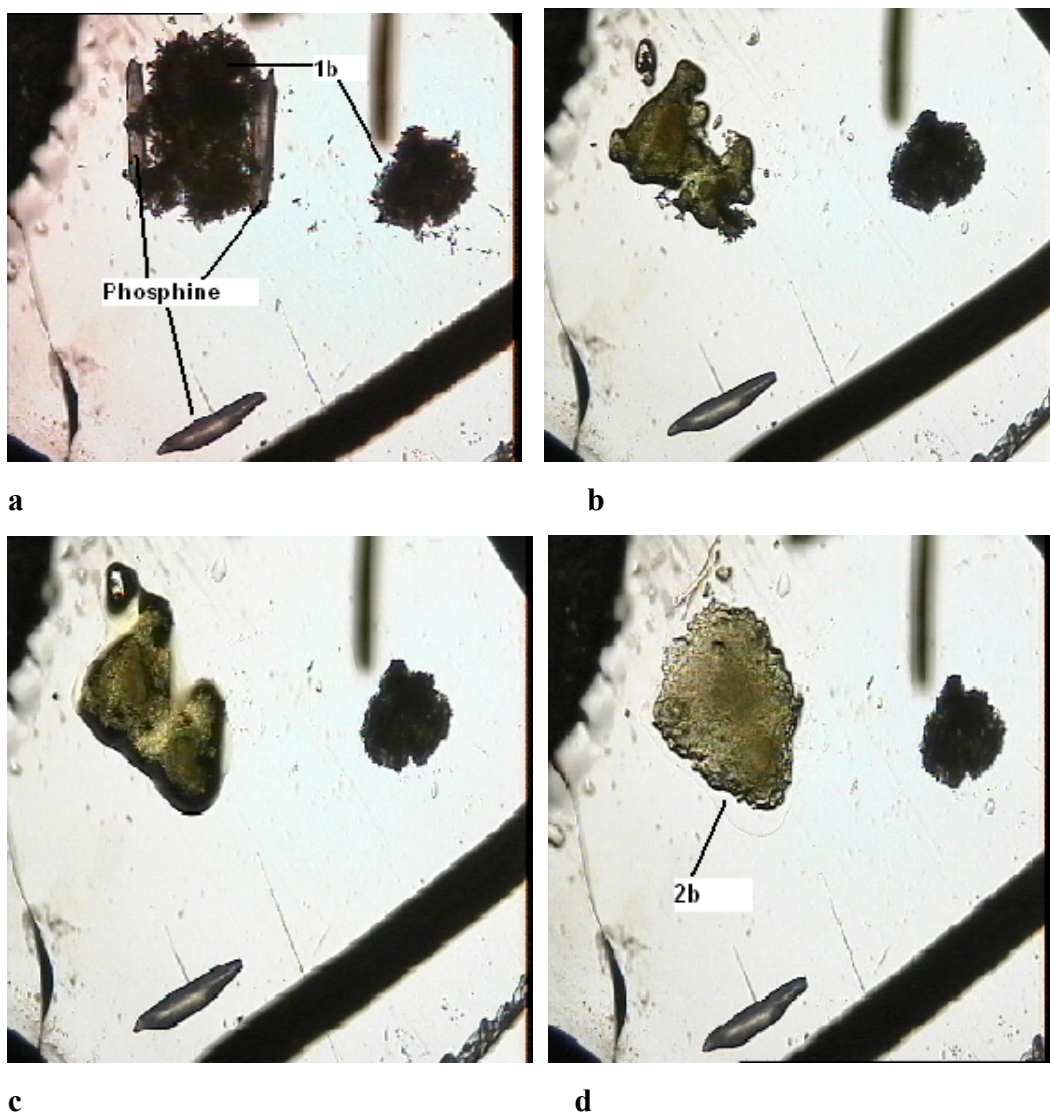


Figure 7.13. Interface melting in the reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Me}$ with $\text{P}(p\text{-FC}_6\text{H}_4)_3$ at 40 °C: (a) room temperature (b) 40 °C / 1 min (c) 40 °C / 2 min (d) 40 °C / 10 min

The DSC profile shown in **Figure 7.14** shows that by simply mixing the two reactants together a melt is induced at a temperature below both reactants' melting points.

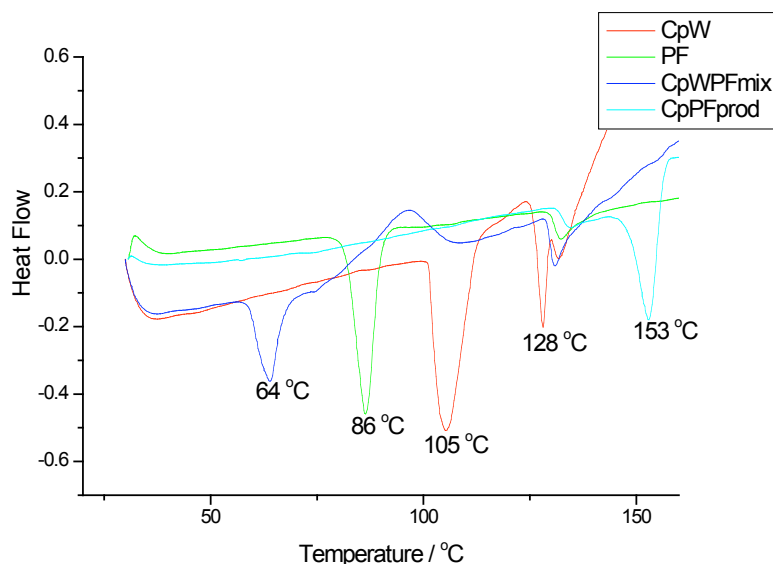


Figure 7.14: The DSC scans of $\text{CpW}(\text{CO})_3\text{Me}$ (**CpW**), the phosphine, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (**PF**), the mixture of the $\text{CpW}(\text{CO})_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (**CpWPFmix**) and the product, $\text{CpW}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$, (**CpWPFprod**).

It is assumed that this melt stage facilitates the progression of the reaction. However, the reaction appears to be unchanged to the naked eye.

It is suggested that in a solvent-free reaction the physical contact between the two reactants, i.e. $(\text{CpR})\text{M}(\text{CO})_3\text{Me}$ and L , lowers the melting point of the mixture. This then permits the mixing that is required for the reaction to occur. The lack of a melt phase at 40 °C is evident in the poor kinetics observed. The formation of a melt indicates the existence of a eutectic mixture with a temperature of fusion below the melting points of both reactants.⁶ Rothenberg and colleagues proposed that the eutectic formation can be a result of the mechanical grinding of the two

reactants.⁶ However, we have observed that this eutectic is achieved by simply mixing two powdered reactants together (see **Figure 7.14**).

7.3.1.5 Comparison of migratory-insertion reaction with W complexes versus Mo complexes

A comparison of the rate constants for the migratory-insertion reaction of $\text{CpW(CO)}_3\text{Me}$ and $\text{CpMo(CO)}_3\text{Me}$, respectively with the $\text{P}(p\text{-FC}_6\text{H}_4)_3$ was done.

Table 7.5 shows that the rate constants for the migratory-insertion reaction at 1:1 and 1:10 molar ratios in the temperature range 40 – 60 °C.

Table 7.5: Comparison of rate constants for $\text{CpW(CO)}_3\text{Me}$ and $\text{CpMo(CO)}_3\text{Me}$

T / °C	W complex (1:1)	Mo complex (1:1)	W complex (1:0)	Mo complex (1:10)
40	7.04	-	2.33	7.53
50	1.11	6.36	2.22	9.38
60	7.23	20.3	7.59	25.2

The above table indicates that the rate for migratory-insertion reaction was much faster for the Mo complex than for the W tungsten complex. This was consistent with previous work done by Adeyemi and Coville², and also consistent with solutions studies.⁷

7.3.2. DRIFTS study of the decarbonylation reaction

The reactants used for the decarbonylation were synthesized by the migratory-insertion reactions described above. The insertion compounds that were generated *in situ* were all *trans* complexes. The migratory-insertion was monitored by following the disappearance of the $\sim 2016\text{ cm}^{-1}$ peak and the appearance of the $\sim 1600\text{ cm}^{-1}$ peak (see **Figure 7.15**). The temperature of the IR cell was then elevated ($100 - 120\text{ }^{\circ}\text{C}$) and the decarbonylation reaction was then monitored. The end of decarbonylation was signalled by the total disappearance of the carbonyl peak at $\sim 1600\text{ cm}^{-1}$ (see **Figure 7.15**)

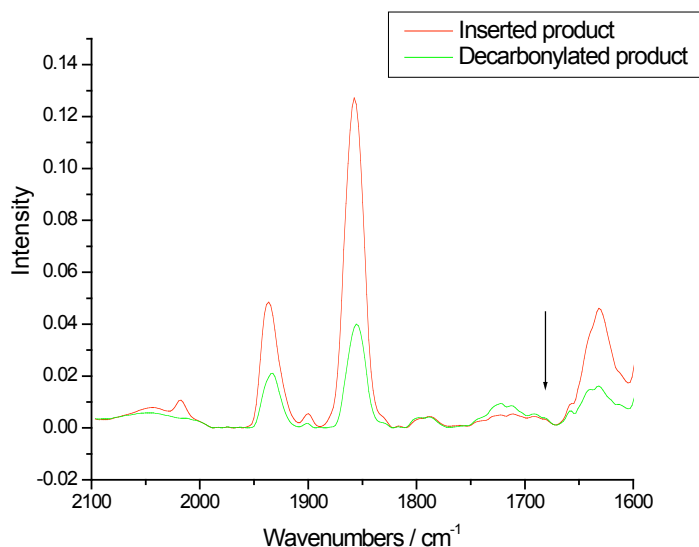


Figure 7.15: Spectra showing the insertion complex, $\text{CpW(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ and finally the decarbonylated product, $\text{CpW(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{Me}$.

The decarbonylation progress was easily monitored by DRIFTS and a typical set of spectra is shown in **Figure 7.16**.

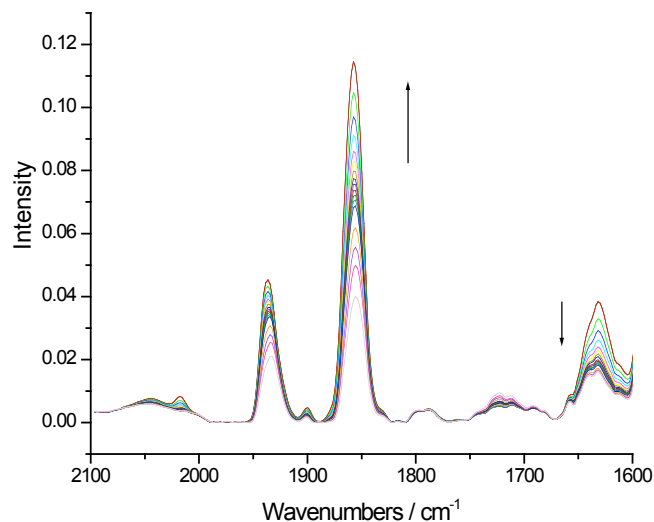


Figure 7.16: DRIFTS spectra showing the decarbonylation of $\text{CpW(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ to $\text{CpW(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{Me}$ at 110 °C.

This data was used to plot a conversion graph as shown in **Figure 7.17**. This was done by following the gradual disappearance of the $\sim 1600 \text{ cm}^{-1}$ peak. The highest absorption peak at $\sim 1600 \text{ cm}^{-1}$ was used as 100 % of $\text{CpW(CO)}_2(\text{L})\text{COMe}$.

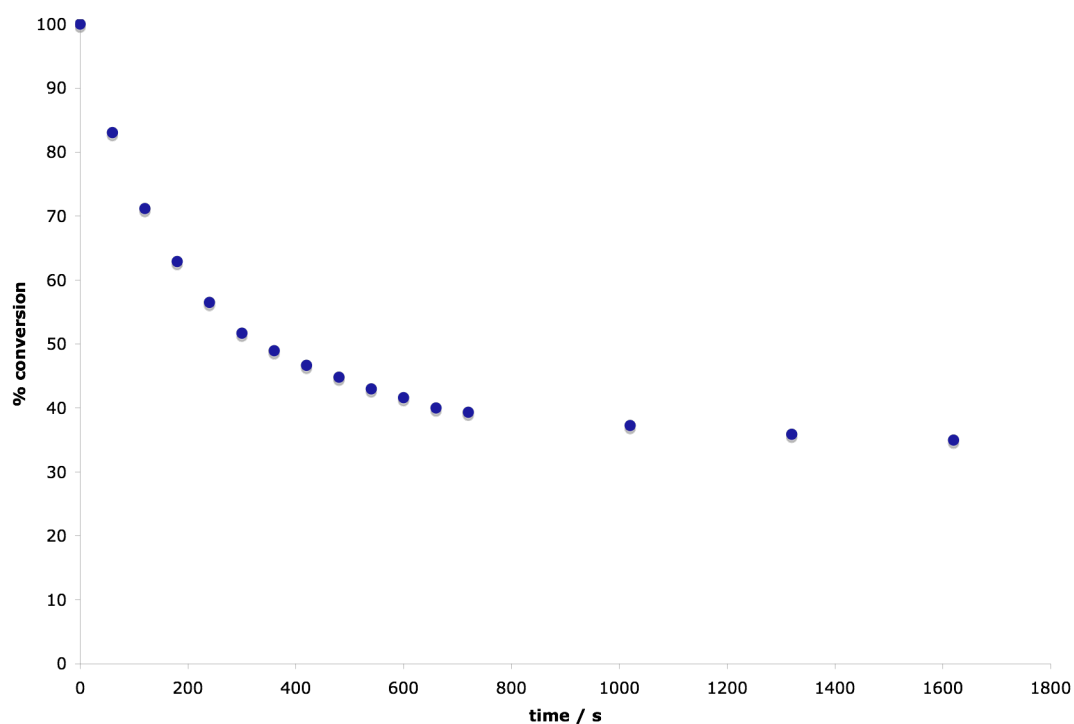


Figure 7.17: The conversion of $\text{CpW(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ to $\text{CpW(CO)}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{Me}$ at $110\text{ }^\circ\text{C}$

It was assumed that the reaction was first order and the conversion graph was used to plot the rate plot ($\ln A - a$) against time) as displayed in **Figure 7.18**. This plot confirmed that the rate was indeed first order.

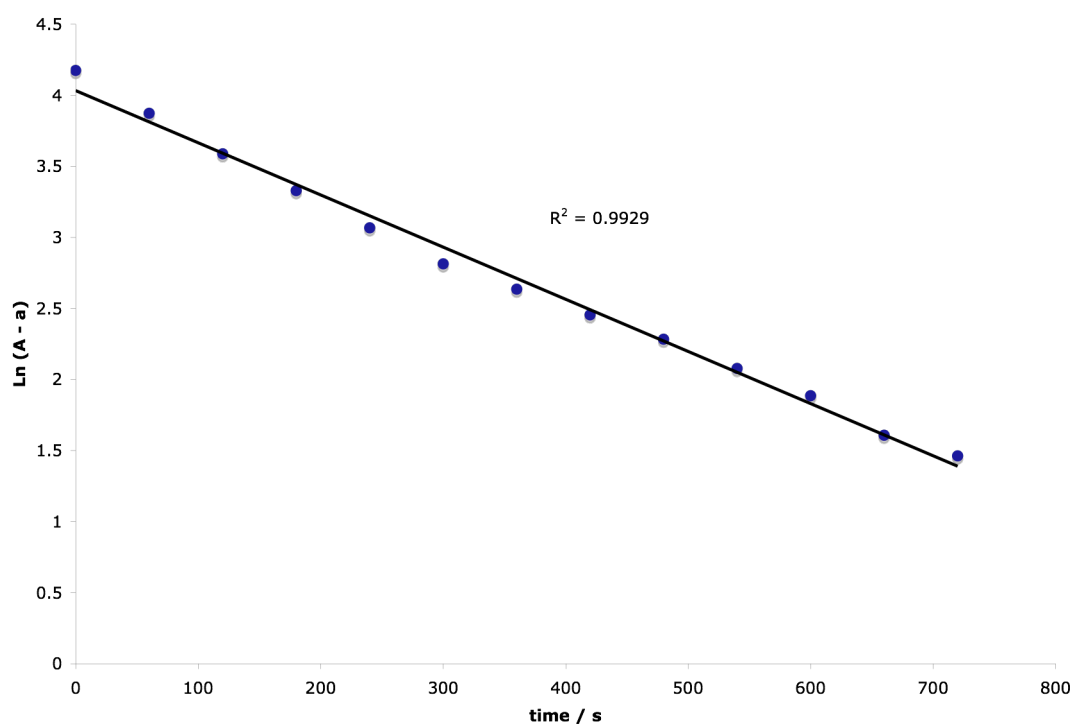


Figure 7.18: First order kinetic plot for the conversion of $\text{CpW}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ to $\text{CpW}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{Me}$ at $110\text{ }^\circ\text{C}$

As discussed in **Chapter 6** for Mo insertion complexes, according to Llewellyn *et al.* the decarbonylation reaction can occur via two mechanisms: one in which the phosphine dissociates from the metal complex allowing the decarbonylation to occur, and then the phosphine re-attaches to the metal complex, or when the CO simply dissociates from the acyl group.⁸ The kinetics of the decarbonylation reaction and the various conditions of temperature and ligand effects were investigated.

7.3.2.1 Temperature study of the decarbonylation reaction

The effect of temperature on the decarbonylation reaction was investigated using $\text{CpW}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ as a model complex. The study was undertaken in the temperature range of 100 - 120 °C. The % reaction conversion and rate plot for the decarbonylation reaction of $\text{CpW}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ at varying temperatures is shown in **Figure 7.19** and **Figure 7.20**, respectively. The data is summarised in **Table 7.6**.

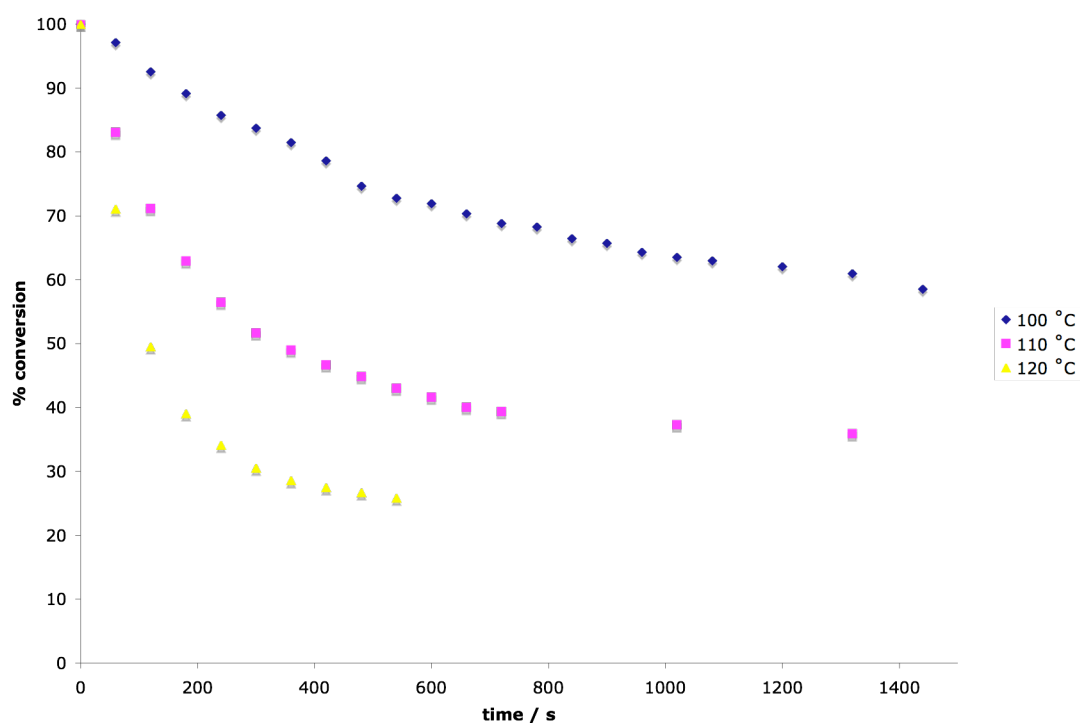


Figure 7.19: The conversion plot for decarbonylation reaction of $\text{CpW}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ at varying temperatures

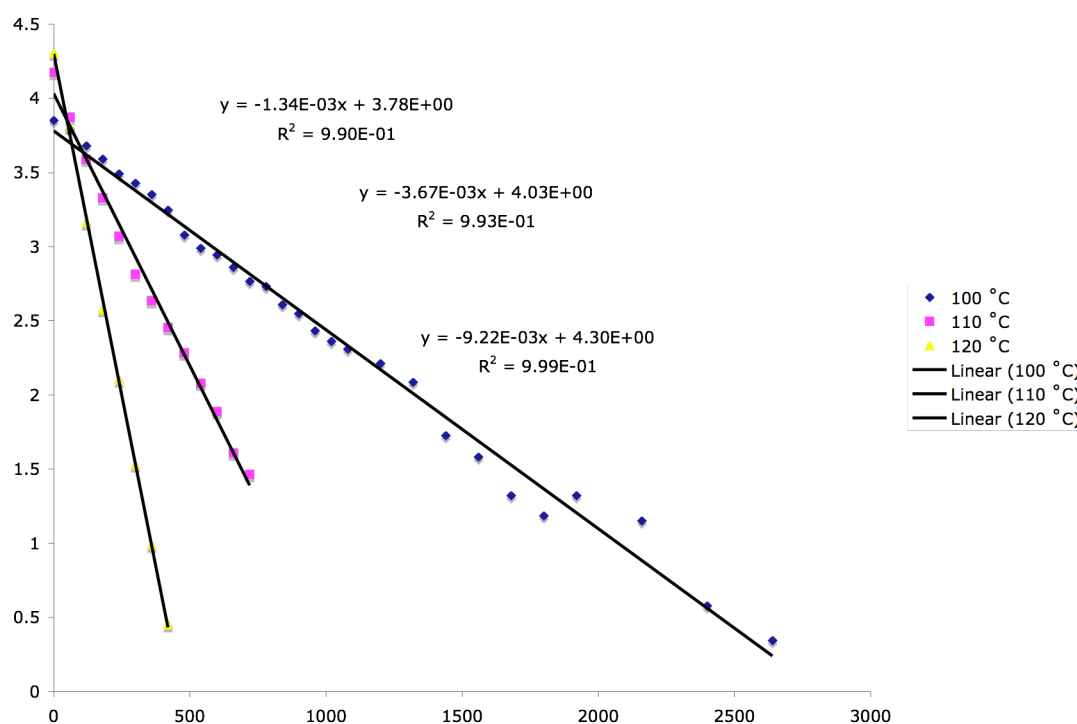


Figure 7.20: The rate plot for decarbonylation reaction of $\text{CpW}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ at varying temperatures

Table 7.6: The rate constants for the decarbonylation reaction of $\text{CpW}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ at varying temperatures

Temperature / °C	$k \times 10^{-3} / \text{s}^{-1}$	% R^2
100	1.34	99
110	3.67	99
120	9.22	100

The rate of the decarbonylation reaction increased with an increase of temperature, as one would have expected.

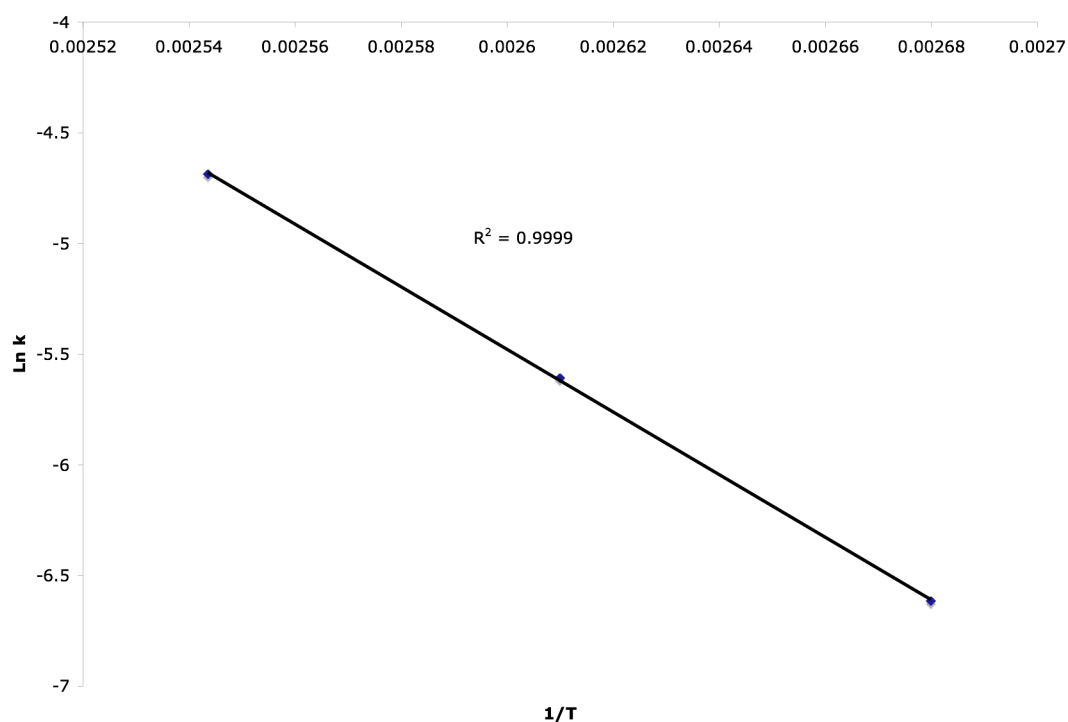


Figure 7.21: The activation energy plot of the decarbonylation reaction of $\text{CpW}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$ with at varying temperatures ($117.24 \text{ kJmol}^{-1}$)

7.3.2.2 Ligand effect study of the decarbonylation reaction

The effect of the phosphine ligand on the rate of the decarbonylation reaction was studied using the following phosphine ligands: $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$ and PPh_3 . Only $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$ did not react with the starting material to form the insertion complex, therefore the decarbonylation reaction involving this phosphine could not be monitored by DRIFTS. The decarbonylation of $\text{CpW}(\text{CO})_2(\text{L})\text{COMe}$, where $\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ and PPh_3 at 110°C is displayed in **Figure 7.22**. The rate of the reaction was assumed to first-order and the data were successfully plotted in **Figure 7.23**. A summary of these results is depicted in **Table 7.6**.

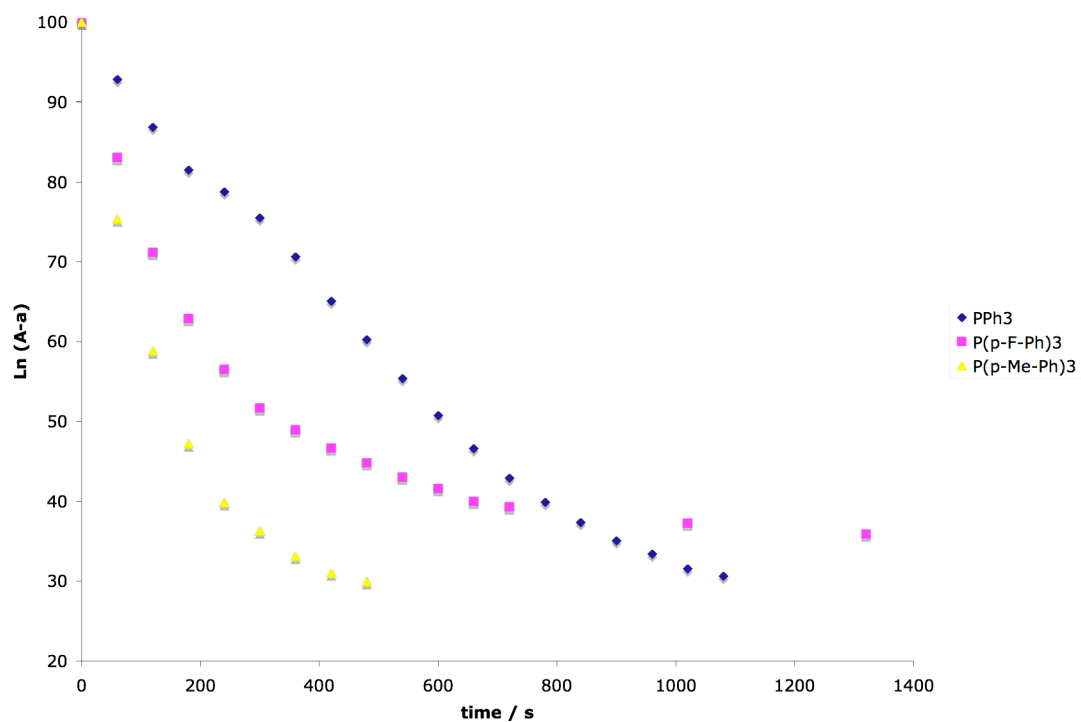


Figure 7.22: The conversion plot for the decarbonylation reaction of $\text{CpW}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{L} = \text{PPh}_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ and $\text{P}(p\text{-MeC}_6\text{H}_4)_3$) at 110°C

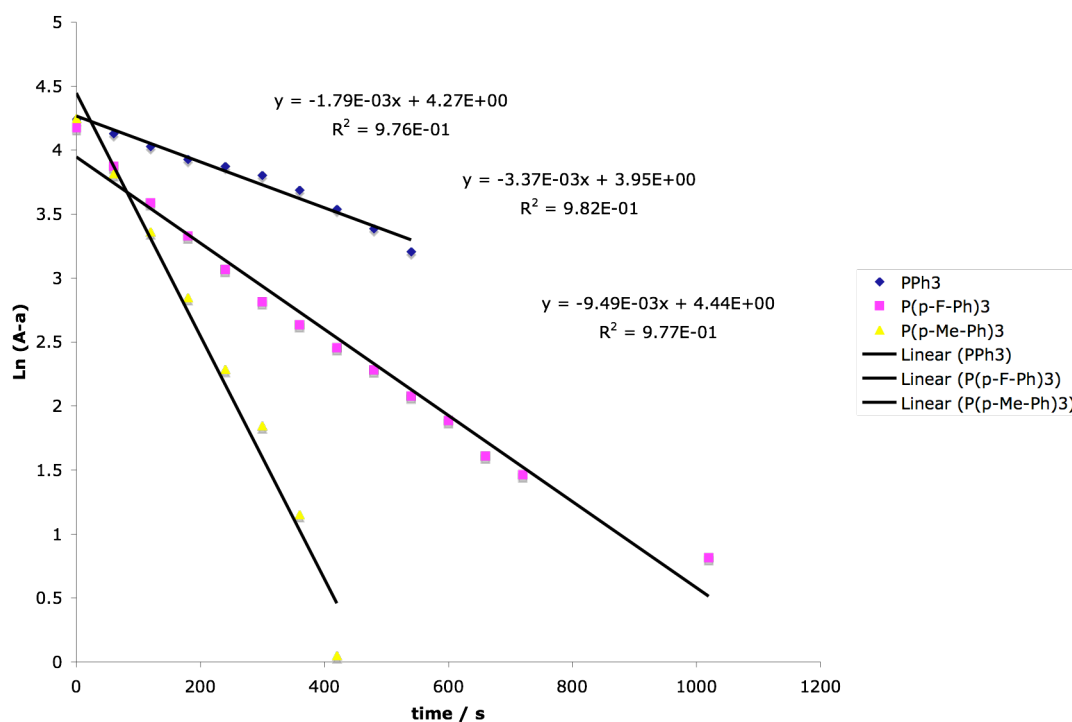


Figure 7.23: The rate plot for the decarbonylation reaction of $\text{CpW}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{L} = \text{PPh}_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ and $\text{P}(p\text{-MeC}_6\text{H}_4)_3$) at 110°C

Table 7.7: The rate constants for the decarbonylation reaction of $\text{CpW}(\text{CO})_2(\text{L})\text{COMe}$ (where $\text{L} = \text{PPh}_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ and $\text{P}(p\text{-MeC}_6\text{H}_4)_3$) at 110°C .

L	$k \times 10^{-3} / \text{s}^{-1}$	% R^2
PPh_3	1.79	98
$\text{P}(p\text{-FC}_6\text{H}_4)_3$	3.37	98
$\text{P}(p\text{-MeC}_6\text{H}_4)_3$	9.49	98

The trend derived from **Table 7.7** for the W complex containing L (in the order of decreasing rate): $\text{P}(p\text{-MeC}_6\text{H}_4)_3 > \text{P}(p\text{-FC}_6\text{H}_4)_3 > \text{PPh}_3$. As discussed in **Chapter 6**, the above phosphines have the same cone angles (therefore the same steric

effects), but they differ in their electronic effects. These electronic effects are different and are depicted in **Table 7.4**.

From **Table 7.4**, the electronic effects of the phosphine ligand decreases in the following manner: $P(p\text{-FC}_6\text{H}_4)_3 > PPh_3 > P(p\text{-MeC}_6\text{H}_4)_3$. No trend in the rate of the decarbonylation, shown above, *versus* the electronic effect of the phosphine can be ascertained. However, it can be noted that electron withdrawing ligand has a faster reaction rate than the reference ligand, PPh_3 , while the electron donating ligand had a faster reaction rate than the electron withdrawing ligand. Thus, it can be assumed that the decarbonylation reaction involving the insertion W complex occurs *via* CO being removed, and not related to the phosphine ligand.

7.4 Conclusions

An investigation of the migratory-insertion reaction of $CpW(CO)_3Me$ and phosphine ligands was studied various reaction conditions, such as, temperature, mole ratio and different ligands. The influence of the temperature and mole ratio on the reaction rate revealed unusual behaviour. An optical microscopy investigation revealed that the migratory-insertion reaction was influenced by the formation of a eutectic melt and product precipitation. Thus, the initiation of the migratory-insertion reaction was due to formation of a melt and then the progression of the rest of the reaction was diffusion-controlled.

From earlier studies (**Chapter 6**), the decarbonylation of $CpMo(CO)_2(L)COMe$ complex occurred in the solid-state and the $CpMo(CO)_2(L)COMe$ complex was

also expected to undergo a solid-state reaction. This study showed that the rate of decarbonylation increased as the temperature increased as expected. The study of the effect of the ligand on the rate of the decarbonylation showed that the electronic effect of the phosphine played no part in the reaction. The rate of the decarbonylation reaction simply depended upon the rate of the removal of CO.

7.5 References

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CHAPTER 8: THE CRYSTAL STRUCTURE ANALYSIS OF SOME Mo COMPLEXES OF THE TYPE, (CpR)Mo(CO)₂(L)COMe (R = H OR Me AND L = PHOSPHINE)

8.1 Introduction

X-ray diffraction by crystals has increased our knowledge of the architecture of a molecule and the method serves to give detailed information of the molecular structure of simple and complex stable chemical species.¹ This method was first used by Bragg in 1913, who elucidated the crystal structure of NaCl.^{1,2}

Once the individual positions of the atom have been determined by X-ray crystallography, calculations of the interatomic distances, bond angles, and other characteristics of molecular geometry, can be done.¹ Thus, crystal structure analysis, allows the unambiguous three-dimensional representation of the atoms in a crystal. This analysis can provide the link between the structure of a crystal and its chemical properties.¹

A successful crystal structure analysis depends on the crystal itself. Crystal growth is a delicate art, and there have been various methods used to achieve crystals: slow

evaporation of a solution, slow cooling of a melt, slow precipitation, and sublimation.¹ Difficulties in growth can arise when the crystal is unstable under ordinary conditions. Thus a complex may react with oxygen or moisture, or may effloresce (lose solvent of crystallisation and form a non-crystalline powder), or deliquesce (take up water from the atmosphere to form a solution) during or subsequent to crystal growth.¹

Herein various crystal structures of the type, $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{R} = \text{H}$, $\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$ and $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$; $\text{R} = \text{Me}$, $\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ and PPh_3), are reported. These insertion complexes were prepared via migratory-insertion reactions of $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ with L .

The crystal structure analysis of these insertion complexes can provide key information on the steric and electronic effects of the phosphine ligand and the R group (as discussed in **Chapter 5**).

8.2 Experimental

Solvent-free procedures, as indicated in **Chapter 3**, were used to produce the following $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ complexes, ($\text{R} = \text{H}$, $\text{L} = \text{P}(p\text{-MeOC}_6\text{H}_4)_3$ **1** and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ **2** and when $\text{R} = \text{Me}$, $\text{L} = \text{P}(p\text{-MeOC}_6\text{H}_4)_3$ **3**, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ **4**, PPh_3 **5** and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ **6**. All the complexes were crystallized using a combination of pentane or hexane and dichloromethane. The solvent was then removed after the

crystal had formed. Some crystals, namely, $\text{CpMo(CO)}_2[\text{P}(p\text{-MeOC}_6\text{H}_4)_3]\text{COMe}$ and $(\text{CpMe})\text{Mo(CO)}_2[\text{P}(p\text{-MeC}_6\text{H}_4)_3]\text{COMe}$, included the solvent of crystallisation. One of the starting materials used in this thesis, $(\text{CpCOMe})\text{Mo(CO)}_3\text{Me}$, which was made by literature methods (see **Chapter 3**) was also successfully crystallised.

The crystals were individually placed at the end of a 0.3 mm Hilgenberg Mark capillary tube and secured in position using a glass fibre. The glass fibre was then glued to the walls of the capillary and left to harden. The mounted crystals were then secured, individually, to a brass-collar before the fibre was moved to a goniometer. Intensity data were collected on a Bruker SMART 1K CCD area detector diffractometer with graphite monochromated Mo $K\alpha$ radiation (50kV, 30mA) was used for the data collection. Data reduction was carried out using the program *SAINT+* and face indexed absorption corrections were made using the program *XPREF*.³ The crystal structure was solved by direct methods using *SHELX*.⁴ Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on F_2 using *SHELX*.⁴ Hydrogen atoms were first located in the difference map then added using a function in *SHELX*.⁴ All tables and diagrams were generated using *SHELX* and *PLATON*.⁴ Details of the data collection and refinement are found in the **Appendix A9**.

8.3 Results and Discussion

Structure determination

The structures of **1** – **7** predicted by ^1H -NMR and IR spectroscopy were confirmed by X-ray analysis. A full account of the ^1H -NMR and IR spectra of the complexes solved by X-ray analysis can be found in **Chapter 3**.

8.3.1 Analysis of structural details of complexes **7**

The crystal structure details of **7**, which is a piano-stool complex used to perform migratory-insertion reactions and subsequent decarbonylation reactions as discussed in **Chapter 5** and **6**, respectively, are shown in **Table 8.1**.

Table 8.1: Crystal data and details of structure refinement for **7**

Empirical formula	$\text{C}_{11}\text{H}_{10}\text{MoO}_4$
Formula weight	302.13
Crystal system,	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 10.2284(2) \text{ \AA}, \alpha = 90^\circ$ $b = 14.216(3) \text{ \AA}, \beta = 93.387(3)^\circ$ $c = 8.1523(4) \text{ \AA}, \gamma = 90^\circ$
Volume ($\text{\AA}^3$)	1183.4(4)
Z	4
Calculated density (g/m^3)	1.696

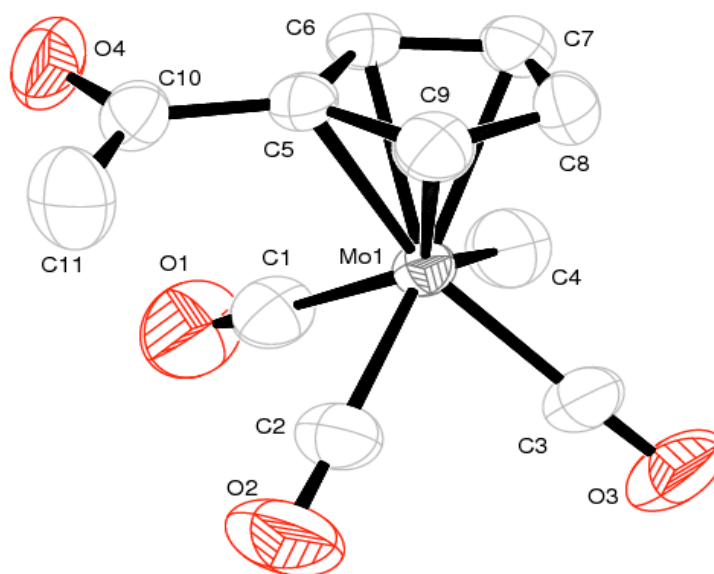


Figure 8.1a: The ORTEP diagram showing the atomic numbering of **7**

The ORTEP (Oak Ridge Thermal Ellipsoid Program) diagram for **7**, is shown in **Figure 8.1a** and the packing diagram is shown in **Figure 8.1b**. The selected bond angles and bond angles and bond lengths for **7** are given in **Table 8.2**.

This crystal structure is an example of a material used to study the migratory-insertion reaction. Numerous other related structures have been reported in the literature and a comparison of these structures with structure **7** is possible.

Table 8.2: Summary of bond distances and bond angles for (CpCOMe)Mo(CO)₃Me **7**

Mo-CO	Cp-R	Avg Mo-Cp	CO	Mo-Me	Avg C-C in Cp
(1) 1.973(4)	1.482(4)	2.344(9)	1.128(5)	2.305(4)	1.414(1)
(2) 1.991(4)			1.136(4)		
(3) 1.990(3)			1.140(4)		
OC-Mo-CO	Mo-C-O	Avg Cp-Mo-Cp	Avg Cp-Cp-C	Cp-C=O	Avg Cp angle
78.87(2)	176.9(4)	35.11(5)	126.6(8)	119.9(3)	108.0(5)
78.46(2)	178.7(4)				
71.20(2)	178.0(4)				

Another interesting characteristic of **7**, can be observed in the packing diagram shown below. The orientation depicted shows a head-to-head or tail-to-tail arrangement, with 180° alternation in the position of the Cp ring.

The angle Me-Mo-CO, is quite small, and the angle CO-Mo-CO is large for an incoming ligand, like a phosphine. This arrangement together with the head-to-head orientation facilitates the migratory-insertion reaction.

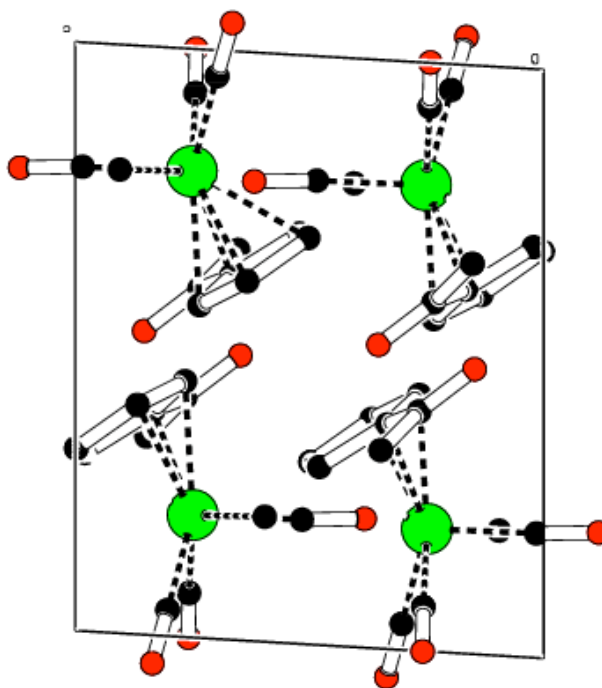


Figure 8.1b: Packing diagram of 7

An evaluation of the literature on crystal structures of piano-stool complexes revealed that the first structure reported was that of the dimer $[\pi-(C_5H_5)Mo(CO)_3]_2$. This information was reported by Chaiwasie and Fenn, who stated that the structure was first determined by Wilson and Shoemaker.⁵ Crystal structure of complexes in which the $CpMo(CO)_3$ unit has also been replaced by various groups such as $-Cl$, and $-Me$ have been reported.⁵ Chaiwasie and Fenn solved the structure of the organometallic complex, $CpMo(CO)_3Cl$, which revealed many equivalent geometric parameters to the structures reported here.⁵ **Table 8.3** lists the bond distances and angles for the

starting material i.e. (CpCOMe)Mo(CO)₃Me is comparison with other piano stool complexes discussed above.

Table 8.3: The comparison of selected bond lengths for some piano-stool complexes

Avg Bond length (Å)	CpMo(CO) ₃ Cl ⁵	CpW(CO) ₃ Cl ⁵	(CpCOMe)Mo(CO) ₃ Me
C-C (ring)	1.362(4)	1.394(9)	1.414(1)
M-C (ring)	2.304(7)	2.326(6)	2.344(9)
M-CO	1.994(1)	1.998(2)	1.982(4)
C-O	1.137(6)	1.140(3)	1.135(1)
M-X	2.498(1)	2.490(2)	2.305(4)

In **Table 8.3**, the C-C distances within the Cp ring and distances between Mo and the Cp ring were compared. **7** differed from the others in that it's average C-C (ring) and Mo-C (ring) distances were greater, probably due to the electron-withdrawing, –COMe substituent on the Cp ring. All have similar distances between Mo and the carbonyl ligands. However, the distance from the Mo atom to the 4th leg of the piano-stool, X, differed greatly. Considering the Mo metal system only, when X = Cl, the distance was 0.193 Å greater, than when X = Me. This is owing to the fact that –Cl is much larger in size than –Me. The metal to Cp ring distance is smaller for the Mo

complex than the W complex. This is also due to Mo atom being relatively smaller in size than the W atom.

8.3.2 Analysis of structural details of complexes 1 to 6

Crystal structures **1** to **6** are piano-stool complexes that are products of migratory-insertion reaction which are of the type, $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$. The crystal structure data are given in **Table 8.4**, and further details on the structure refinement, and intermolecular bond distances and angles can be found in **Appendix A9**.

Table 8.4: Crystal data details for complexes **1** - **6**

	1	2	3	4	5	6
Empirical formula	C ₃₂ H ₃₃ Cl ₃ MoO ₆ P	C ₂₇ H ₂₀ F ₃ MoO ₃ P	C ₃₁ H ₃₁ MoO ₆ P	C ₃₃ H ₃₅ Cl ₃ MoO ₃ P	C ₂₈ H ₂₅ MoO ₃ P	C ₂₈ H ₂₂ F ₃ MoO ₃ P
fw	746.84	576.34	626.47	712.87	536.39	590.37
T (K)	173(2)	293(2)	173(2)	173(2)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	P-1	P2 ₁ /n	P-1	P-1	C2/c	P2 ₁ /n
Unit cell dimensions (Å)	a = 10.766(3) α = 61.734(5) b = 13.622(4) β = 73.360(5) c = 13.665 (4) γ = 70.702(4)	a = 8.0218(3) α = 90 b = 30.0925(13) β = 104.695(3) c = 10.5945(18) γ = 90	a = 10.5126(17) α = 97.066(3) b = 10.8213(17) β = 106.301(3) c = 13.486(2) γ = 101.087(3)	a = 10.5328(5) α = 100.247(3) b = 13.6117 (8) β = 112.240(3) c = 13.7658(7) γ = 111.528(3)	a = 26.294(4) α = 90 b = 12.436 (3) β = 122.046(17) c = 17.658(4) γ = 90	a = 10.0597(4) α = 90 b = 24.400(10) β = 112.500(3) c = 11.1315(5) γ = 90
Volume (Å³)	1645.4(8)	2473.81(18)	1419.2(4)	1580.14(14)	4894.3(16)	2524.36(18)
Z	2	4	2	2	8	4
D_x calc (g/cm⁻³)	1.508	1.547	1.466	1.498	1.456	1.553

The ORTEP plots of the (CpR)Mo(CO)₂(L)COMe complexes, (R = H, L = P(*p*-FC₆H₄)₃ and P(*p*-MeOC₆H₄)₃ ; R = Me, L = P(*p*-FC₆H₄)₃, P(*p*-MeOC₆H₄)₃, P(*p*-MeC₆H₄)₃ and PPh₃), are depicted in **Figures 8.2 - 8.7**. They reveal that all the structures had *trans*-geometries.

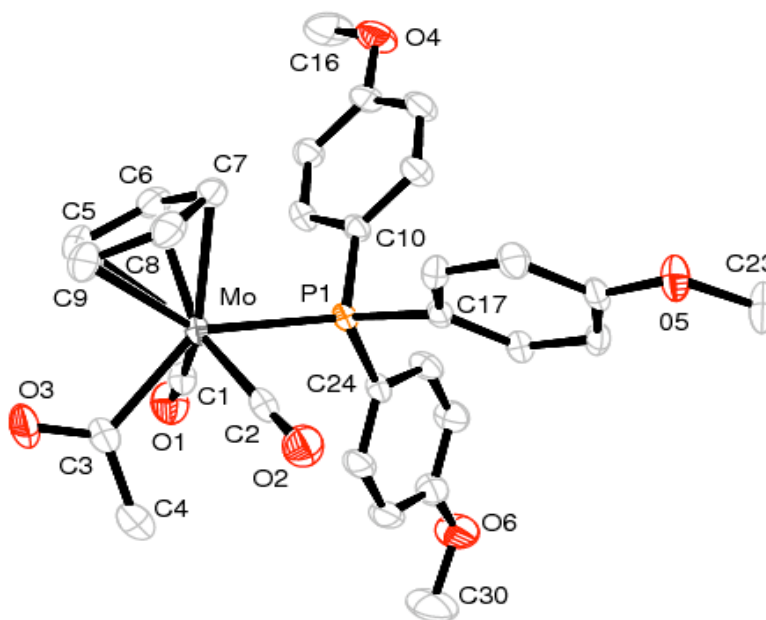


Figure 8.2a: The ORTEP diagram showing the atomic numbering of **1**

Structure **1** is a piano-stool complex containing an unsubstituted Cp ring and a $P(p\text{-MeOC}_6\text{H}_4)_3$ ligand. It was crystallized from a mixture of dichloromethane and hexane, and contains a solvent molecule in the crystal structure. It is found in the triclinic crystal system with a space group P-1, and has 2 molecules in its unit cell (as seen in the packing diagram **Figure 8.2b**).

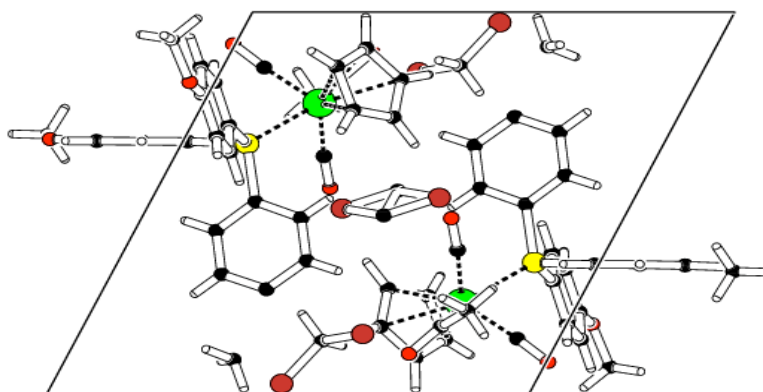


Figure 8.2b: The packing diagram of **1**

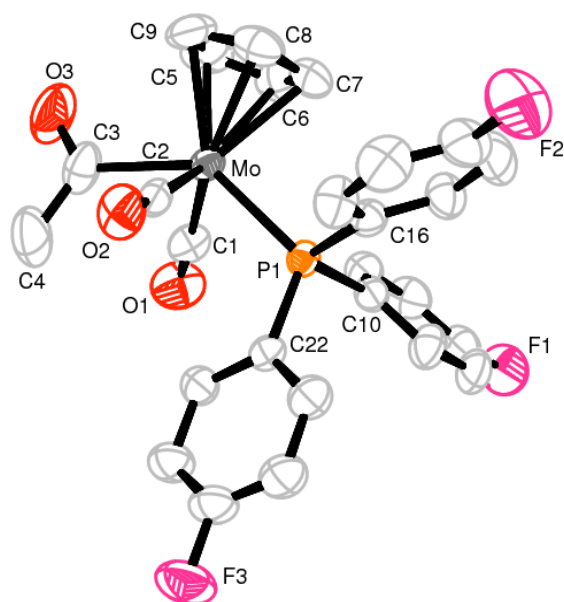


Figure 8.3a: The ORTEP diagram showing the atomic numbering of **2**

Structure **2** is a piano-stool complex containing a Cp ring and a $P(p\text{-FC}_6\text{H}_4)_3$ ligand. This complex crystallized in a monoclinic crystal system with a $P2_1/n$ space group. It can accommodate four molecules in the unit cell (see packing diagram **Figure 8.3b**)

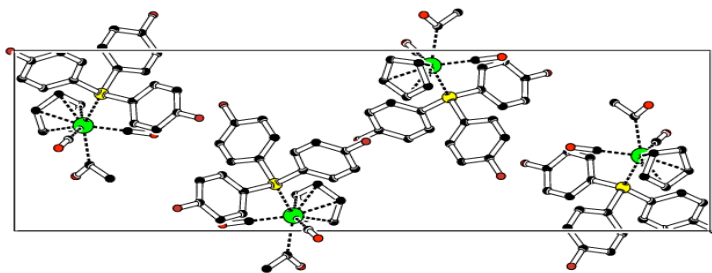


Figure 8.3b: The packing diagram of **2**

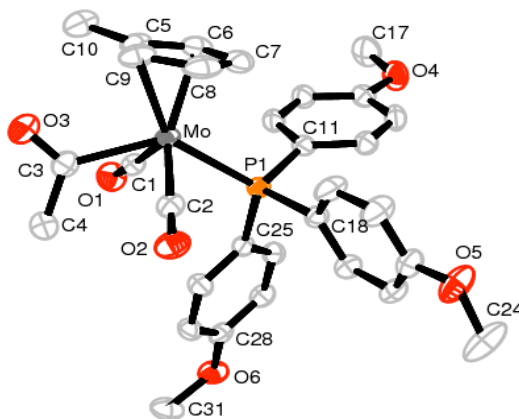


Figure 8.4a: The ORTEP diagram showing the atomic numbering of **3**

Structure **3** is a methyl-substituted Cp ring piano-stool complex, with a $P(p\text{-MeOC}_6\text{H}_4)_3$ ligand. Similar to **1**, it crystallizes in the triclinic crystal system with the

space group P-1, and contains two molecules in the unit cell (see packing diagram **Figure 8.4b**).

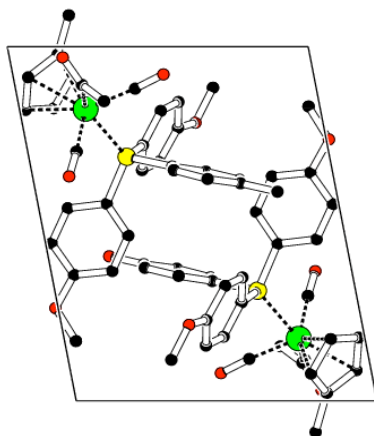


Figure 8.4b: The packing diagram of **3**

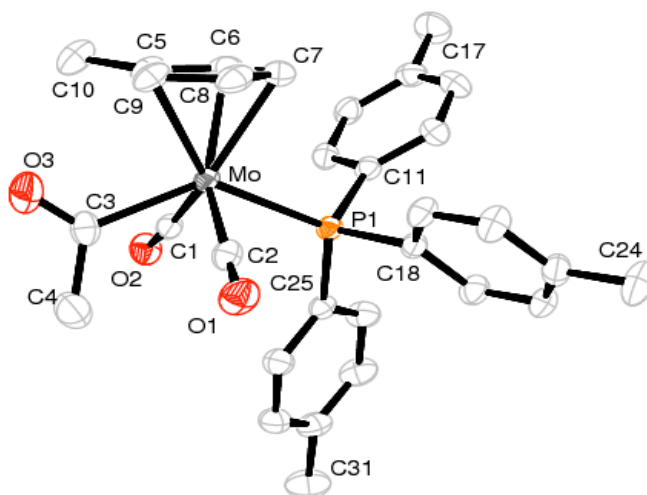


Figure 8.5a: The ORTEP diagram showing the atomic numbering of **4**

Structure **4** is a methyl-substituted Cp ring piano-stool complex with a $P(p\text{-MeC}_6\text{H}_4)_3$ ligand. **4** is similar to **1** and **3**, because they have a triclinic crystal system with a P-1

space group, and has two molecules in the unit cell (see packing diagram **Figure 8.5b**). **4** also contains a solvent molecule, which is similar to **1**.

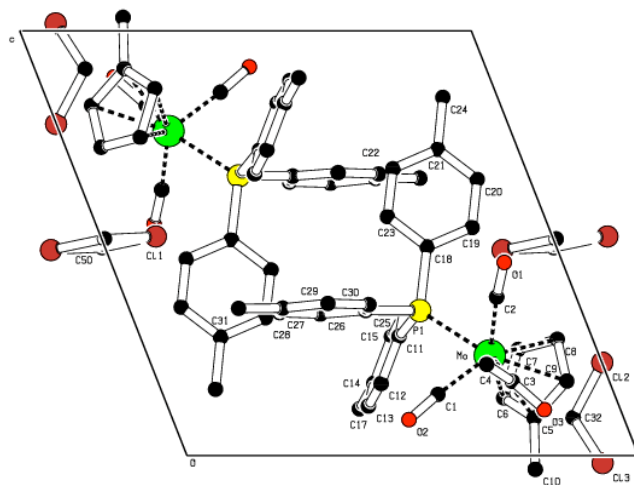


Figure 8.5b: The packing diagram of **4**

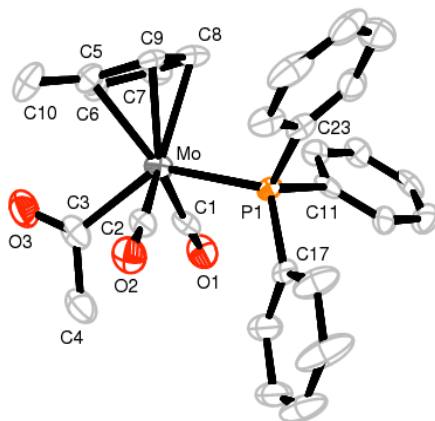


Figure 8.6a: The ORTEP diagram showing the atomic numbering of **5**

Structure **5** is a methyl-substituted piano stool complex containing a PPh₃ ligand. It has a monoclinic crystal system like **1**, but it has a C2/c space group. Unlike the rest

of the structures, it can accommodate eight molecules in the unit cell (see packing diagram **Figure 8.6b**).

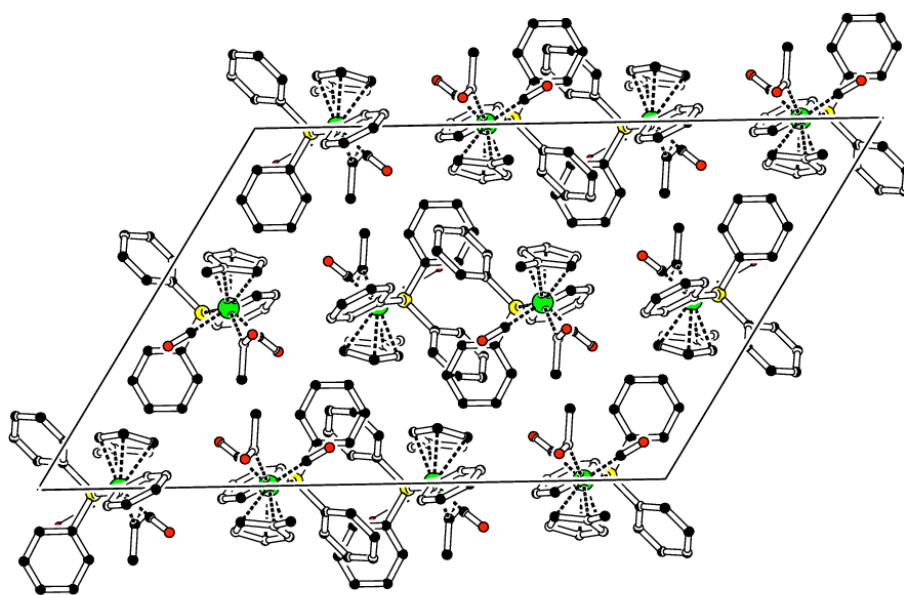


Figure 8.6b: The packing diagram of **5**

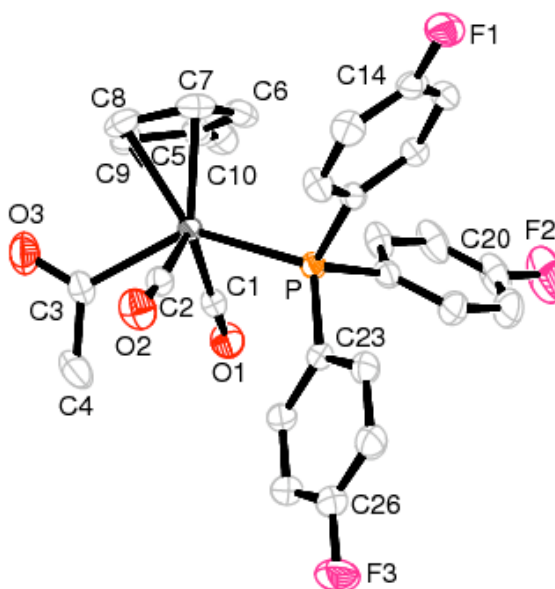


Figure 8.7a: The ORTEP diagram showing the atomic numbering of **6**

Structure **6** is a methyl-substituted Cp ring piano-stool complex containing a $P(p\text{-FC}_6\text{H}_4)_3$ ligand. It is found in a monoclinic crystal system with a $P2_1/n$ and has four molecules in the unit cell. **6** shares the above characteristics with **2**, which only differ from each other by a methyl-substitution on Cp ring for **6** (see packing diagram **Figure 8.7b**).

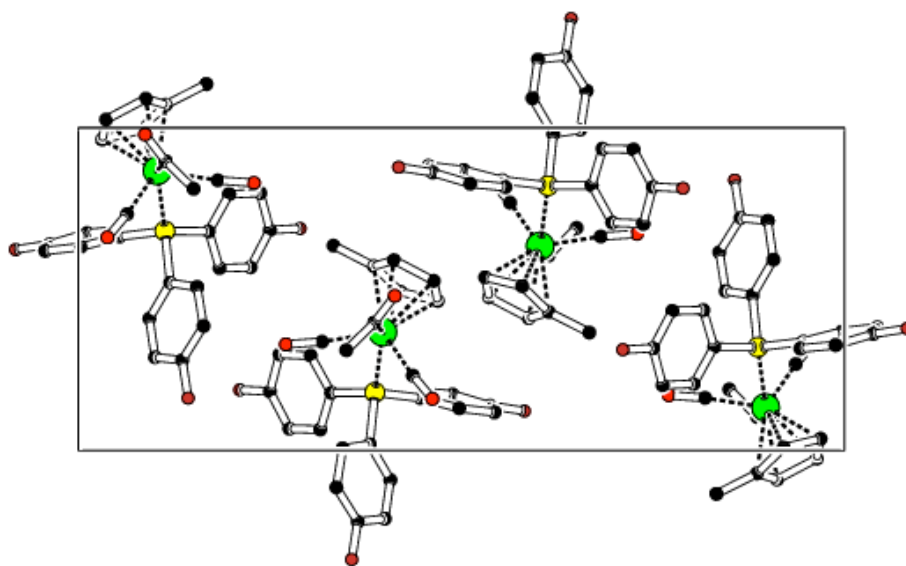


Figure 8.7b: The packing diagram of **6**

A summary of bond distances and bond angles for $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ complexes ($\text{R} = \text{Me}$ and $\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ and PPh_3 and $\text{R} = \text{H}$, $\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$ and $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$) are displayed in **Tables 8.5** and **8.6** respectively. More detailed tables of the bond angles and distances can be found in the **Appendix A9**.

Table 8.5: Summary of structural data (bond lengths, Å) (CpR)Mo(CO)₂(L)COMe
(R = H with L = and P(*p*-MeOC₆H₄)₃ **1** and P(*p*-FC₆H₄)₃ **2**; R = Me with L = P(*p*-
MeOC₆H₄)₃ **3**, P(*p*-MeC₆H₄)₃ **4**, PPh₃ **5** and P(*p*-FC₆H₄)₃ **6**).

	Avg CO-Mo	Avg C-O	C-C in Cp	Mo- ring	Cp-R	Mo-P	C=O	Me-CO	Mo-CO
	R = H								
1	1.972(1)	1.154(6)	1.418(1)	2.354(6)	-	2.468(1)	1.209(6)	1.525(7)	2.269(4)
2	1.956(9)	1.153(9)	1.400(6)	2.338(1)	-	2.419(9)	1.207(5)	1.502(6)	2.263(4)
	R = Me								
3	1.966(7)	1.157(8)	1.417(6)	2.358(7)	1.516(4)	2.476(9)	1.215(3)	1.526(4)	2.270(8)
4	1.971(4)	1.155(6)	1.422(2)	2.342(7)	1.500(5)	2.4794(8)	1.203(4)	1.534(6)	2.267(4)
5	1.960(6)	1.165(14)	1.423(2)	2.341(1)	1.496(2)	2.466(3)	1.223(2)	1.508(2)	2.275(2)
6	1.966(7)	1.155(8)	1.423(2)	2.347(4)	1.506(3)	2.4670(5)	1.215(3)	1.510(4)	2.275(2)

Table 8.6: Summary of structural data (bond angles, Å) for (CpR)Mo(CO)₂(L)COMe (R = H with L = P(*p*-MeOC₆H₄)₃ **1** ; P(*p*-FC₆H₄)₃) **2** and R = Me with L = P(*p*-MeOC₆H₄)₃ **3**, P(*p*-MeC₆H₄)₃ **4**, PPh₃ **5** and P(*p*-FC₆H₄)₃ **6**.

Complex	P-Mo-Acetyl	Avg P-Mo-CO	C1-Mo-C2	Avg OC-Mo-Acetyl
	R = H			
1	133.12(2)	79.60(1)	109.09(1)	73.82(2)
2	135.42(2)	81.39(1)	106.64(5)	72.58(2)
	R = Me			
3	133.1(7)	80.05(7)	106.13(1)	72.44(1)
4	133.60(1)	80.42(1)	108.34(1)	73.10(1)
5	133.6(4)	79.6(4)	108.2(2)	73.84(5)
6	134.56(6)	80.61(1)	107.99(9)	73.50(4)

Selected torsion angles for structures **1 – 6** are depicted in **Table 8.7**, and **Figures 8.2a - 8.7a** can be used to ascertain the torsion angles being measured for the six complexes.

Table 8.7: The torsion angles around selected atoms for structures **1 - 6**

	1	2	3	4	5	6
Cp-Mo-P-C _{P1} *	34.017(2)	44.447(2)	39.594(1)	38.183(5)	38.127(1)	39.919(2)
Cp-Mo-P-C _{P2} *	83.982(2)	74.316(2)	82.111(1)	82.217(5)	83.280(1)	78.011(2)
Cp-Mo-P-C _{P3} *	152.795(2)	164.176(2)	156.644(8)	153.75(4)	156.432(1)	159.436(2)
Cp-Mo-C ₃ -C ₄	164.123(2)	173.645(2)	172.544(1)	172.192(5)	173.115(2)	163.430(2)
Cp-Mo-C ₃ -O ₃	13.508(4)	6.819(3)	8.871(1)	8.889(7)	3.371(1)	20.763(3)

*Note C_{P1}, C_{P2} and C_{P3} refers to the 1st, 2nd and 3rd C atom attached to the P atom

A search for similar acyl complexes in the Cambridge Crystallographic Database Centre (CCDC) yielded no results for similar products containing a substituted Cp ring.⁶ However structural studies have been performed on complexes of the type $\text{CpM}(\text{CO})_2(\text{X})(\text{COMe})$ (M= transition metal, X = any molecule). The crystal data of these complexes are summarized in **Table 8.8**.

Table 8.8: Selected bond lengths and angles of literature crystals of the type $\text{CpM}(\text{CO})_n(\text{X})\text{COMe}$ complexes⁶

	M=Mo X = PPh₃	M = Mo X = PPh₂COMe	M = Fe X = P(<i>p</i>-MeC₆H₄)₃	M = Fe X = P(<i>p</i>-FC₆H₄)₃
Bond lengths, Å				
Avg CO-M	1.947(1)	1.950(4)	1.746(3)	1.748(3)
Avg C-O	1.148(2)	1.152(5)	1.149(3)	1.151(3)
C-C in Cp	1.406(2)	-	1.391(5)	1.406(4)
M-ring	2.347(1)	2.331(5)	2.113(3)	2.118(3)
M-P	2.473(3)	2.446(2)	2.193	2.194(8)
C=O	1.211(2)	1.203(7)	1.202(3)	1.203(3)
Me-CO	1.550(2)	1.506(7)	1.535(4)	1.518(4)
M-CO	2.264(1)	2.259(6)	1.953(3)	1.956(3)
Bond angles, °				
P-M-Acetyl	132.7(4)	136.3(1)	89.0(8)	90.16(8)
Avg P-M-CO	79.1(4)	80.4(2)	93.04(8)	91.72(9)
C1-M-C2	107.9(5)	106.4(2)	-	-
Avg OC-M-Acetyl	73.7(5)	74.0(2)	94.70(12)	94.41(1)

In 1968, Churchill and Fennessey, solved the crystal structure of $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{COMe}$.⁷ This was the first crystal structure of a Mo complex with an acyl group formed in a migratory-insertion reaction. Structures **1** to **6** have a similar arrangement of ligands to that of $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{COMe}$. More importantly structures **5** and $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{COMe}$ differ only in the substituent attached to

the Cp ring (H or Me). Interestingly **5** and $\text{CpMo(CO)}_2(\text{PPh}_3)\text{COMe}$ also have a monoclinic $C2/c$ space group.⁷

8.3.3 Effect of the Cp ring substituent on the intermolecular bond lengths and angles of the complexes $(\text{CpR})\text{Mo(CO)}_2(\text{L})\text{COMe}$

The crystal structure study was used to make a comparison between structures containing similar phosphine ligands, but different Cp ring substituents, R. **Table 8.9** shows selected geometries for the comparison of the complexes that share a common phosphine ligand.

Table 8.9: Selected bond lengths and angles ($\text{\AA}$) associated with the R group in $(\text{CpR})\text{Mo(CO)}_2(\text{L})\text{COMe}$, where R = H and L = $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$ **1** and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ **2**; R = Me and L = $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$ **3** and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ **6**; R = Me, L = PPh_3 **5** and $\text{CpMo(CO)}_2(\text{PPh}_3)\text{COMe}$ **a**

Length	1	3	2	6	5	a
Avg CO-Mo	1.972(1)	1.966(7)	1.956(9)	1.966(7)	1.961(1)	1.955(1)
Avg C-O	1.154(6)	1.157(8)	1.153(9)	1.155(8)	1.165(13)	1.148(2)
C-C in Cp	1.418(1)	1.417(6)	1.400(6)	1.423(2)	1.423(2)	1.406(2)
Mo-ring	2.354(6)	2.358(7)	2.338(1)	2.347(4)	2.341(1)	2.347(1)
Cp1-R*	1.000	1.516(4)	1.000	1.506(3)	1.496(2)	1.000
Mo-P	2.468(1)	2.476(9)	2.419(9)	2.4670(5)	2.466(3)	2.473(3)
C=O	1.209(6)	1.215(3)	1.207(5)	1.215(3)	1.223(2)	1.211(2)
Me-CO	1.525(7)	1.526(4)	1.502(6)	1.510(4)	1.508(5)	1.550(2)
Mo-CO	2.269(4)	2.270(8)	2.263(4)	2.275(2)	2.275(1)	2.264(1)

Angle	1	3	2	6	5	a
P-Mo-Acetyl	133.12(1)	133.1(7)	135.42(1)	134.56(6)	133.6(4)	132.7(4)
Avg P-Mo-CO	79.60(1)	80.05(7)	81.39(1)	80.61(1)	79.6(4)	79.1(3)
C1-Mo-C2	109.09(1)	106.13(1)	106.64(2)	107.99(9)	108.3(5)	107.9(5)
Avg OC-Mo-Acetyl	73.82(2)	72.44(1)	72.58(2)	73.50(4)	73.85(4)	73.7(5)
Cp2-Cp1-R*	125.8	123.9(3)	125.8	127.7(2)		
Cp3-Cp1-R*	125.8	128.7(3)	125.8	125.2(2)		

Note: * *Cp1* is the C from the Cp ring attached to the R group and *Cp2* and *Cp3* are carbons on the Cp ring adjacent to *Cp1*.

Comparison of **1** and **3** (similar P(*p*-MeOC₆H₄)₃ ligand, differing only by R)

The comparison of **1** and **3**, shows that the distance from the Cp to the R group is greater for **3**. It should be noted that Cp-H distance is fixed by SHELX³ and not a true indication of the Cp-H distance found in the crystal. The average CO-Mo distance is greater for **3** than **1**.

They share the following similarities: C-C bond distance on the Cp ring, Mo-C=O bond distance, P-Mo-acetyl angle, the average angle between P-Mo-CO and the average angle between OC-Mo-acetyl.

From **Table 8.9** above, **3** has lower bond distances for the following: average C-O distance, distance of the Mo to the Cp ring and to the P atom, and C=O bond distance. The angle about the mutual C atom attached to both the Cp ring and the R group also differs. The -Me group is bent 2 ° closer to the Cp ring than -H.

Comparison of **2** and **6** (similar P(*p*-FC₆H₄)₃ ligand, differing only by R)

When **2** and **6** are compared, it can be seen that most bond angles and distances are greater for **6** than **2**.

From **Table 8.9**, it is observed that they both share the following similarities: average C-O distance, P-Mo-Acetyl angle, average P-Mo-CO angle, C1-Mo-C2 angle, and average OC-Mo-acetyl bond angle. As in the comparison of **1** and **3** above, the angle about the mutual C atom attached to both the Cp ring and the R group also differs. The -Me group is bent slightly closer to the Cp ring than -H.

Comparison of 5 and a (CpMo(CO)₂(PPh₃)COMe) (similar PPh₃ ligand, differing only by R)

5 and CpMo(CO)₂(PPh₃)COMe complex found in the literature⁷, share similar intermolecular features e.g. the average distance from the Mo to the carbonyl ligands, the Mo to the ring, the average angle of P-Mo-CO and acetyl-Mo-CO and the angle between the two carbonyls. **5** has similar geometric parameters to other related piano-stool complexes. For example, the angle P-Mo-COMe is 133.6° (**4**) compares well with the corresponding *trans*-(OC-Mo-X) angles: 132.7° (**4**) in CpMo(CO)₂(PPh₃)COMe, 131.6° in [(C₁₀H₅)Mo(CO)₃CH₃]₂, and 131.8° in CpMo(CO)₃C₂H₅.⁷

The differences in the two structures are as follows: the average carbonyl (C-O) distance and the average C-C distance in the Cp ring is ~ 0.02 Å greater in **5**, the Cp-Me distance (**5**) is larger than Cp-H distance, the C=O distance and Mo-CO distance is greater in **5**, and **5** has a smaller distance in Mo-P and Me-C=O.

8.3.4 Summary of significant features noted from the crystallographic data

Mo-Cp distances

Distances from the individual Mo-C in the Cp ring range from 2.338 to 2.356 Å, which is a similar range as that found in the literature complexes, CpMo(CO)₂(PPh₃)COMe.⁷

M-Phosphine distances

In **5**, the Mo-P distance (2.466(3) Å) is also found to be similar to CpMo(CO)₂(PPh₃)COMe (2.473(3) Å) which is longer than other observations cited.⁸ It is this that gives evidence for the d_π-p_π metal-phosphorus back donation.⁷ Similar to CpMo(CO)₂(PPh₃)COMe, the P-C bond lengths and angles showed no evidence of back donation and this was also found in crystal structures containing PPh₃.⁷

When we compare the different phosphine ligand for the methyl-substituted Cp insertion complexes, the P atom distance to Mo increases in the following trend: P(*p*-MeC₆H₄)₃ **3** ≥ P(*p*-MeOC₆H₄)₃ **4** > P(*p*-FC₆H₄)₃ **6** ≥ PPh₃ **5**, and for the unsubstituted Cp complexes : P(*p*-MeOC₆H₄)₃ **1** ≥ P(*p*-FC₆H₄)₃ **2**. All 6 insertion complexes have similar average bond angle between the phosphine-Mo-CO. All phosphines, but P(*p*-F-Ph)₃, share the ~ 133 ° angle between P-Mo-Acetyl. In P(*p*-FC₆H₄)₃, on the other

hand, the angle is 134.6 ° and 135.4 °, in the Me-substituted Cp and unsubstituted Cp complexes, respectively.

MC(Me)O angle

The bond angles about the ketonic carbon atom shown in **Table 8.10** for Mo-C3-C4, Mo-C3-O3 and C4-C3-O3 are connected with an sp^2 bond angle of about 120° as found for CpMo(CO)₂(PPh₃)COMe (120.9(1)° , 121.2(1)° and 117.7(1)° respectively.⁷

Table 8.10: Bond angles about the ketonic carbon atom for **1 - 6**

	1	2	3	4	5	6	a
Mo-C3-C4	122.7(3)	123.4(3)	121.3(3)	122.05(2)	122.0(1)	122.6(2)	120.9(1)
Mo-C3-O3	120.7(4)	119.9(4)	122.4(3)	121.0(2)	120.3(1)	119.7(2)	121.2(1)
C4-C3-O3	116.6(4)	116.7(4)	116.4(4)	116.4(4)	117.5(1)	117.6(2)	117.7(1)

M-COMe distances and angles

The C(3)-O(3) bond distance of 1.223(2) Å for **5** agrees with 1.211(2) Å in CpMo(CO)₂(PPh₃)COMe and with the accepted “ketonic-carbonyl” bond distance.⁷ The rest of the complexes were also in the range 1.204 - 1.223 Å. The C(3)-C(4) distance range of 1.503-1.535 Å is also within the standard deviation of ideal C(sp^2)-C(sp^2) value of 1.51.⁷ When comparing the different phosphine ligand for the methyl-substituted Cp insertion complexes, the C3-C4 distance increases as

following: $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ **3** > $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$ **4** > $\text{P}(p\text{-FC}_6\text{H}_4)_3$ **6** $\geq$ PPh_3 **5** and for the unsubstituted Cp complexes : $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$ **1** $\geq$ $\text{P}(p\text{-FC}_6\text{H}_4)_3$ **2**.

The Mo-acetyl bond distance of 2.275(1) Å for **5** is within standard deviation of $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{COMe}$. The range of this bond distance for the six insertion complexes is 2.263 – 2.275 Å. Only **2** had a smaller distance, and differed by 0.01 to the others. Churchill and Fennessey compared their Mo-acyl linkage of 2.264(1) Å to a larger Mo-alkyl distance of 2.383(1) Å $[\text{C}_{10}\text{H}_5]\text{Mo}(\text{CO})_3\text{CH}_3]_2$ and concluded that this suggested $d_\pi\text{-p}_\pi$ back donation in transition metal acyl complexes.⁷ Our data also shows this, owing to the short distance between the Mo-acetyl bond.

8.3.5 Steric and electronic effect of phosphines as detected by the X-ray crystallography study

According to Tolman, the cone angles of *para*-substituted phosphines are all 145 °, and their solid angles are all 129 °. Interestingly, when the observed co-ordinates of atoms for $(\text{CpMe})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ (where L = $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$ **3**, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ **4**, PPh_3 **5** and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ **6**), were used in the program STERIC⁸, the calculated Tolman cone angles and solid angles obtained were slightly different from the expected 145 ° (see **Table 8.7**). This shows that the geometry of the phosphine

changes according to the chemical environment it is in. The cavity formed by the rest of the molecule is affected by the phosphine.

Table 8.11: Calculated Tolman cone angles⁹ and solid angles¹⁰ for L from (CpMe)Mo(CO)₂(L)COMe, where L = P(*p*-MeOC₆H₄)₃ **3**, P(*p*-MeC₆H₄)₃ **4**, PPh₃ **5** and P(*p*-FC₆H₄)₃ **6**

L	Calculated Tolman cone angle / °	Calculated solid angle / steradians	Tolman cone angle ^a / °	Solid angle / °
P(<i>p</i> -MeOC ₆ H ₄) ₃	149	3.201	145	129
P(<i>p</i> -MeC ₆ H ₄) ₃	148	3.282	145	129
P(<i>p</i> -FC ₆ H ₄) ₃	148	3.244	145	129
PPh ₃	147	3.259	145	129

Note (a) Ref. Tolman calculated using Ni system

Tolman also quantified the electronic effect using the electronic parameter as discussed in **Chapter 5**, which is listed in **Table 8.12**.⁹ This shows that the Tolman electronic parameter decreases as follows: P(*p*-FC₆H₄)₃ > PPh₃ > P(*p*-MeC₆H₄)₃ > P(*p*-OMeC₆H₄)₃.

Table 8.12: The Tolman electronic parameters,⁹ calculated Tolman cone angles and electron donating and withdrawing ability¹¹ of phosphine ligands used in this decarbonylation study

Phosphine ligand	Tolman Electronic parameter (ν) ⁹ / cm^{-1}	Calculated Tolman cone angle / °	Electron donating / withdrawing ¹¹
P(<i>p</i> -OMeC ₆ H ₄) ₃	2066.1	149	donating
P(<i>p</i> -MeC ₆ H ₄) ₃	2066.7	148	donating
PPh ₃	2068.9	147	reference ligand
P(<i>p</i> -FC ₆ H ₄) ₃	2071.3	148	withdrawing

More interesting data extracted from the crystal structures of **3** - **6**, are the structural characteristics associated with the various phosphines attached to the Mo system. Since the metal system remains the same for all four complexes, the geometry of the varying phosphines should differ, and thus are indicative of the steric and electronic effects of the phosphines. **Table 8.13** lists various bond lengths and angles around the phosphorous atom.

Table 8.13: Selected bond lengths and angles associated with the phosphine ligand

	3	4	5	6
Mo-P1	2.4766(9)	2.4794(8)	2.466(3)	2.4670(5)
P1-C(1P)	1.829(2)	1.835(3)	1.835(1)	1.836(2)
P1-C(2P)	1.834(2)	1.837(3)	1.821(1)	1.838(2)
P1-C(3P)	1.834(2)	1.836(3)	1.843(1)	1.834(2)
CO-Mo-P1	79.14(7)	81.05(1)	79.4(4)	79.67(6)
Mo-P1-C(1P)	114.07(8)	110.32(1)	112.4(4)	116.42(7)
Mo-P1-C(2P)	116.71(8)	118.40(1)	115.0(4)	118.99(8)
Mo-P1-C(3P)	117.27(8)	117.70(1)	112.4(4)	116.42(2)
C(1P)-P1-C(2P)	102.46(2)	103.13(2)	101.5(5)	101.58(1)
C(2P)-P1-C(3P)	102.19(2)	102.40(2)	103.7(5)	101.86(1)
C(3P)-P1-C(2P)	102.33(2)	102.87(2)	103.6(5)	104.16(1)
	X = MeO	X = Me		X = F
C-X1	1.371(3)	1.520(5)	-	1.354(3)
C-X2	1.364(3)	1.516(5)	-	1.362(2)
C-X3	1.368(3)	1.514(5)	-	1.363(3)

The above table indicates the following points:

- 1) The bond length between the Mo-P decreases in the following manner: **4** > **3** > **6** > **5**. This is identical to the sequence of solid angle measurements (**Table 8.11**), thus it can be said that the greater the solid angle of the phosphine, the greater the bond length between the phosphine and the Mo.
- 2) The shortest and longest bond distance between the P atom and the C atom (of the phenyl ring) can be found in **5**, which contains the PPh₃ ligand.
- 3) All have similar angles between the carbonyl-Mo-P.

- 4) The angle between Mo-P-C_{phenyl} decreases in the following way: **6** > **3** > **4** > **5**.

The first three complexes in the sequence indicate that the smaller the electronic effect, the greater the Mo-P-C_{phenyl} angle. Also, considering **6**, **3** and **4**, as the angle between Mo-P-C_{phenyl} decreases, the solid angle of the phosphine increases. Thus, the greater the steric effect, the smaller the Mo-P-C_{phenyl} angle.

- 5) All have similar C_{phenyl}-P-C_{phenyl} angles.
- 6) The bond lengths of the C_{phenyl}-X decreases (X = Me, MeO and F; substituents on the phenyl ring) in the following sequence of X: Me **4** > MeO **3** > F **6**, which is indicative of the electronic effect. Thus, the greater the electronic effect of X, the greater the bond length of X to the carbon on the phenyl ring.

8.3.6 Steric and electronic effects of substituent, R as detected from crystallographic study

The two complexes with common phosphines (**1** and **3** with P(*p*-MeOC₆H₄)₃ and **2** and **6** with P(*p*-FC₆H₄)₃) were used to determine the effect of the R group on the structure of the complexes. The cone angles and electronic parameters for the R groups (as mentioned in **Chapter 5**) are shown in **Table 8.14**.

Table 8.14: The cone angles and solid angles for $C_5H_4R^{10}$ and electronic factors for CH_2R^{12}

R	θ_1 (°)	θ_2 (°)	Ω_{av} (°)	F	σ_I	σ_R
H	128	55	131	0.03	0	-
Me	141	64	144	0.01	-0.05	-0.13

8.3.7 The steric and electronic effect of the phosphine and R group on the decarbonylation reaction

An attempt was made to relate the structural data of the crystal study of the insertion complexes to the decarbonylation reaction, the subsequent reaction after the migratory-insertion reaction. A summary of rate constants derived from DRIFTS investigations on the decarbonylation reaction (see **Chapter 6**) is displayed in **Table 8.15**.

Table 8.15: The rate constants ($\times 10^{-3} \text{ s}^{-1}$) for the decarbonylation reaction of $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ complexes ($\text{R} = \text{H}$, $\text{L} = \text{P}(p\text{-MeOC}_6\text{H}_4)_3$ **1** and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ **2** and when $\text{R} = \text{Me}$ and $\text{L} = \text{P}(p\text{-MeOC}_6\text{H}_4)_3$ **3**, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ **4**, PPh_3 **5** and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ **6**

R \ L	$\text{P}(p\text{-MeOC}_6\text{H}_4)_3$	$\text{P}(p\text{-MeC}_6\text{H}_4)_3$	PPh_3	$\text{P}(p\text{-FC}_6\text{H}_4)_3$
H	1.25	n/a	n/a	3.18
Me	2.93	3.24	2.21	4.99

According to the decreases of the rate of decarbonylation, the above table shows that when $\text{R} = \text{H}$, **2** > **1**, and when $\text{R} = \text{Me}$, **6** > **4** > **3** > **5**. The trends are explained below.

8.3.7.1 Effect of phosphines

The trend of the decrease of the rate of the decarbonylation reaction, as seen in **Table 8.15**, is similar to the trend of the decrease in the size of the $\text{Mo-P-C}_{\text{phenyl}}$ angle. As stated above a comparison of **3**, **4** and **6**, shows that the greater the electronic effect and the smaller the steric effect (considering the calculated cone angles in **Table 8.11**), the greater the size of the aforementioned angle, and so the faster the rate of decarbonylation.

The Mo-P distance decreases in the following way: **4** > **3** > **6** > **5**. Then if **6** ignored, as the Mo-P distance decreases, the rate of the decarbonylation also decreases. Thus,

the greater the bond distance between the Mo-P the faster the decarbonylation reaction.

The rate of decarbonylation is therefore affected by size of the Mo-P-C_{phenyl} angle, Mo-P distance, the electronic parameter and the cone angles of the phosphine. As stated in **Chapter 6**, the initial step for the decarbonylation reaction to take place is the dissociation of phosphine, thereafter the phosphine displaces the CO.¹³ For the faster rate of the decarbonylation reaction the following structural characteristics play a key role: the greater the size of the Mo-P-C_{phenyl} angle, the greater the distance between the Mo-P, the greater the electronic and the smaller the steric effect of the phosphine (to allow the incoming phosphine to displace the CO), the faster the decarbonylation reaction.

8.3.7.2 Effect of the R group

Table 8.15 shows that the Me group has a greater steric effect, and a greater electronic effect relative to H. When the electron donating, P(*p*-MeOC₆H₄)₃ ligand (lower electronic parameter and 1 ° larger cone angle size) is used then the rate of decarbonylation is: Me > H. The opposite is true when the phosphine ligand is P(*p*-FC₆H₄)₃. It can also be visualised that the increased interaction of the P(*p*-MeOC₆H₄)₃ and the Me group, would cause the faster dissociation of the phosphine, thus the faster the rate of decarbonylation reaction. It was found that in the comparison of **3** and **1**; **2** and **6**, and **5** and CpMo(CO)₂(PPh₃)COMe) above, that the

Me group is bent closer to the Cp ring than H. Hence steric and electronic effects can be used to control the rate of the decarbonylation reaction.

Also, according to **Table 8.5**, **3** has a the longer Cp-Me bond distance than **6**. Therefore, steric and/or electronic interaction may exist between the phosphine and the Me group to cause a faster dissociation than H. Additionally, $P(p\text{-FC}_6\text{H}_4)_3$ has a larger electronic effect and is electron-withdrawing. This indicates that the steric and electronic effects both control the bond length and the bond angle for R group on the Cp ring, which in turn affect the rate of the decarbonylation reaction.

8.4 Conclusions

Crystal structures of the type $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ complexes ($\text{R} = \text{H}$, $\text{L} = P(p\text{-MeOC}_6\text{H}_4)_3$ **1** and $P(p\text{-FC}_6\text{H}_4)_3$ **2** and when $\text{R} = \text{Me}$ and $\text{L} = P(p\text{-MeOC}_6\text{H}_4)_3$ **3**, $P(p\text{-MeC}_6\text{H}_4)_3$ **4**, PPh_3 **5** and $P(p\text{-FC}_6\text{H}_4)_3$ **6** and the starting material, $(\text{CpCOMe})\text{Mo}(\text{CO})_3\text{Me}$ **7**, were successfully determined.

The Tolman cone angles for L were calculated for the complexes, $(\text{CpMe})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{L} = P(p\text{-MeOC}_6\text{H}_4)_3$ **3**, $P(p\text{-MeC}_6\text{H}_4)_3$ **4**, PPh_3 **5** and $P(p\text{-FC}_6\text{H}_4)_3$) using STERIC. These differed by 2 – 4 ° from the Tolman cone angle of 145 ° that was calculated using a Ni system.

The geometries of the insertion Mo structures showed that the rate of the decarbonylation reaction was controlled by the steric and electronic effects of the phosphine ligand and the ring substituent, R.

The effect of the phosphine, in particular was as follows. For a faster rate of the decarbonylation reaction the following structural characteristics played a role: the greater the size of the Mo-P-C_{phenyl} angle and the greater the distance between the Mo-P (which lead to a greater electronic yet smaller steric effect of the phosphine). The effect of the ring substituent, R, on the rate was observed by the larger Me-Cp bond distance relative to H-Cp bond distance and that the Me group is bent closer to the Cp ring than H, which could increase the steric and electronic interaction of R with the ligand, causing the rate of decarbonylation, according to R to be: Me > H.

Thus, the geometries obtained from the crystal structure data were utilised to explain the steric and electronic effects of the phosphine and the R group on the observed rate of the decarbonylation reaction.

8.5 References

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CHAPTER 9: CONCLUSIONS AND FUTURE SUGGESTIONS

9.1 Conclusions

A study of the solvent-free migratory-insertion reactions between $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ and L ($\text{R} = \text{Me}$, $\text{L} = \text{PPh}_3$; $\text{R} = \text{COH}$, H , $\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$) was investigated using NMR spectroscopy. Their rate constants for the reactions were found to be $2.75 \times 10^{-4} \text{ s}^{-1}$ ($42 - 43^\circ\text{C}$), $3.06 \times 10^{-4} \text{ s}^{-1}$ ($74 - 75^\circ\text{C}$) and $11.6 \times 10^{-4} \text{ s}^{-1}$ ($72 - 73^\circ\text{C}$), respectively. This method of investigating the kinetics of a reaction was found to be labour intensive and only a limited set of data could be obtained. The various factors, that controlled the reaction including temperature, mole ratio, ligand effects and ring substituent effects, required a more rapid technique of investigation.

The DRIFTS technique was implemented to investigate systematically the factors that controlled the solvent-free migratory-insertion reaction between $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ and $(\text{R} = \text{H}, \text{Me}, \text{COH}, \text{COMe})$ and L ($\text{L} = \text{P}(p\text{-MeOC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, PPh_3). A temperature study was done in the range $40 - 60^\circ\text{C}$ as this was below the melting points of the individual reactants. The temperature study indicated complexities in monitoring the reaction at 40°C . However, at $T > 40^\circ\text{C}$, the reaction proceeded well and the reaction rate increased as the temperature and the mole ratio

increased. The activation energy for the reaction at 50 °C for 1:10 mole ratio was found to be 52.0 kJmol⁻¹ (L = P(*p*-FC₆H₄)₃).

The migratory-insertion reaction was observed under an optical microscope and digital photographs revealed that the reaction was facilitated by a eutectic melt at T > 40 °C upon contact of the two reactants. It was observed also that no reaction took place between reactants that did not touch and consequently had not melted. The eutectic melt was dependent on the nature of the reactant. For example, when the reaction of (CpCOMe)Mo(CO)₃Me and L (L = P(*p*-MeOC₆H₄)₃, P(*p*-MeC₆H₄)₃, P(*p*-FC₆H₄)₃, PPh₃), took place, the eutectic melting point decreased in the following manner: P(*p*-MeC₆H₄)₃ > P(*p*-MeOC₆H₄)₃ > P(*p*-FC₆H₄)₃ > PPh₃. This eutectic melting point trend correlated with the melting points of the respective phosphines. The lack of a melt phase explained the complexities obtained in the kinetic data obtained at 40 °C.

The study of the effect of the ligand on the migratory-insertion reaction revealed that electron-donating ligands have faster rates than electron withdrawing ligands. It is believed that the electron-donating group on the phosphine adds electron density to the phosphorus atom, facilitating an interaction between the phosphine and the electrophilic site of the metal complex. Alternatively, an electron-withdrawing group of a phosphine makes the phosphorus atom electron deficient and this facilitates an interaction between the nucleophilic sites of the metal complex. Although, both types of ligands lead to a reaction by a melt process, the reaction of electron donating

phosphine will be faster because the first step involves an attack at an electrophilic site, which is the metal atom.

The ring substituent, R, also controlled the rate of the reaction and both electronical and sterical factors were found to be important. Electron donating R groups (R = Me) show faster reaction rates than electron withdrawing R groups (R = COMe). If R is electron donating it adds electron density to the Cp ring. This strengthens the Cp-Mo bond and weakens the Mo-Me and Mo-CO bonds. When the phosphine interacts with the metal complex, the already weakened bond between Mo and the alkyl groups breaks, allowing for a faster rate of alkyl migration. The opposite is true for electron withdrawing R groups. Steric effects associated with R are also important. The size of R as measured by the cone angle associated with the ring substituent, may control the access to the reaction site on the metal. It has been observed that a larger groups like R = COMe and COH, have slower reaction rates when compared to R = H and Me, which have faster reaction rates.

A mechanism for the migratory-insertion reaction for solid reactants was proposed that involved both a phosphine interaction with the metal complex and alkyl migration in the melt followed by solidification of the insertion complex.

The reverse of migratory-insertion reaction involving, the decarbonylation reaction of $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ (R = H, Me, COH, COMe) and L (L = $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, PPh_3) was also studied at 80 – 100 °C using the DRIFTS

technique. It was found that the rate of decarbonylation reaction increased as the temperature increased. The activation energy for $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{R} = \text{H}$; $\text{L} = \text{P}(p\text{-OMeC}_6\text{H}_4)_3, \text{P}(p\text{-FC}_6\text{H}_4)_3$) was found to be 67 and 135 kJmol^{-1} respectively. The progression of the decarbonylation reaction under the optical microscope revealed that it involved a solid-state reaction. The ligand effect study showed that electron-withdrawing ligands have faster rates than electron donating ligands, which was the opposite to that found for the migratory-insertion reactions. It indicates that the greater the electron withdrawing power on the phosphine, the easier it is for the phosphine to dissociate from the metal complex which is believed to be the first step in the decarbonylation reaction.

The steric and electronic effect of the R group also played a role in the rate of the decarbonylation reaction. The overall effect of the Cp ring substituent, R on the reaction rate is as follows: $\text{COH} > \text{COMe} > \text{Me} > \text{H}$. This trend correlates with the decrease in steric effect (θ_1 and θ_2), the increase of electronic effect (as defined by F and σ_{R}) yet a decrease of electronic effect (as defined by $\nu(\text{CO})$)

It is believed that the smaller the steric effect and electronic effect of the R group, the easier the dissociation of the phosphine from the metal complex and that thus facilitates the decarbonylation process.

The migratory-insertion reaction between $\text{CpW(CO)}_3\text{Me}$ and L ($\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3$) at 40 – 60 °C at varying mole ratios via DRIFTS was also investigated. The activation energy for the reaction with $\text{P}(p\text{-FC}_6\text{H}_4)_3$ at 40 °C was found to be 50.75 kJmol⁻¹. The study again showed complexities in the kinetic data. An optical microscopy study revealed that this reaction also occurred via a melt phase reaction (> 40 °C) that required the reactants to “touch” for a reaction to take place. This explained the complexities in the kinetic data at 40 °C.

A ligand effect study showed that electron-donating ligands have faster rates than electron withdrawing ligands, which was the same as found for the similar Mo complexes. The mechanism of the reaction was proposed to be similar for the both the Mo and W complexes.

The decarbonylation reactions of $\text{CpW(CO)}_2(\text{L})\text{COMe}$ ($\text{L} = \text{P}(p\text{-MeC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ and PPh_3) were done using DRIFTS at 100 – 120 °C. The rate of the decarbonylation increased as the temperature increased.

A ligand effect study showed that no trend in the rate of the decarbonylation results *versus* the electronic effect of the phosphine could be ascertained. Thus, it can be assumed that the decarbonylation reaction involving the insertion W complex occurs *via* dissociation of CO ligand, and is not related to the phosphine ligand (as it was for the Mo complex above).

The final investigation involved the crystal structure analysis of some Mo complexes of the type $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{R} = \text{H}$, $\text{L} = \text{P}(p\text{-MeOC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ and $\text{R} = \text{Me}$, $\text{L} = \text{P}(p\text{-MeOC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ ($\text{L} = \text{P}(p\text{-MeC}_6\text{H}_4)_3$, PPh_3) and $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$ ($\text{R} = \text{COMe}$). This provided the necessary intermolecular information to make suggestions on the steric and electronic effect of the phosphine ligands and the ring substituent, R on the rate of the decarbonylation reaction. The study of the steric and electronic effect of the phosphine yielded the following results: the greater the solid angle of the phosphine, the greater the bond length between the phosphine and the Mo; the greater the electronic and steric effect, the greater the Mo-P-C_{phenyl} angle; the greater the electronic effect of X (ring substituent on the phosphine), the greater the bond length of X to the carbon of the phenyl ring. It was found that the greater the size of the Mo-P-C_{phenyl} angle, the greater the distance between the Mo-P and this lead to a greater the electronic, yet smaller the steric effect of the phosphine. This, in turn allows the incoming phosphine to displace the CO more rapidly and thus the faster the decarbonylation reaction.

The study of the steric and electronic effect of the ring substituent, R indicated the following points. When the electron donating, $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$ ligand (lower electronic parameter and 1 ° higher cone angle size) is used then the rate of decarbonylation is: $\text{Me} > \text{H}$. This could be due to the Me group, which has a greater steric effect, and a greater electron donating effect relative to H. The rate of reaction was found to be $\text{H} > \text{Me}$ for the electron withdrawing ligand, $\text{P}(p\text{-FC}_6\text{H}_4)_3$. The Cp-R bond distance was found to be longer than Cp-H bond distance and the Me group is

bent slightly closer to the Cp ring than H. Therefore, interaction may exist between the phosphine and the Me group to cause a faster rate of decarbonylation for H.

Thus the crystal structure analysis showed that both the steric and electronic effects of both the ring substituent, R and the phosphine, in combination, control the rate of the decarbonylation reaction.

9.2 Future suggestions

1. The kinetics of the solvent-free migratory-insertion reaction of $(\text{CpR})\text{M}(\text{CO})_3\text{X}$ (R = hydrocarbon, M = metal, X = alkyl group) and L (L = phosphine) could be extended to include:
 - a) A variation of alkyl groups to evaluate the influence of the steric and electronic effect of the alkyl group on the rate of the migratory-insertion reaction, as it has been proven that the alkyl migration is the key step in the reaction;
 - b) A variation of phosphines to incorporate liquid phosphines that differ sterically as well as electronically measures to evaluate the role of the steric and electronic effect of the phosphines on the rate of the migratory-insertion reaction;
 - c) A variation of M to ascertain the influence of the metal on the rate of the migratory-insertion reaction

2. Competition reactions between two different phosphines that have either constant steric effects (i.e. same cone angle), and different electronic effects that undergo migratory-insertion reaction with the same metal complex. This would confirm which phosphine prefers to undergo migratory-insertion reaction.
3. The kinetics of the solvent-free decarbonylation reaction of $(\text{CpR})\text{M}(\text{CO})_2(\text{L})\text{COX}$ (R = hydrocarbon, M = metal, L = phosphine and X = alkyl group) could be extended to evaluate the various parameters that control the rate of the decarbonylation reaction as stated for the migratory-insertion reaction in 1 above.
4. The successful growth of crystals of the type $(\text{CpR})\text{M}(\text{CO})_2(\text{L})\text{COX}$, provide information on the intermolecular interactions within the crystal structure and the relationship to the steric and electronic effect of R , M , L and X , and the effect of these on the rate of reaction. The growth and study of suitable crystals of the type $(\text{CpR})\text{M}(\text{CO})_2(\text{L})\text{COX}$ could provide valuable information about the decarbonylation reaction.
5. A study on the migratory-insertion and decarbonylation reactions stated above, but using a variation of solvents could be useful to draw a better comparison between reactions in solvent and solvent-free reactions.

APPENDIX

A1: The synthesis of insertion complexes, $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$

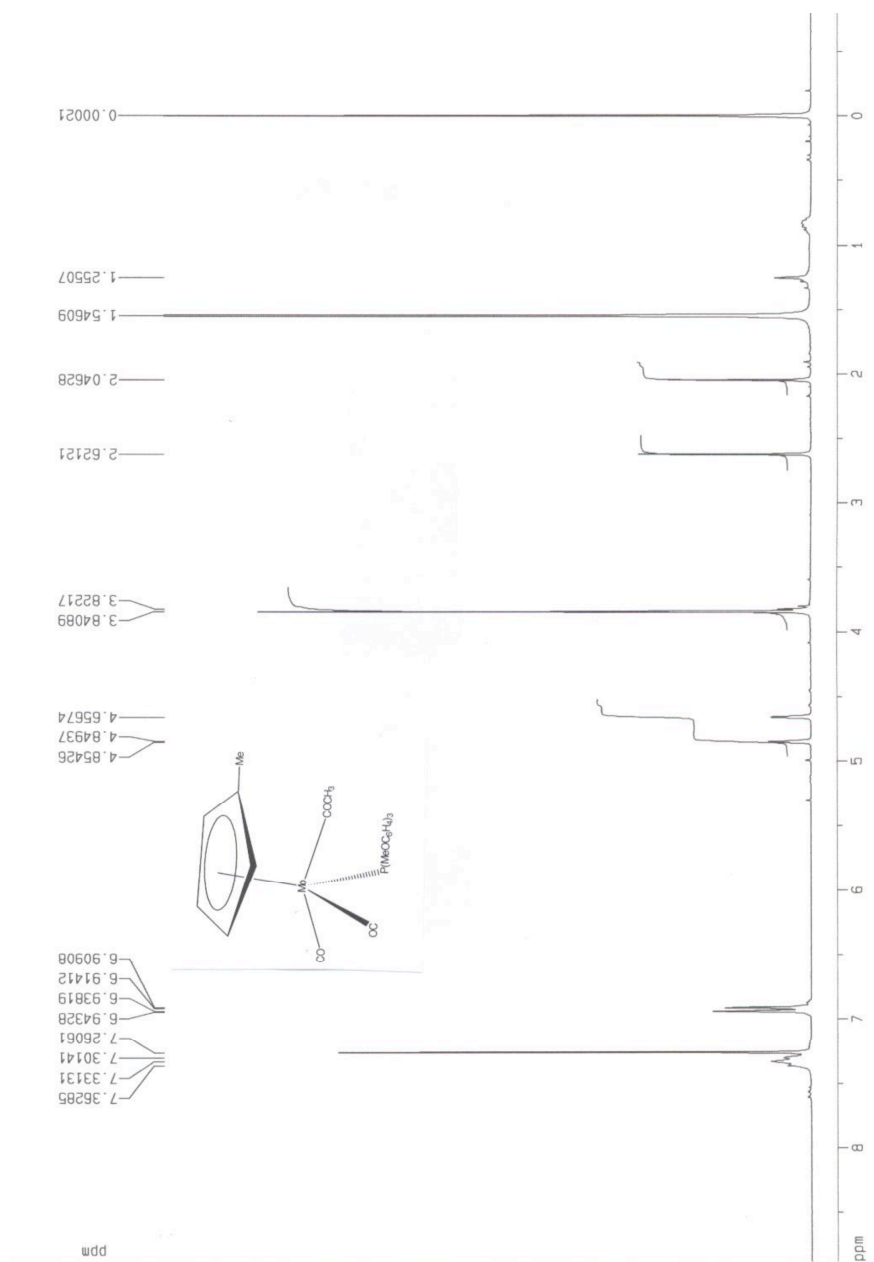


Figure A1: The ^1H -NMR spectrum for the insertion complex, $\text{CpMo}(\text{CO})_2[\text{P}(p\text{-MeOC}_6\text{H}_4)_3]\text{COMe}$

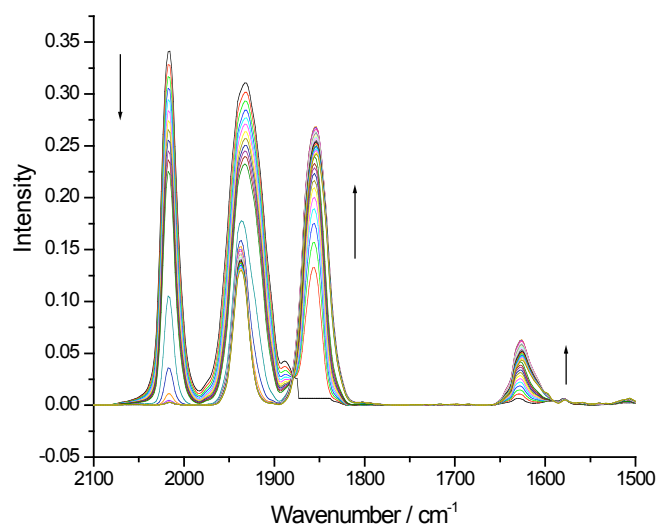


Figure A2: The DRIFTS spectrum showing the conversion to the insertion product, **(CpR)Mo(CO)₂(L)COMe**

A2 The synthesis of decarbonylated complexes, (CpR)Mo(CO)₂(L)Me

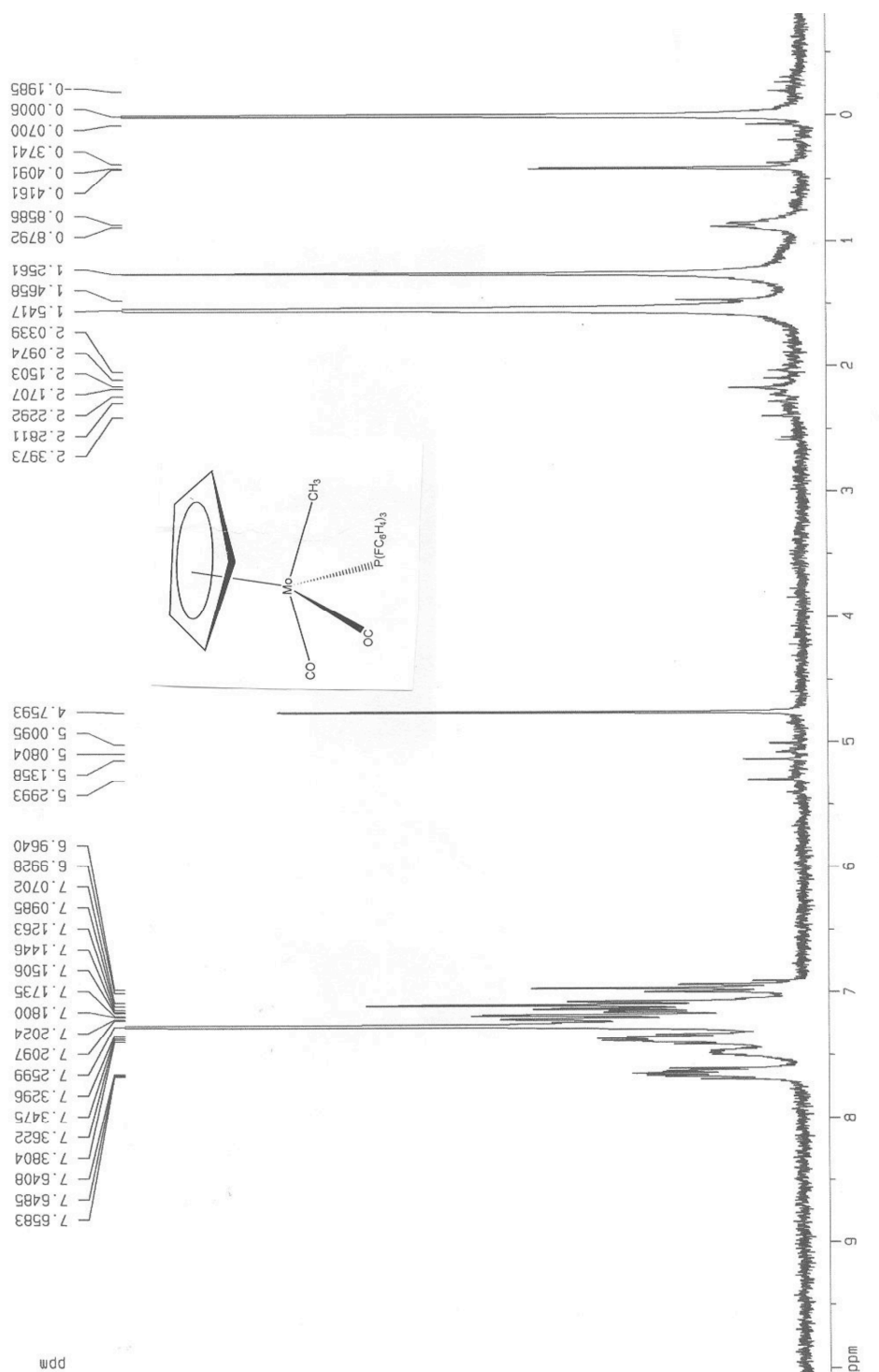


Figure A3: The ¹H-NMR spectrum for the decarbonylated complex, CpMo(CO)₂[P(*p*-FC₆H₄)₃]Me

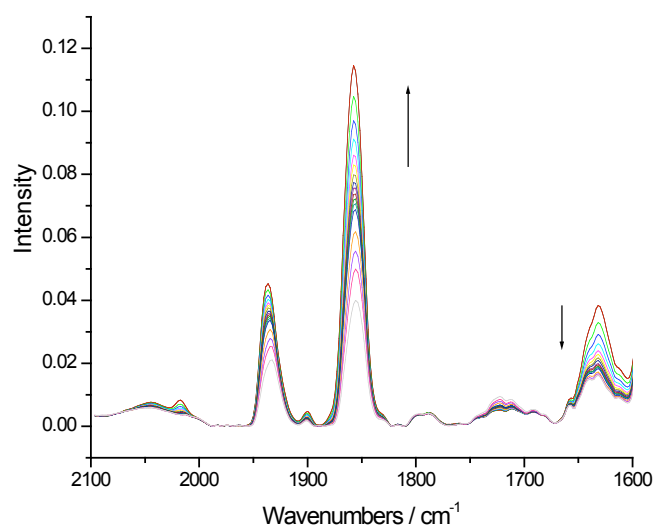


Figure A4: The DRIFTS spectrum showing the conversion to the decarbonylated product, $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{Me}$

A3: Optical microscopy pictures of the melt between $(\text{CpCOMe})\text{Mo}(\text{CO})_3\text{Me}$ and L ($\text{L} = \text{P}(p\text{-MeOC}_6\text{H}_4)_3, \text{P}(p\text{-MeC}_6\text{H}_4)_3, \text{PPh}_3$)

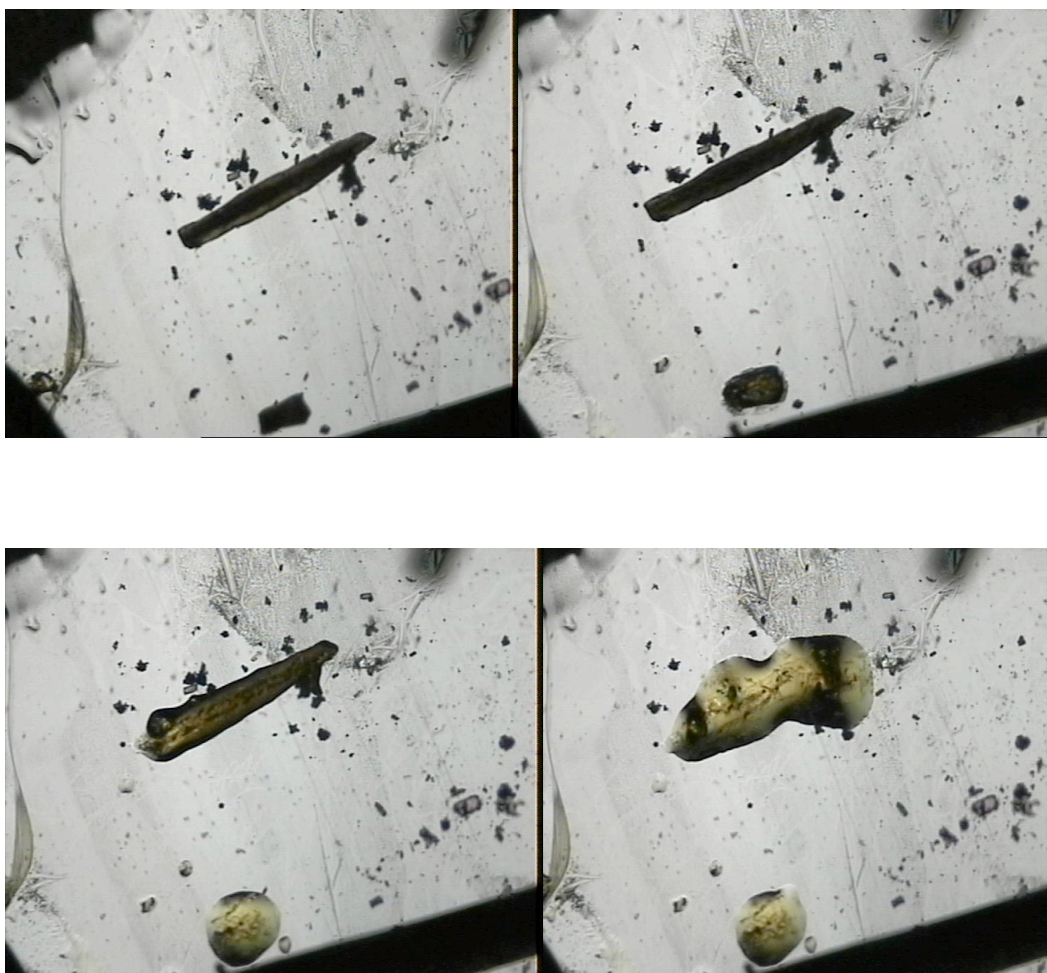


Figure A5a: Optical microscopy pictures showing the eutectic melt at 48 °C for the reaction of $(\text{CpMe})\text{Mo}(\text{CO})_3\text{COMe}$ and $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$.

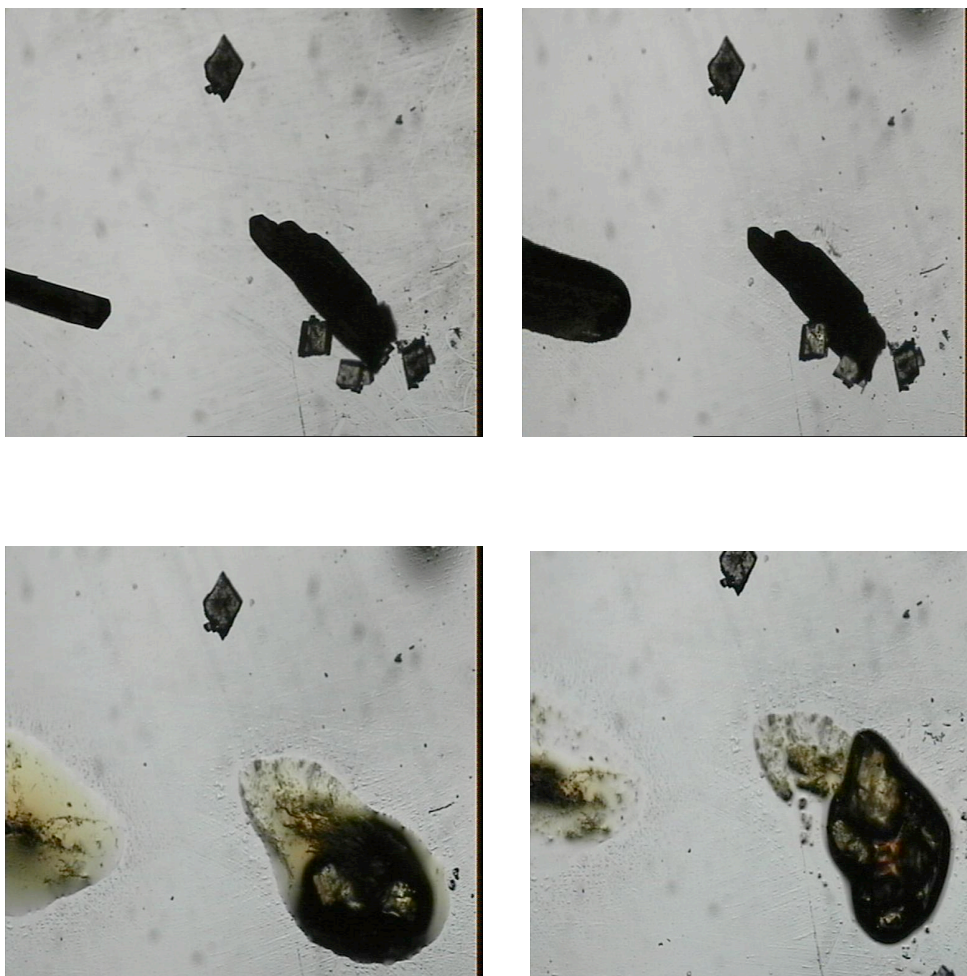


Figure A5b: Optical microscopy pictures showing the eutectic melt at 56 °C for the reaction of $(\text{CpCOMe})\text{Mo}(\text{CO})_3\text{COMe}$ and $\text{P}(p\text{-MeC}_6\text{H}_4)_3$.

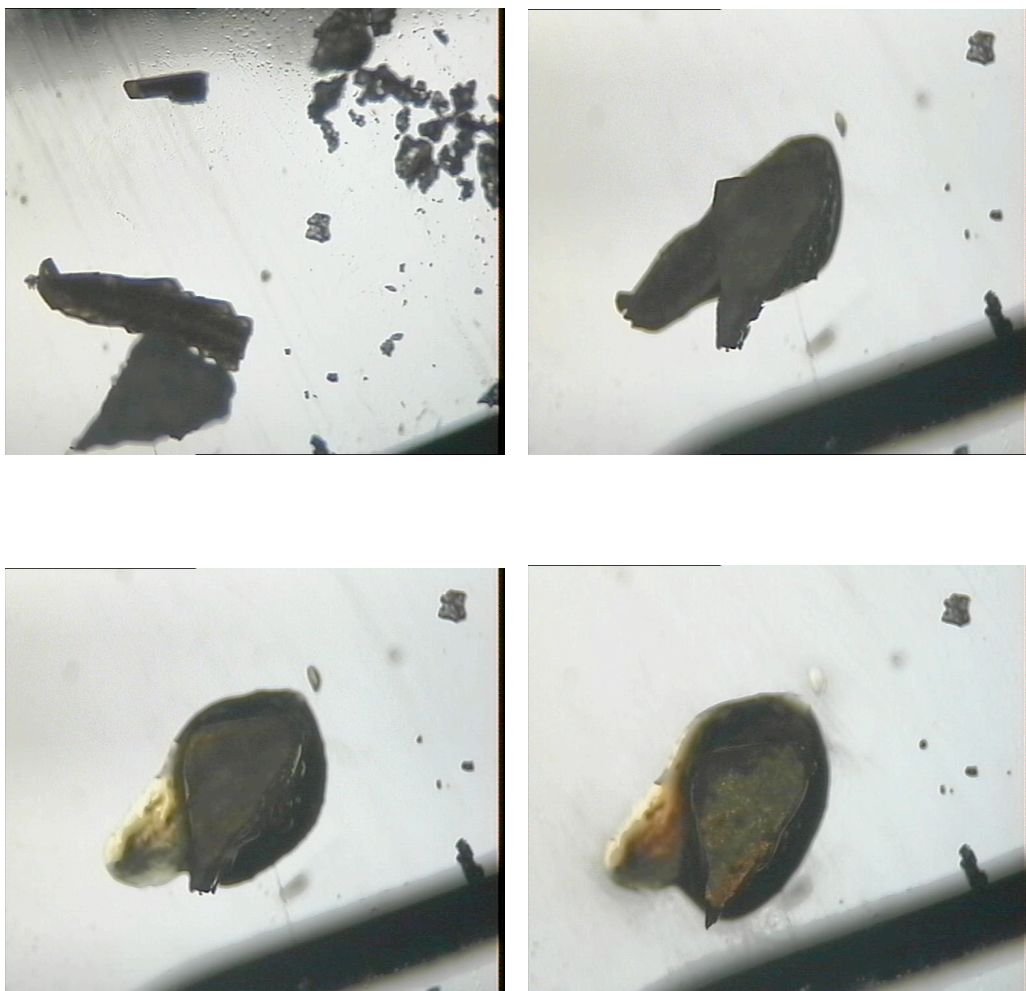


Figure A5c: Optical microscopy pictures showing the eutectic melt at 42 °C for the reaction of (CpCOMe)Mo(CO)₃COMe and PPh₃

A4 - Rate plots for the migratory-insertion reaction of $(\text{CpR})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{R} = \text{H, Me, COH, COMe}$) and L ($\text{L} = \text{P}(p\text{-FC}_6\text{H}_4)_3, \text{P}(p\text{-MeC}_6\text{H}_4)_3, \text{P}(p\text{-MeOC}_6\text{H}_4)_3$ and PPh_3)

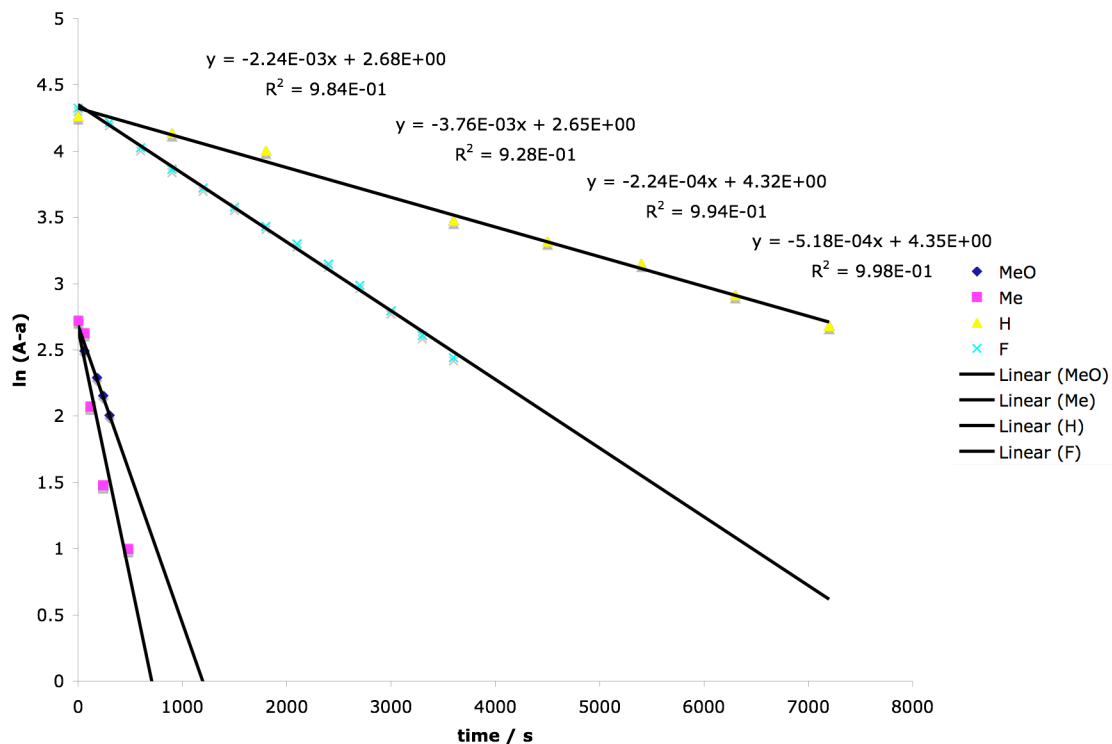


Figure A6a: The rate plot for the migratory-insertion reaction of $(\text{CpMe})\text{Mo}(\text{CO})_3\text{COMe}$ and L ($\text{L} = \text{PPh}_3, \text{P}(p\text{-FC}_6\text{H}_4)_3, \text{P}(p\text{-MeC}_6\text{H}_4)_3, \text{P}(p\text{-MeOC}_6\text{H}_4)_3$) at 40°C in 1:10 molar ratio.

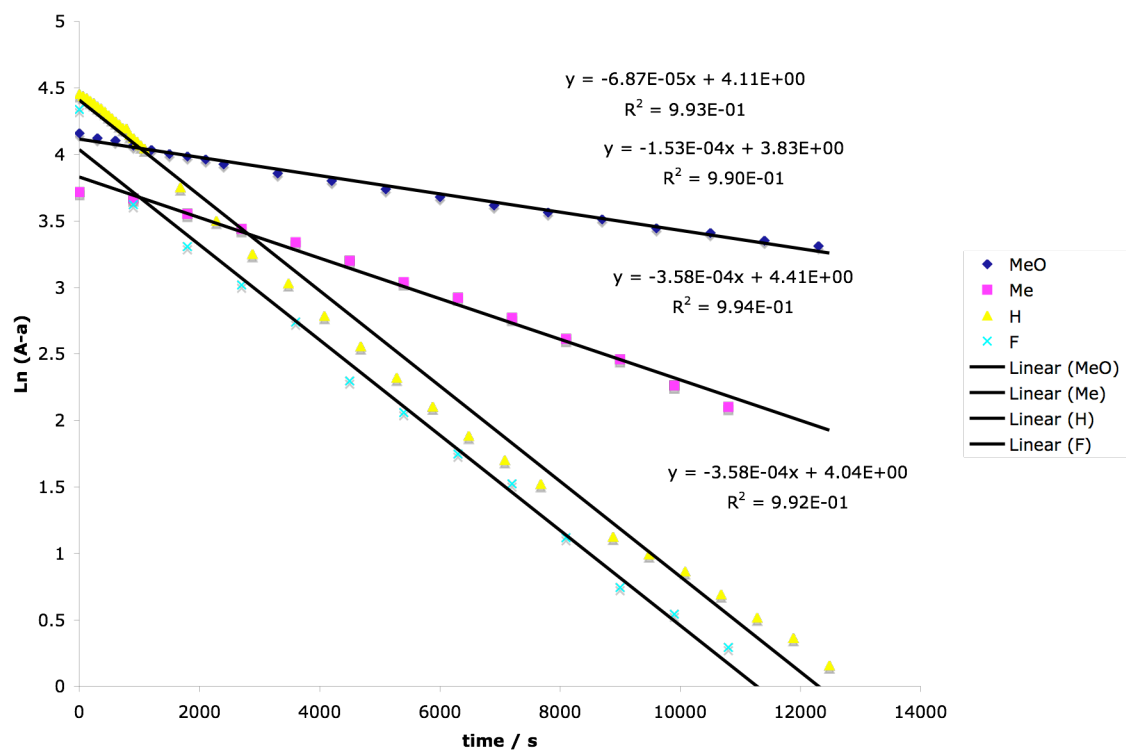


Figure A6b: The rate plot for the migratory-insertion reaction of $(\text{CpCOH})\text{Mo}(\text{CO})_3\text{COMe}$ and L ($L = \text{PPh}_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$) at 40°C in 1:10 molar ratio.

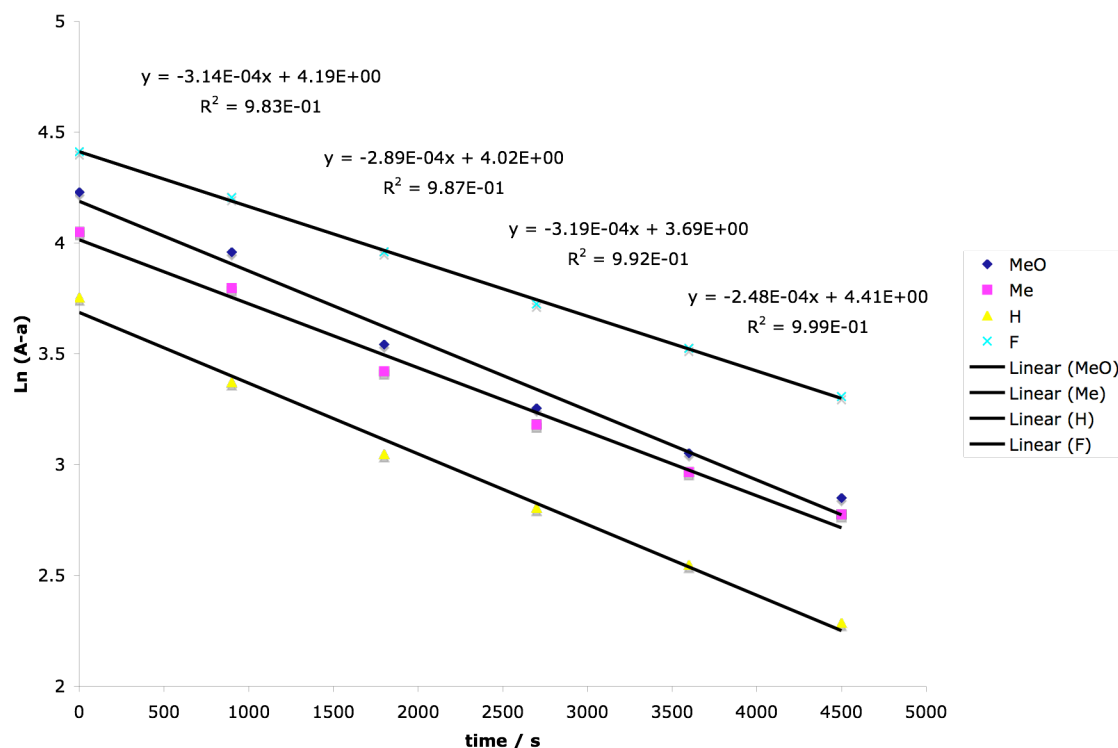


Figure A6c: The rate plot for the migratory-insertion reaction of $(\text{CpCOMe})\text{Mo}(\text{CO})_3\text{COMe}$ and L ($\text{L} = \text{PPh}_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$) at 40°C in 1:10 molar ratio.

A5: Taft equation showing the steric effects of the R group in $(\text{CpR})\text{Mo}(\text{CO})_3\text{Me}$

Henderson et al, used the Taft equation, $\log k$ against σ^* (σ^* represents the Taft parameter), to indicate if there were steric effects, resonance effects or changes in hybridization when any deviation from a straight line was observed. The Taft parameters for the four phosphine ligands were obtained from Wilson et al and the plot of $\log k$ against σ^* is shown in the **Figure A8**, which is similar to the plot of k versus the Tolman electronic parameter (**Chapter 5, Figure 5.25**). This deviation

from straight line indicates that there are steric effects brought about by the phosphine ligands.

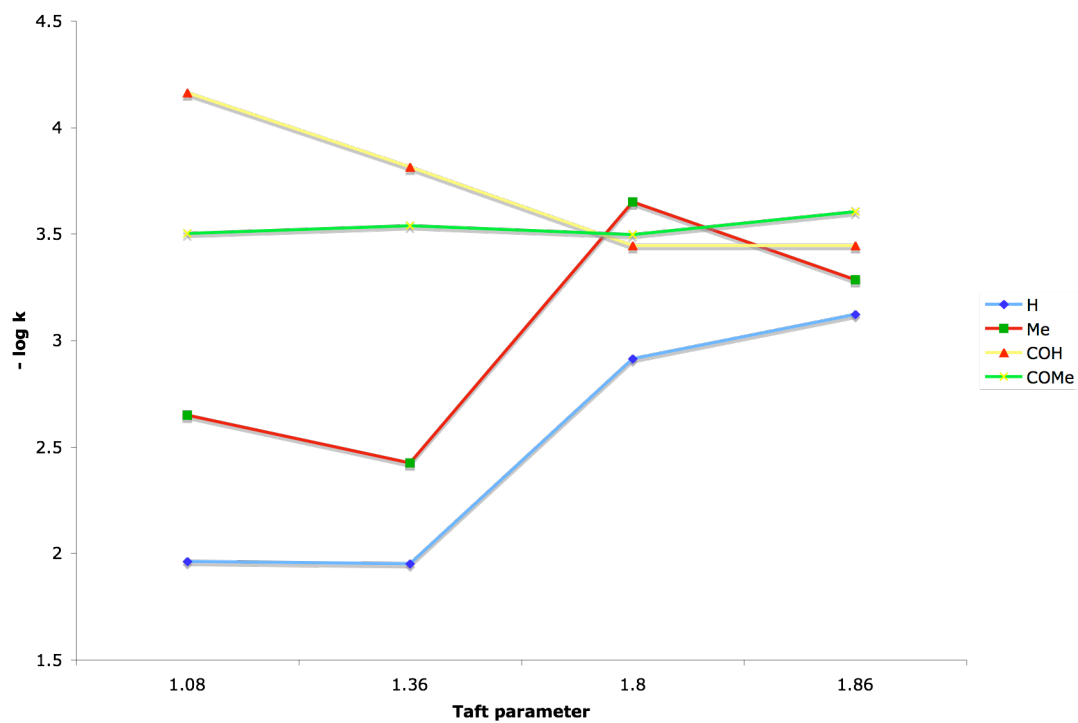


Figure A8: The graph of $-\log k$ against $\Sigma\sigma^*$

A6: The 3D plots of the relationship between the steric (Tolman cone angle of R) and electronic (electronic parameter, F) and the rate of the migratory-insertion reaction

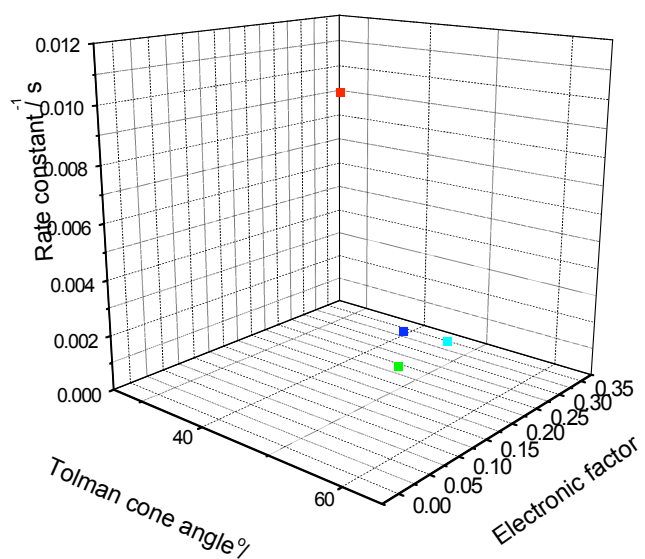


Figure A9a: The 3D plot showing the relationship between the Tolman cone angle for R and the Electronic factor for R on the rate of the migratory-insertion reaction of CpR)Mo(CO)₃Me and P(*p*-FC₆H₄)₃

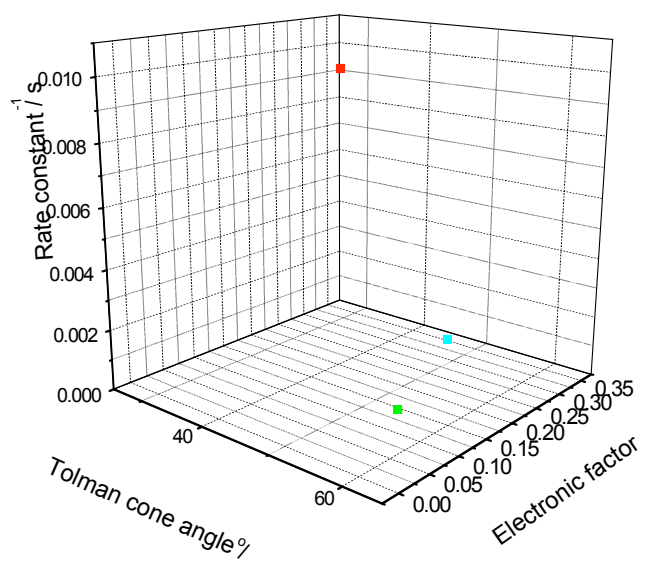


Figure A9b: The 3D plot showing the relationship between the Tolman cone angle for R and the Electronic factor for R on the rate of the migratory-insertion reaction of $\text{CpR)Mo(CO)}_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$

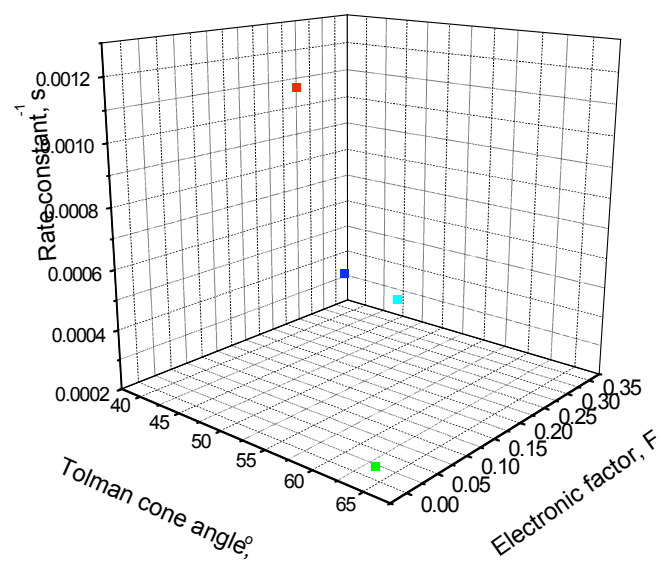


Figure A9c: The 3D plot showing the relationship between the Tolman cone angle for R and the Electronic factor for R on the rate of the migratory-insertion reaction of $\text{CpR)Mo(CO)}_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$

A7: The Effect of the diluent on the migratory-insertion reaction of $\text{CpMo(CO)}_3\text{Me}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ using DRIFTS.

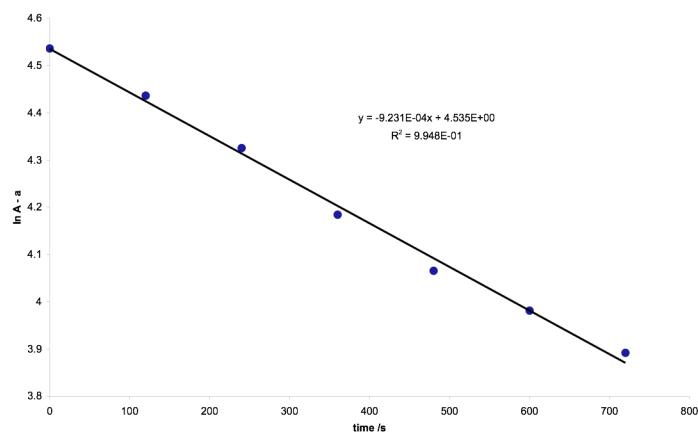


Figure A10: The rate plot for the migratory-insertion reaction of $\text{CpMo(CO)}_3\text{COMe}$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ at 50 °C in 1:11 molar ratio performed by DRIFTS using CaSO_4 as the diluent.

A8: The rate plots for the decarbonylation reaction of (CpR)Mo(CO)₂(L)COMe

((L = P(*p*-MeOC₆H₄)₃, P(*p*-MeC₆H₄)₃, PPh₃, P(*p*-FC₆H₄)₃) at 110 °C

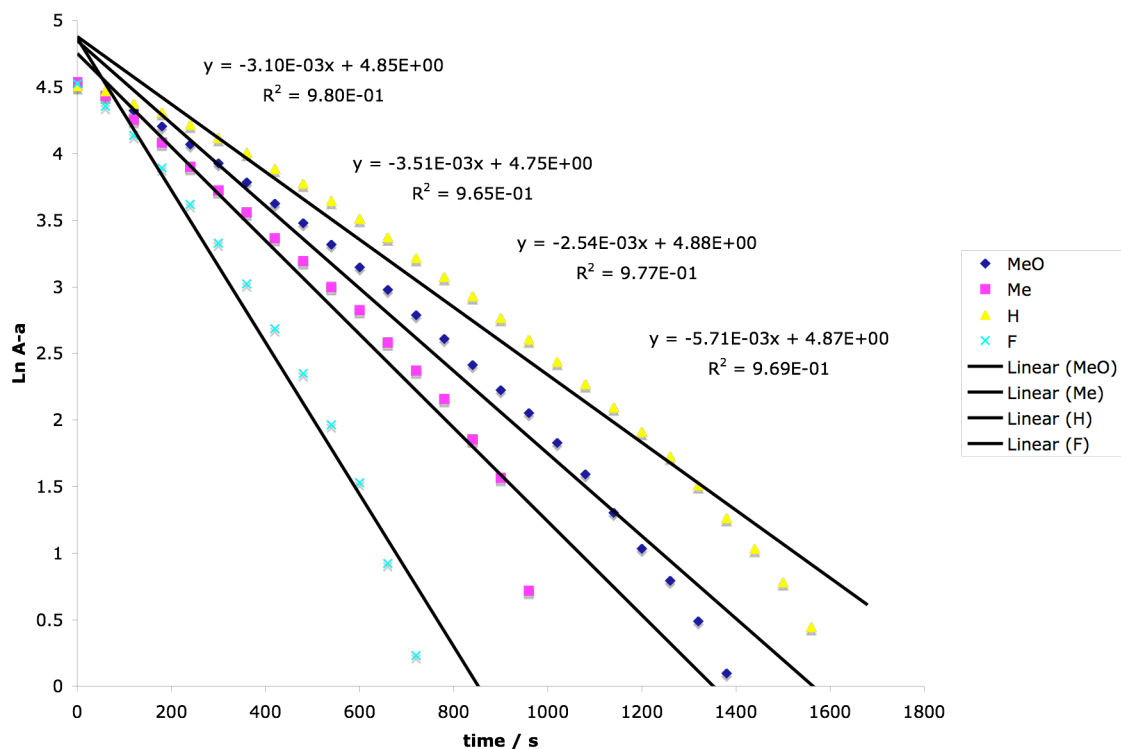


Figure A11a: The rate plot for the decarbonylation reaction of (CpMe)Mo(CO)₂(L)COMe (L = PPh₃, P(*p*-FC₆H₄)₃, P(*p*-MeC₆H₄)₃, P(*p*-MeOC₆H₄)₃) at 100 °C

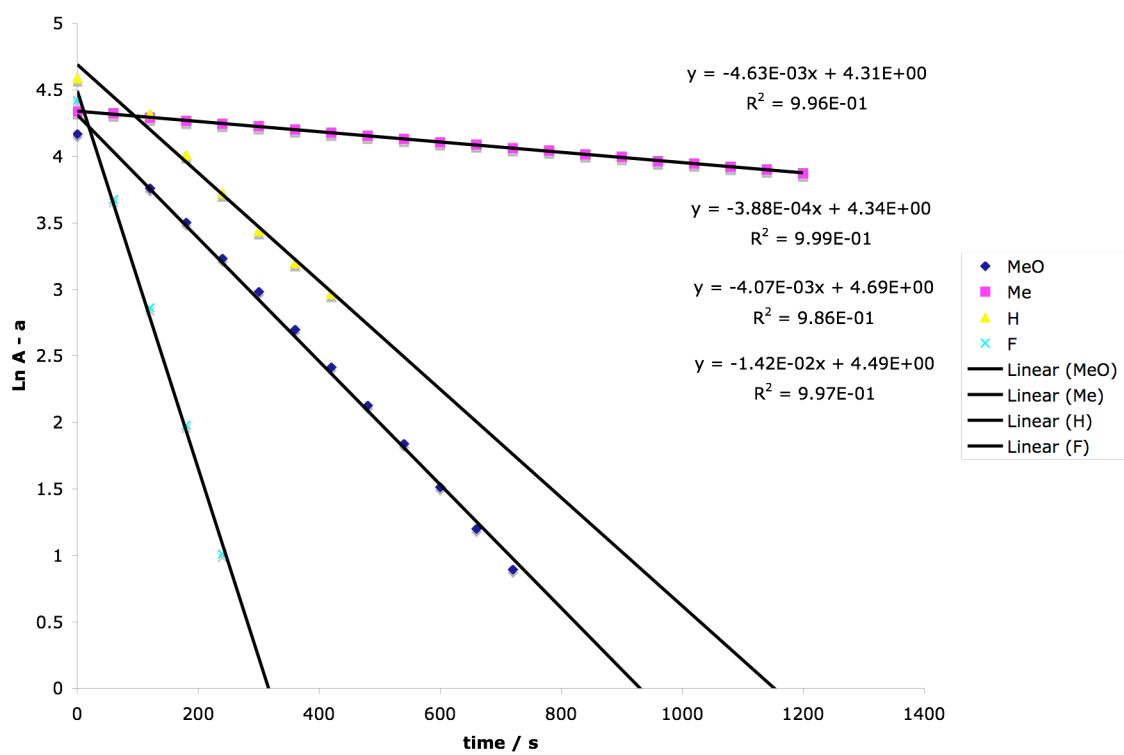


Figure A11b: The rate plot for the decarbonylation reaction of $(\text{CpCOH})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{L} = \text{PPh}_3, \text{P}(p\text{-FC}_6\text{H}_4)_3, \text{P}(p\text{-MeC}_6\text{H}_4)_3, \text{P}(p\text{-MeOC}_6\text{H}_4)_3$) at $100\text{ }^\circ\text{C}$

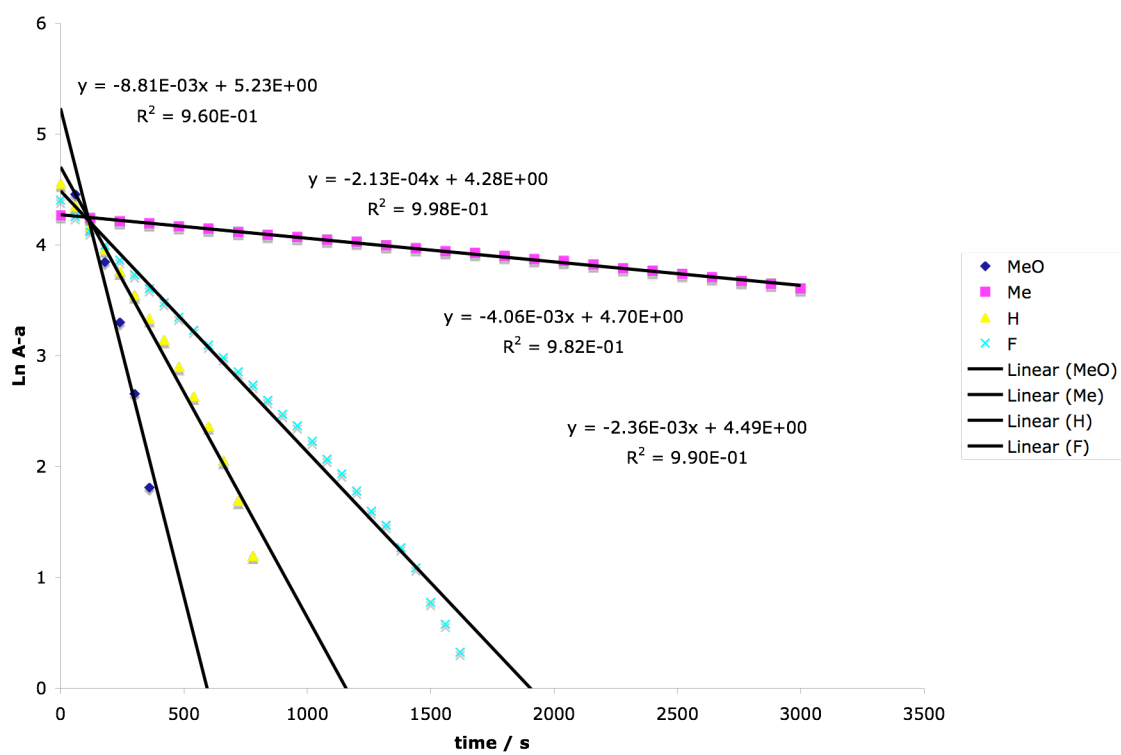


Figure A11c: The rate plot for the decarbonylation reaction of $(\text{CpCOMe})\text{Mo}(\text{CO})_2(\text{L})\text{COMe}$ ($\text{L} = \text{PPh}_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeC}_6\text{H}_4)_3$, $\text{P}(p\text{-MeOC}_6\text{H}_4)_3$) at 100°C

**A9: Crystal structure refinement and bond lengths and bond angles for some
CpR)Mo(CO)₂(L)COMe complexes and (CpCOMe)Mo(CO)₃Me**

Table A1: Details of structure refinement for complexes 1-6

	1	2	3	4	5	6
D_x calc (g/cm⁻³)	1.508	1.547	1.466	1.498	1.456	1.553
Abs coeff (mm⁻¹)	0.733	0.644	0.561	0.752	0.629	0.633
F(000)	762	1160	644	730	2192	1192
cryst size (mm)	0.40 x 0.30 x 0.26	0.20 x 0.20 x 0.17	0.20 x 0.20 x 0.17	0.50 x 0.30 x 0.26	0.48 x 0.28 x 0.24	0.40 x 0.40 x 0.22
θ range for data collection	1.71-27.0	1.35-25.0	1.60-28.0	1.72-28.0	1.83-25.0	2.15-28.0
Index ranges	-13 ≤ h ≤ 13 -17 ≤ k ≤ 15 -15 ≤ l ≤ 17	-9 ≤ h ≤ 9 -33 ≤ k ≤ 35 -12 ≤ l ≤ 12	-13 ≤ h ≤ 13 -14 ≤ k ≤ 12 -16 ≤ l ≤ 17	-13 ≤ h ≤ 13 -17 ≤ k ≤ 17 -18 ≤ l ≤ 17	-31 ≤ h ≤ 30 -11 ≤ k ≤ 14 -20 ≤ l ≤ 20	-13 ≤ h ≤ 12 -32 ≤ k ≤ 32 -14 ≤ l ≤ 14
No. of reflns collected	13021	10895	12448	22998	12239	25119
No. of ind reflns	7123 [R _{int} = 0.0308]	4347 [R _{int} = 0.0436]	6780 [R _{int} = 0.0336]	7621 [R _{int} = 0.0209]	4304 [R _{int} = 0.0456]	6086 [R _{int} = 0.0266]
No. of data/restraints/parameters	7123 / 7 / 383	4347 / 0 / 317	6780 / 0 / 352	7621 / 3 / 365	4304 / 0 / 298	6086 / 0 / 325
Goodness-of-fit	1.009	0.854	0.966	1.062	1.478	1.005
Final R indices [I > 2σ(I)]	R ₁ = 0.0561 wR ₂ = 0.1511	R ₁ = 0.0356 wR ₂ = 0.0788	R ₁ = 0.0329 wR ₂ = 0.0869	R ₁ = 0.0481 wR ₂ = 0.1354	R ₁ = 0.0946 wR ₂ = 0.2480	R ₁ = 0.0272 wR ₂ = 0.0741
R indices (all data)	R ₁ = 0.0725 wR ₂ = 0.1646	R ₁ = 0.0620 wR ₂ = 0.0872	R ₁ = 0.0451 wR ₂ = 0.0941	R ₁ = 0.0543 wR ₂ = 0.1410	R ₁ = 0.1029 wR ₂ = 0.2521	R ₁ = 0.0333 wR ₂ = 0.0827
Largest diff peak and hole/ eÅ⁻³	1.827 & - 1.232	0.294 & - 0.357	0.676 & - 0.721	0.720 & - 1.821	1.880 & - 1.453	0.531 & - 0.465

Table A2: Crystal data and details of structure refinement for **7**

Empirical formula	C ₁₁ H ₁₀ MoO ₄
Absorption coefficient (mm ⁻¹)	1.103
F(000)	600
Crystal size/ mm	0.28 x 0.14 x 0.11
Theta range for data collection	1.99 to 27.50 deg.
Limiting indices	-13<=h<=12, -16<=k<=18, -10<=l<=10
Reflections collected / unique	7513 / 2714 [R(int) = 0.0338]
Completeness to theta = 27.50	99.4 %
Absorption correction	Integration
Max. and min. transmission	0.8883 and 0.7476
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2714 / 0 / 145
Goodness-of-fit on F ²	1.010
Final R indices [I>2σ (I)]	R1 = 0.0275, wR2 = 0.0654
R indices (all data)	R1 = 0.0450, wR2 = 0.0703
Largest diff. peak and hole (eÅ ⁻³)	0.777 and -0.383

Table A3: Bond distances within (η^5 -C₅H₅)Mo(CO)₂[P(*p*-MeOC₆H₄)₃]COMe

Atoms	Distance, Å	Atoms	Distance, Å
(i) Distances from Molybdenum atom			
Mo-P(1)	2.4686(11)	C(3)-Mo	2.269(4)
Mo...O(1)		C(5)-Mo	2.329(4)
Mo...O(2)		C(6)-Mo	2.340(4)
Mo...O(3)		C(7)-Mo	2.364(4)
C(1)-Mo	1.966(4)	C(8)-Mo	2.392(4)
C(2)-Mo	1.977(5)	C(9)-Mo	2.352(4)
(ii) Distances within Carbonyl groups			
C(1)-O(1)	1.155(6)	C(2)-O(2)	1.153(6)
(iii) Distances within the Acetyl group			
C(3)-O(3)	1.209(6)	C(3)-C(4)	1.525(7)
(iv) Distances within the Cp ring			
C(5)-C(6)	1.416(7)	C(8)-C(9)	1.409(7)
C(6)-C(7)	1.427(6)		
C(7)-C(8)	1.420(7)	C(5)-C(9)	1.415(7)
(v) Distances in the PPh ₃ ligand			
P-C(10)	1.838(4)	C(19)-C(20)	1.402(6)
P-C(17)	1.838(4)	C(20)-C(21)	1.382(6)
P-C(24)	1.833(4)	C(21)-C(22)	1.292(6)
C(10)-C(11)	1.398(6)	C(17)-C(22)	1.398(6)
C(11)-C(12)	1.387(6)	C(20)-O(5)	1.370(5)
C(12)-C(13)	1.398(6)	C(23)-O(5)	1.431(5)

C(13)-C(14)	1.387(6)	C(25)-C(26)	1.384(6)
C(14)-C(15)	1.393(6)	C(26)-C(27)	1.392(7)
C(15)-C(10)	1.403(6)	C(27)-C(28)	1.392(7)
C(20)-O(5)	1.370(5)	C(28)-C(29)	1.394(7)
C(23)-O(5)	1.431(5)	C(17)-C(18)	1.393(6)
C(18)-C(19)	1.383(6)	C(29)-C(24)	1.384(6)
C(13)-O(4)	1.363(5)		
C(16)-O(4)	1.432(7)	C(24)-C(25)	1.401(6)
C(27)-O(6)	1.360(6)	C(30)-O(6)	1.435(7)
(vi) Intramolecular contacts from Cp group to other ligands (cyclically)			

Table A4: Bond angles in $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2[\text{P}(p\text{-MeOC}_6\text{H}_4)_3]\text{COMe}$

Atoms	degrees	Atoms	degrees
(i) Around Molybdenum atom			
P-Mo-C(1))	79.96(12)	C(5)-Mo-C(6)	35.31.(17)
P-Mo-C(2)	79.24(12)	C(6)-Mo-C(7)	35.32(15)
P-Mo-C(3)	133.12(12)	C(7)-Mo-C(8)	34.73(16)
C(1)-Mo-C(2)	109.09(19)	C(8)-Mo-C(9)	34.54(16)
C(1)-Mo-C(3)	71.83(17)	C(9)-Mo-C(5)	35.19(17)
C(2)-Mo-C(3)	75.81(17)	O(1)...Mo...O(2)	
P-Mo...O(1)		O(1)...Mo...O(3)	
P-Mo...O(2)		O(2)...Mo...O(3)	
(ii) In Carbonyl groups			
Mo-C(1)-O(1)	175.5(4)	Mo-C(2)-O(2)	174.2(4)
(iii) In Acetyl group			
Mo-C(3)-C(4)	122.7(3)	C(4)-C(3)-O3	116.6(4)
Mo-C(3)-O3	120.7(4)		
(iv) In the Cp ring			
C(5)-C(6)-C(7)	107.7(4)	C(8)-C(9)-C(5)	108.7(4)
C(6)-C(7)-C(8)	107.9(4)	C(9)-C(5)-C(6)	107.9(4)
C(7)-C(8)-C(9)	107.8(4)		
(v) In the PPh ₃ ligand			
Mo-P-C(10)	112.07(13)	C(18)-C(19)-C(20)	119.6(4)
Mo-P-C(17)	117.12(13)	C(19)-C(20)-C(21)	119.9(4)
Mo-P-C(24)	118.47(13)	C(20)-C(21)-C(22)	119.8(4)

C(15)-C(10)-C(11)	117.9(4)	C(21)-C(22)-C(17)	121.2(4)
C(10)-C(11)-C(12)	121.8(4)	C(22)-C(17)-C(18)	118.0(4)
		C(21)-C(20)-O(5)	124.5(4)
		C(19)-C(20)-O(5)	115.7(4)
		C(20)-O(5)-C(23)	116.7(3)
C(11)-C(12)-C(13)	119.3(4)	C(24)-C(25)-C(26)	121.0(4)
C(12)-C(13)-C(14)	119.9(4)		
C(13)-C(14)-C(15)	120.3(4)	C(25)-C(26)-C(27)	120.3(4)
C(14)-C(15)-C(10)	120.7(4)	C(26)-C(27)-C(28)	119.3(4)
C(16)-O(4)-C(13)	118.7(4)	C(27)-C(28)-C(29)	119.9(4)
C(12)-C(13)-O(4)	124.7(4)	C(28)-C(29)-C(24)	121.4(4)
C(14)-C(13)-O(4)	115.5(4)	C(27)-O(6)-C(30)	117.5(4)
C(22)-C(17)-C(18)	118.0(4)		
C(17)-C(18)-C(19)	121.5(4)	C(28)-C(27)-O(6)	125.1(4)
		C(26)-C(27)-O(6)	115.6(4)

Table A5: Bond distances within (η^5 -C₅H₅)Mo(CO)₂[P(*p*-FC₆H₄)₃]COMe

Atoms	Distance, Å	Atoms	Distance, Å
(i) Distances from Molybdenum atom			
Mo-P(1)	2.4719(9)	C(3)-Mo	2.263(4)
Mo...O(1)		C(5)-Mo	2.320(4)
Mo...O(2)		C(6)-Mo	2.371(4)
Mo...O(3)		C(7)-Mo	2.364(6)
C(1)-Mo	1.962(4)	C(8)-Mo	2.338(4)
C(2)-Mo	1.951(4)	C(9)-Mo	2.295(4)
(ii) Distances within Carbonyl groups			
C(1)-O(1)	1.148(4)	C(2)-O(2)	1.159(4)
(iii) Distances within the Acetyl group			
C(3)-O(3)	1.207(5)	C(3)-C(4)	1.502(6)
(iv) Distances within the Cp ring			
C(5)-C(6)	1.393(6)	C(8)-C(9)	1.399(6)
C(6)-C(7)	1.384(6)		
C(7)-C(8)	1.402(6)	C(5)-C(9)	1.422(7)
(v) Distances in the PPh ₃ ligand			
P-C(10)	1.838(3)	C(19)-C(20)	1.351(6)
P-C(16)	1.832(4)	C(20)-C(21)	1.376(6)
P-C(22)	1.834(4)	C(21)-C(16)	1.393(5)
C(10)-C(11)	1.384(5)	C(19)-F(2)	1.357(5)
C(11)-C(12)	1.400(5)		
C(12)-C(13)	1.357(6)	C(22)-C(23)	1.391(5)

C(13)-C(14)	1.351(6)	C(23)-C(24)	1.378(5)
		C(24)-C(25)	1.358(6)
C(14)-C(15)	1.375(5)	C(25)-C(26)	1.363(5)
C(15)-C(10)	1.386(5)	C(26)-C(27)	1.386(5)
		C(27)-C(22)	1.382(5)
C(13)-F(1)	1.356(4)	C(25)-F(3)	1.355(4)
C(16)-C(17)	1.379(5)		
C(17)-C(18)	1.392(6)		
C(18)-C(19)	1.359(6)		
(vi) Intramolecular contacts from Cp group to other ligands (cyclically)			

Table A6: Bond angles in $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]\text{COMe}$

Atoms	degrees	Atoms	degrees
(i) Around Molybdenum atom			
P-Mo-C(1)	83.16(11)	C(5)-Mo-C(6)	34.53(15)
P-Mo-C(2)	79.62(11)	C(6)-Mo-C(7)	33.99(14)
P-Mo-C(3)	135.42(12)	C(7)-Mo-C(8)	34.69(14)
C(1)-Mo-C(2)	106.64(16)	C(8)-Mo-C(9)	35.15(16)
C(1)-Mo-C(3)	71.46(16)	C(9)-Mo-C(5)	35.90(16)
C(2)-Mo-C(3)	73.70(15)	O(1)...Mo...O(2)	
P-Mo...O(1)		O(1)...Mo...O(3)	
P-Mo...O(2)		O(2)...Mo...O(3)	
(ii) In Carbonyl groups			
Mo-C(1)-O(1)	176.7(3)	Mo-C(2)-O(2)	174.6(3)
(iii) In Acetyl group			
Mo-C(3)-C(4)	123.4(3)	C(4)-C(3)-O3	116.7(4)
Mo-C(3)-O3	119.9(4)		
(iv) In the Cp ring			
C(5)-C(6)-C(7)	108.3(4)	C(8)-C(9)-C(5)	107.1(4)
C(6)-C(7)-C(8)	108.7(4)	C(9)-C(5)-C(6)	107.9(4)
C(7)-C(8)-C(9)	108.0(4)		
(v) In the PPh ₃ ligand			
Mo-P-C(10)	118.06(12)	C(18)-C(19)-C(20)	122.3(4)
Mo-P-C(16)	112.23(11)	C(19)-C(20)-C(21)	119.0(4)
Mo-P-C(22)	116.87(11)	C(20)-C(21)-C(16)	121.3(4)

C(15)-C(10)-C(11)	117.3(4)	C(20)-C(19)-F(2)	119.5(5)
C(10)-C(11)-C(12)	121.1(4)		
C(11)-C(12)-C(13)	117.8(4)		
		C(18)-C(19)-F(2)	118.2(5)
		C(22)-C(23)-C(24)	121.2(4)
		C(23)-C(24)-C(25)	118.8(4)
		C(24)-C(25)-C(26)	122.8(4)
C(12)-C(13)-C(14)	123.0(4)		
C(13)-C(14)-C(15)	118.9(4)		
C(14)-C(15)-C(10)	121.3(4)	C(25)-C(26)-C(27)	117.6(4)
		C(26)-C(27)-C(22)	122.2(3)
F(1)-C(13)-C(14)	118.7(4)	C(27)-C(22)-C(23)	117.4(3)
F(1)-C(13)-C(12)	118.3(4)	C(24)-C(25)-F(3)	118.7(4)
C(21)-C(16)-C(17)	117.1(4)	C(26)-C(25)-F(3)	118.4(4)
C(16)-C(17)-C(18)	121.0(4)		
C(17)-C(18)-C(19)	118.7(4)		

Table A7: Bond distances within (η^5 -C₅H₄Me)Mo(CO)₂[P(*p*-MeOC₆H₄)₃]COMe 3

Atoms	Distance, Å	Atoms	Distance, Å
(i) Distances from Molybdenum atom			
Mo-P(1)	2.4766(9)	C(3)-Mo	2.270(3)
Mo...O(1)		C(5)-Mo	2.345(2)
Mo...O(2)		C(6)-Mo	2.355(2)
Mo...O(3)		C(7)-Mo	2.372(3)
C(1)-Mo	1.962(2)	C(8)-Mo	2.376(3)
C(2)-Mo	1.971(2)	C(9)-Mo	2.344(3)
(ii) Distances within Carbonyl groups			
C(1)-O(1)	1.159(3)	C(2)-O(2)	1.156(3)
(iii) Distances within the Acetyl group			
C(3)-O(3)	1.215(3)	C(3)-C(4)	1.526(4)
(iv) Distances within the Cp ring			
C(5)-C(6)	1.411(4)	C(8)-C(9)	1.410(4)
C(6)-C(7)	1.426(4)	C(5)-C(10)	1.516(4)
C(7)-C(8)	1.412(4)	C(5)-C(9)	1.427(4)
(v) Distances in the PPh ₃ ligand			
P-C(11)	1.829(2)	C(19)-C(20)	1.384(2)
P-C(18)	1.834(2)	C(20)-C(21)	1.392(4)
P-C(25)	1.834(2)	C(21)-C(22)	1.384(4)
C(11)-C(12)	1.393(3)	C(17)-C(22)	
C(12)-C(13)	1.390(3)	C(22)-C(23)	1.394(3)
C(13)-C(14)	1.391(3)	C(21)-C(24)	

C(14)-C(15)	1.389(4)	C(25)-C(26)	1.395(3)
C(15)-C(16)	1.383(4)	C(26)-C(27)	1.383(3)
C(11)-C(16)	1.395(30)	C(27)-C(28)	1.395(3)
C(14)-C(17)		C(28)-C(29)	1.382(3)
C(18)-C(19)	1.404(3)	C(29)-C(30)	1.391(3)
C(18)-C(23)	2.383(3)	C(25)-C(30)	1.393(3)
C(17)-O(4)	1.425(4)		
C(28)-O(6)	1.368(3)	C(14)-O(4)	1.371(3)
C(24)-O(5)	1.416(4)	C(31)-O(6)	1.429(3)

Table A8: Bond angles in (η^5 -C₅H₄Me)Mo(CO)₂[P(*p*-MeOC₆H₄)₃]COMe 3

Atoms	degrees	Atoms	degrees
(i) Around Molybdenum atom			
P-Mo-C(1))	80.96(7)	C(5)-Mo-C(6)	34.94(10)
P-Mo-C(2)	79.14(7)	C(6)-Mo-C(7)	35.12(9)
P-Mo-C(3)	133.15(7)	C(7)-Mo-C(8)	34.59(11)
C(1)-Mo-C(2)	106.13(10)	C(8)-Mo-C(9)	34.74(11)
C(1)-Mo-C(3)	70.76(10)	C(9)-Mo-C(5)	35.43(9)
C(2)-Mo-C(3)	74.12(10)	O(1)...Mo...O(2)	
P-Mo...O(1)		O(1)...Mo...O(3)	
P-Mo...O(2)		O(2)...Mo...O(3)	
(ii) In Carbonyl groups			
Mo-C(1)-O(1)	175.7(2)	Mo-C(2)-O(2)	176.5(2)
(iii) In Acetyl group			
Mo-C(3)-C(4)	122.05(18)	C(4)-C(3)-O3	116.9(2)
Mo-C(3)-O3	121.0(2)		
(iv) In the Cp ring			
C(5)-C(6)-C(7)	108.3(2)	C(8)-C(9)-C(5)	108.2(3)
C(6)-C(7)-C(8)	107.6(3)	C(9)-C(5)-C(6)	107.5(2)
C(7)-C(8)-C(9)	108.4(2)	C(10)-C(5)-C(6)	123.9(3)
		C(9)-C(5)-C(10)	128.4(3)
(v) In the PPh ₃ ligand			
Mo-P-C(11)	114.07(8)	C(18)-C(19)-C(20)	121.7(2)
Mo-P-C(18)	116.71(8)	C(19)-C(20)-C(21)	119.8(3)
Mo-P-C(25)	117.27(8)	C(20)-C(21)-C(22)	119.5(2)

C(16)-C(11)-C(12)	118.1(2)	C(21)-C(22)-C(23)	120.0(2)
C(11)-C(12)-C(13)	121.8(2)	C(22)-C(23)-C(18)	121.8(2)
		C(22)-C(21)-O(5)	124.9(2)
		C(20)-C(21)-O(5)	115.6(2)
		C(21)-O(5)-C(24)	117.8(3)
C(12)-C(13)-C(14)	118.9(2)		
C(13)-C(14)-C(15)	120.2(2)		
C(14)-C(15)-C(16)	120.2(2)	C(25)-C(26)-C(27)	121.7(2)
C(15)-C(16)-C(11)	120.8(2)	C(26)-C(27)-C(28)	119.8(2)
C(17)-O(4)-C(14)	118.4(2)	C(27)-C(28)-C(29)	119.7(2)
C(13)-C(14)-O(4)	124.2(2)	C(28)-C(29)-C(30)	119.7(2)
C(15)-C(14)-O(4)	115.6(2)	C(28)-O(6)-C(31)	117.0(2)
C(23)-C(18)-C(19)	117.2(2)	C(29)-C(30)-C(25)	121.7(2)
C(26)-C(25)-C(30)	117.4(2)	C(29)-C(28)-O(6)	124.2(2)
		C(27)-C(28)-O(6)	116.1(2)

Table A9: Bond distances within (η^5 -C₅H₄Me)Mo(CO)₂[P(*p*-MeC₆H₄)₃]COMe **4**

Atoms	Distance, Å	Atoms	Distance, Å
	(i) Distances from Molybdenum atom		
Mo-P(1)	2.4794(8)	C(3)-Mo	2.267(4)
Mo...O(1)		C(5)-Mo	2.358(3)
Mo...O(2)		C(6)-Mo	2.341(3)
Mo...O(3)		C(7)-Mo	2.356(4)
C(1)-Mo	1.970(4)	C(8)-Mo	2.380(8)
C(2)-Mo	1.972(4)	C(9)-Mo	2.352(3)
	(ii) Distances within Carbonyl groups		
C(1)-O(1)	1.157(4)	C(2)-O(2)	1.154(4)
	(iii) Distances within the Acetyl group		
C(3)-O(3)	1.203(5)	C(3)-C(4)	1.534(6)
	(iv) Distances within the Cp ring		
C(5)-C(6)	1.420(5)	C(8)-C(9)	1.418(6)
C(6)-C(7)	1.430(6)	C(5)-C(10)	1.500(5)
C(7)-C(8)	1.412(6)	C(5)-C(9)	1.428(5)
	(v) Distances in the PPh ₃ ligand		
P-C(11)	1.835(3)	C(19)-C(20)	1.397(5)
P-C(18)	1.837(3)	C(20)-C(21)	1.394(5)
P-C(25)	1.836(3)	C(21)-C(22)	1.390(5)
C(11)-C(12)	1.401(5)	C(17)-C(22)	

C(12)-C(13)	1.387(5)	C(22)-C(23)	1.392(5)
C(13)-C(14)	1.393(5)	C(21)-C(24)	1.516(5)
C(14)-C(15)	1.391(5)	C(25)-C(26)	1.399(5)
C(15)-C(16)	1.407(5)	C(26)-C(27)	1.390(5)
C(11)-C(16)	1.397(5)	C(27)-C(28)	1.393(6)
C(14)-C(17)	1.520(5)	C(28)-C(29)	1.392(6)
C(18)-C(19)	1.392(5)	C(29)-C(30)	1.393(5)
		C(28)-C(31)	1.514(5)
		C(25)-C(30)	1.387(5)

Table A10: Bond angles in (η^5 -C₅H₄Me)Mo(CO)₂[P(*p*-MeC₆H₄)₃]COMe **4**

Atoms	degrees	Atoms	degrees
(i) Around Molybdenum atom			
P-Mo-C(1))	79.78(9)	C(5)-Mo-C(6)	35.18(13)
P-Mo-C(2)	81.05(10)	C(6)-Mo-C(7)	35.36(14)
P-Mo-C(3)	133.60(10)	C(7)-Mo-C(8)	34.68(14)
C(1)-Mo-C(2)	108.34(14)	C(8)-Mo-C(9)	34.87(13)
C(1)-Mo-C(3)	71.32(13)	C(9)-Mo-C(5)	35.31(13)
C(2)-Mo-C(3)	74.88(14)	O(1)...Mo...O(2)	
P-Mo...O(1)		O(1)...Mo...O(3)	
P-Mo...O(2)		O(2)...Mo...O(3)	
(ii) In Carbonyl groups			
Mo-C(1)-O(1)	175.9(3)	Mo-C(2)-O(2)	174.5(3)
(iii) In Acetyl group			
Mo-C(3)-C(4)	121.3(3)	C(4)-C(3)-O3	116.4(4)
Mo-C(3)-O3	122.4(3)		
(iv) In the Cp ring			
C(5)-C(6)-C(7)	108.2(3)	C(8)-C(9)-C(5)	109.2(3)
C(6)-C(7)-C(8)	108.4(3)	C(9)-C(5)-C(6)	106.8(3)
C(7)-C(8)-C(9)	107.4(3)	C(10)-C(5)-C(6)	126.4(4)
		C(9)-C(5)-C(10)	126.5(4)
(v) In the PPh ₃ ligand			
Mo-P-C(11)	110.32(10)	C(18)-C(19)-C(20)	120.8(3)
Mo-P-C(18)	118.40(11)	C(19)-C(20)-C(21)	121.1(3)
Mo-P-C(25)	117.70(11)	C(20)-C(21)-C(22)	117.8(3)

C(16)-C(11)-C(12)	118.3(3)	C(21)-C(22)-C(23)	121.5(3)
C(11)-C(12)-C(13)	120.7(3)	C(22)-C(23)-C(18)	120.6(3)
		C(24)-C(21)-C(22)	120.6(3)
		C(20)-C(21)-C(24)	121.5(4)
C(12)-C(13)-C(14)	121.2(3)		
C(13)-C(14)-C(15)	118.3(3)		
C(14)-C(15)-C(16)	121.3(3)	C(25)-C(26)-C(27)	120.8(3)
C(15)-C(16)-C(11)	119.8(3)	C(26)-C(27)-C(28)	121.2(4)
C(17)-C(14)-C(15)	121.6(4)	C(27)-C(28)-C(29)	117.7(3)
C(17)-C(14)-C(13)	120.2(4)	C(28)-C(29)-C(30)	121.3(3)
C(23)-C(18)-C(19)	118.3(3)	C(29)-C(30)-C(25)	119.5
C(26)-C(25)-C(30)	118.0(3)	C(31)-C(28)-C(29)	120.9(4)
		C(31)-C(28)-C(27)	121.5(4)

Table A12: Bond distances within (η^5 -C₅H₄Me)Mo(CO)₂(PPh₃)COMe **5**

Atoms	Distance, Å	Atoms	Distance, Å
(i) Distances from Molybdenum atom			
Mo-P	2.466(3)	C(3)-Mo	2.275(13)
Mo...O(1)		C(5)-Mo	2.349(12)
Mo...O(2)		C(6)-Mo	2.338(10)
Mo...O(3)		C(7)-Mo	2.383(11)
C(1)-Mo	1.962(12)	C(8)-Mo	2.360(11)
C(2)-Mo	1.959(11)	C(9)-Mo	2.275(13)
(ii) Distances within Carbonyl groups			
C(1)-O(1)	1.170(14)	C(2)-O(2)	1.160(13)
(iii) Distances within the Acetyl group			
C(3)-O(3)	1.223.224(17)	C(3)-C(4)	1.508(18)
1.507v) Distances within the Cp ring			
C(5)-C(6)	1.445(16)	C(8)-C(9)	1.428(17)
C(6)-C(7)	1.401(18)	C(9)-C(5)	1.423(17)
C(7)-C(8)	1.418(18)	C(5)-C(10)	1.496(18)
(v) Distances in the PPh ₃ ligand			
P-C(11)	1.835(10)	C(19)-C(20)	1.41(2)
P-C(17)	1.821(11)	C(20)-C(21)	1.36(2)
P-C(23)	1.843(11)	C(21)-C(22)	1.400(18)
C(11)-C(12)	1.393(15)	C(17)-C(22)	1.397(18)

C(12)-C(13)	1.393(17)	C(23)-C(24)	1.350(18)
C(13)-C(14)	1.366(18)	C(24)-C(25)	1.412(17)
C(14)-C(15)	1.380(17)	C(25)-C(26)	1.35(2)
C(15)-C(16)	1.378(17)	C(26)-C(27)	1.39(2)
C(11)-C(16)	1.390(16)	C(27)-C(28)	1.403(17)
C(17)-C(18)	1.396(17)	C(23)-C(28)	1.412(17)

Table A13: Bond angles in $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{COMe } \mathbf{5}$

Atoms	degrees	Atoms	degrees
(i) Around Molybdenum atom			
P-Mo-C(1)	79.8(4)	C(5)-Mo-C(6)	35.9(4)
P-Mo-C(2)	79.4(4)	C(6)-Mo-C(7)	34.5(5)
P-Mo-C(3)	133.6(4)	C(7)-Mo-C(8)	34.8(4)
C(1)-Mo-C(2)	108.2(5)	C(8)-Mo-C(9)	35.3(4)
C(1)-Mo-C(3)	75.0(5)	C(9)-Mo-C(5)	35.3(4)
C(2)-Mo-C(3)	72.6(4)	O(1)...Mo...O(2)	
P-Mo...O(1)		O(1)...Mo...O(3)	
P-Mo...O(2)		O(2)...Mo...O(3)	
(ii) In Carbonyl groups			
Mo-C(1)-O(1)	175.2(10)	Mo-C(2)-O(2)	175.3(10)
(iii) In Acetyl group			
Mo-C(3)-C(4)	122.0(10)	C(4)-C(3)-O3	117.5(12)
Mo-C(3)-O3	120.3(10)		
(iv) In the Cp ring			
C(5)-C(6)-C(7)	108.8(11)	C(8)-C(9)-C(5)	109.2(10)
C(6)-C(7)-C(8)	108.6(11)	C(9)-C(5)-C(6)	106.0(11)

C(7)-C(8)-C(9)	107.4(12)	C(10)-C(5)-C(6)	125.6(11)
		C(9)-C(5)-C(10)	128.2(12)
(v) In the PPh ₃ ligand			
Mo-P-C(11)	118.7(4)	C(18)-C(19)-C(20)	119.2(14)
Mo-P-C(17)	115.0(4)	C(19)-C(20)-C(21)	120.1(12)
Mo-P-C(23)	112.4(4)	C(20)-C(21)-C(22)	121.2(15)
C(16)-C(11)-C(12)	119.1(10)	C(21)-C(22)-C(17)	119.3(14)
C(11)-C(12)-C(13)	119.0(12)	C(28)-C(23)-C(24)	119.6(11)
C(12)-C(13)-C(14)	120.8(11)	C(23)-C(24)-C(25)	121.5(14)
C(13)-C(14)-C(15)	120.8(12)	C(24)-C(25)-C(26)	119.6(16)
C(14)-C(15)-C(16)	118.9(12)	C(25)-C(26)-C(27)	120.2(12)
C(15)-C(16)-C(11)	121.4(11)		
C(22)-C(17)-C(18)	119.4(11)	C(26)-C(27)-C(28)	120.5(14)
C(17)-C(18)-C(19)	120.7(13)	C(27)-C(28)-C(23)	118.6(14)

Table A14: Bond distances within (η^5 -C₅H₄Me)Mo(CO)₂[P(*p*-FC₆H₄)₃]COMe **6**

Atoms	Distance, Å	Atoms	Distance, Å
(i) Distances from Molybdenum atom			
Mo-P(1)	2.4670(5)	C(3)-Mo	2.275(2)
Mo...O(1)		C(5)-Mo	2.407(2)
Mo...O(2)		C(6)-Mo	2.371(2)
Mo...O(3)		C(7)-Mo	2.328(2)
C(1)-Mo	1.970(2)	C(8)-Mo	2.305(2)
C(2)-Mo	1.965(2)	C(9)-Mo	2.325(2)
(ii) Distances within Carbonyl groups			
C(1)-O(1)	1.158(3)	C(2)-O(2)	1.153(3)
(iii) Distances within the Acetyl group			
C(3)-O(3)	1.215(3)	C(3)-C(4)	1.510(4)
(iv) Distances within the Cp ring			
C(5)-C(6)	1.415(3)	C(8)-C(9)	1.426(4)
C(6)-C(7)	1.425(4)	C(5)-C(9)	1.425(3)
C(7)-C(8)	1.423(4)	C(5)-C(10)	1.506(3)
(v) Distances in the PPh ₃ ligand			
P-C(11)	1.836(2)	C(19)-C(20)	1.376(5)
P-C(17)	1.838(2)	C(20)-C(21)	1.364(5)
P-C(23)	1.834(2)	C(21)-C(22)	1.393(4)
C(11)-C(12)	1.394(3)	C(17)-C(22)	1.400(3)
C(12)-C(13)	1.394(3)	C(20)-F(2)	1.363(3)
C(13)-C(14)	1.396(3)	C(23)-C(24)	1.400(3)

		C(24)-C(25)	1.384(3)
C(14)-C(15)	1.371(3)	C(25)-C(26)	1.377(4)
C(15)-C(16)	1.395(3)	C(26)-C(27)	1.380(4)
C(11)-C(16)	1.389(3)	C(27)-C(28)	1.389(3)
C(14)-F(1)	1.362(2)	C(28)-C(23)	1.403(3)
C(17)-C(18)	1.386(3)	C(26)-F(3)	1.354(3)
C(18)-C(19)	1.395(3)		

Table A17: Bond angles in (η^5 -C₅H₄Me)Mo(CO)₂[P(*p*-FC₆H₄)₃]COMe **6**

Atoms	degrees	Atoms	degrees
(i) Around Molybdenum atom			
P-Mo-C(1))	81.54(6)	C(5)-Mo-C(6)	34.44(8)
P-Mo-C(2)	79.67(6)	C(6)-Mo-C(7)	35.28(9)
P-Mo-C(3)	134.56(6)	C(7)-Mo-C(8)	35.76(9)
C(1)-Mo-C(2)	107.99(9)	C(8)-Mo-C(9)	35.88(9)
C(1)-Mo-C(3)	77.87(9)	C(9)-Mo-C(5)	34.98(8)
C(2)-Mo-C(3)	69.12(8)	O(1)...Mo...O(2)	
P-Mo...O(1)		O(1)...Mo...O(3)	
P-Mo...O(2)		O(2)...Mo...O(3)	
(ii) In Carbonyl groups			
Mo-C(1)-O(1)	174.8(2)	Mo-C(2)-O(2)	175.21(19)
(iii) In Acetyl group			
Mo-C(3)-C(4)	122.56(17)	C(4)-C(3)-O3	117.6(2)
Mo-C(3)-O3	119.70(18)		
(iv) In the Cp ring			
C(5)-C(6)-C(7)	109.1(2)	C(8)-C(9)-C(5)	108.8(2)
C(6)-C(7)-C(8)	107.6(2)	C(9)-C(5)-C(6)	107.0(2)
C(7)-C(8)-C(9)	107.5(2)	C(10)-C(5)-C(6)	127.7(2)
		C(9)-C(5)-C(10)	125.2(2)
(v) In the PPh ₃ ligand			
Mo-P-C(11)	117.79(7)	C(18)-C(19)-C(20)	117.5(3)
Mo-P-C(17)	118.99(8)	C(19)-C(20)-C(21)	123.6(2)
Mo-P-C(23)	116.42(7)	C(20)-C(21)-C(22)	118.4(3)

C(16)-C(11)-C(12)	118.9(2)	C(21)-C(20)-F(2)	119.2(3)
C(11)-C(12)-C(13)	120.5(2)		
		C(19)-C(20)-F(2)	117.2(3)
		C(23)-C(24)-C(25)	121.2(2)
		C(24)-C(25)-C(26)	118.4(2)
C(12)-C(13)-C(14)	118.6(2)		
C(13)-C(14)-C(15)	123.0(2)		
C(14)-C(15)-C(16)	118.0(2)	C(25)-C(26)-C(27)	122.7(2)
C(15)-C(16)-C(11)	120.0(2)	C(26)-C(27)-C(28)	118.3(2)
F(1)-C(14)-C(15)	118.7(2)	C(27)-C(28)-C(23)	120.9(2)
F(1)-C(14)-C(13)	118.4(2)	C(27)-C(26)-F(3)	118.4(2)
C(22)-C(17)-C(18)	119.0(2)	C(25)-C(26)-F(3)	118.8(2)
C(17)-C(18)-C(19)	121.2(3)		

Table A18: Bond distances within (η^5 -C₅H₄COCH₃)Mo(CO)₃Me **7**

Atoms	Distance, Å	Atoms	Distance, Å
(i) Distances from Molybdenum atom			
		C(3)-Mo	1.990(3)
		C(4)-Mo	2.305(4)
Mo...O(1)		C(5)-Mo	2.306(3)
Mo...O(2)		C(6)-Mo	2.330(3)
Mo...O(3)		C(7)-Mo	2.373(3)
C(1)-Mo	1.973(4)	C(8)-Mo	2.385(3)
C(2)-Mo	1.991(4)	C(9)-Mo	2.329(3)
(ii) Distances within Carbonyl groups			
C(1)-O(1)	1.128(5)	C(2)-O(2)	1.136(4)
C(3)-O(3)	1.140(4)		
(iv) Distances within the Cp ring			
C(5)-C(6)	1.423(4)	C(8)-C(9)	1.390(5)
C(6)-C(7)	1.413(5)	C(5)-C(9)	1.440(4)
C(7)-C(8)	1.407(5)	C(5)-C(10)	1.482(4)
C(10)-O(4)	1.216(4)	C(10)-C(11)	1.505(5)

Table A20: Bond angles in $(\eta^5\text{-C}_5\text{H}_4\text{COCH}_3)\text{Mo}(\text{CO})_3\text{Me}$ **7**

Atoms	degrees	Atoms	degrees
(i) Around Molybdenum atom			
C(1)-Mo-C(2)	78.87(18)	C(5)-Mo-C(6)	35.74(11)
C(1)-Mo-C(3)	108.39(16)	C(6)-Mo-C(7)	34.96(11)
C(2)-Mo-C(3)	78.46(15)	C(7)-Mo-C(8)	34.40(12)
C(4)-Mo-C(1)	72.76(17)	C(8)-Mo-C(9)	34.28(12)
C(4)-Mo-C(2)	128.43(16)	C(9)-Mo-C(5)	36.19(11)
C(4)-Mo-C(3)	71.20(15)	O(1)...Mo...O(2)	
P-Mo...O(1)		O(1)...Mo...O(3)	
P-Mo...O(2)		O(2)...Mo...O(3)	
(ii) In Carbonyl groups			
Mo-C(1)-O(1)	176.9(4)	Mo-C(2)-O(2)	178.7(4)
Mo-C(3)-O(3)	178.0(4)		
(iv) In the Cp ring			
C(5)-C(6)-C(7)	108.0(3)	C(8)-C(9)-C(5)	108.4(3)
C(6)-C(7)-C(8)	108.3(3)	C(9)-C(5)-C(6)	106.7(3)
C(7)-C(8)-C(9)	108.7(3)	C(10)-C(5)-C(6)	125.1(3)
		C(10)-C(5)-C(9)	128.2(3)
O(4)-C(10)-C(5)	119.9(3)	O(4)-C(10)-C(11)	121.8(3)
C(5)-C(10)-C(11)	118.3(3)		