SYNTHESIS AND CHARACTERIZATION OF PENTAMETHYLCYCLOPENTADIENYL AND PYRAZOLYLBORATE RHENIUM CARBONYL COMPLEXES

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
in the Department
of
Chemistry

Simon Fraser University
August 1997

0-612-24326-5

APPROVAL

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ABSTRACT

This thesis describes the synthesis, characterization, and reactivity of pentamethylcyclopentadienyl rhenium carbonyl complexes and pyrazolylborate rhenium carbonyl complexes and compares their reactivity.

The cationic complexes of the general formula $[Cp^*Re(CO)_2\{P(OR)_3\}X]^+$ ((R = Me or Et, X = Cl, Br, and I) have been synthesized by reactions of $Cp^*Re(CO)_2\{P(OR)_3\}$ with either halogens or $SbCl_5$. In each case a mixture of cis and trans isomers of a typical "four-legged" piano-stool geometry was obtained. It is observed that under appropriate conditions these cationic complexes undergo transformation to the corresponding neutral dialkylphosphonate complexes of general formula *trans*-$Cp^*Re(CO)_2\{PO(OR)_2\}X$.

The photochemical reactions of $Cp^*Re(CO)(L)N_2$ (L = $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$, $P(OCH_2)_3CMe$, PPh_3) complexes were studied in order to investigate the ability of rhenium dinitrogen phosphite complexes to activate C-H bonds in saturated and unsaturated hydrocarbons. In this study, there was observed for the first time in a rhenium system, an *agostic* interaction prior to intramolecular C-H activation of one of the R groups in the phosphite ligand. In the photochemical reaction of $Cp^*Re(CO)\{P(OMe)_3\}N_2$ with hydrocarbons, no C-H activation was observed. Instead, methyl migration from one of the methyl groups in the phosphite ligand to the rhenium center was observed.

Irradiation of $Cp^*Re(CO)(L)N_2$ (L = $P(OMe)_3$, $P(OEt)_3$, $P(OCH_2)_3CMe$, and PMe_2Ph) under UV light with chlorobenzene produced stable phenyl halide complexes.

However, the photolysis of Cp*Re(CO){P(OPh)$_3$}N$_2$ in chlorobenzene produced only the intramolecular C-H activation complex *cis*$_{(P-H)}$-Cp*Re(CO){η^2-P(OC$_6$H$_4$)(OPh)$_2$}H. The reactivity of the phenyl halide rhenium complexes in chlorinated solvents was also investigated.

The photochemical study of Cp*Re(CO)$_2$MeR (R = *p*-Tolyl, Ph, and Me) complexes in hydrocarbons and chlorinated solvents was carried out in order to determine the primary photoproduct and to understand the process of formation of Cp*Re(CO)$_3$.

Attempts to synthesize pyrazolylborate rhenium aryldiazenido complexes with the general formula [Tp(CO)L(N$_2$R)]$^+$ (Tp = HB(C$_3$H$_3$N$_2$)$_3$), where L is a 2-electron donor ligand such as CO or PR$_3$ are described. The reaction of the complex TpRe(CO)$_2$(THF) (**6.2**) with the nitrosonium ion produced the pyrazolylborate rhenium nitrosyl complex [TpRe(CO)$_2$(NO)]$^+$ (**6.3**). The reactions of **6.3** with different nucleophiles are also described.

DEDICATION

Para mi querida y santa madre, Gladys
Mis hermanas Maria Verónica y Evelyn

y a "mi esposo perfecto"

ACKNOWLEDGEMENTS

I would like to thanks my supervisor Dr. Derek Sutton for his guidance, patience and assistance during these years. I appreciate the time he spent with me and all those long discussions "Gracias Jefe".

It has been pleasure to associated with Drs. F. W. B. Einstein, S. Holdcroft, R. H. Hill, A. H. Klahn-Oliva, N. Lowe, L. K. Peterson, J. Walkley and X. Yan, I am indebted to you for all your help.

I also wish to thank Marcelline M. Tracey for her efficient and friendly service in the course of obtaining several NMR spectra, for her friendship and the wealth of all the invaluable knowledge and "technical advice". I would also like to thank Dr. Alan S. Tracey for the NMR knowledge and discussion.

The expert work of Greg L. Owen (Mass Spectroscopy), Mr. M. K. Yang (Microanalyses), Elizabeth M. Brion (Graduate Secretary), Gerry Rynders and Les Wakida (Glass Shop) is greatly appreciated. I would also like to thank Fred H. Chin for the computer consultancy (on innumerable occasions), teaching and friendship.

I would like to thank my labmate Dr. Yingxia He for her friendship and great memories during this "journey". All those long hours in front of the fumehood. The support of my friends Alice, Jorge and Laura was a constant source of inspiration, thanks to all of you.

Finally, thanks to Mutley for the advice and support and all the quality time spent together doing chemistry in these year and to my family for their unconditional love.

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LIST OF ABBREVIATION AND SYMBOLS

Ar	aryl or aromatic
atm	atmosphere
CI	chemical ionization
Cy	cyclohexyl (C_6H_{11})
COSY	homonuclear chemical-shift correlated
Cp	cyclopentadienyl (η^5-C_5H_5)
Cp*	pentamethylcyclopentadienyl (η^5-C_5Me_5)
EI	electron impact
FAB	fast atom bombardment
GC	gas chromatography
IR	infrared
L	monodentate ligand
M^+	parent ion
M	central transition metal in complex
MS	mass spectroscopy
Me	methyl (CH_3)
NMR	nuclear magnetic resonance
NOBA	*m*-nitrobenzyl alcohol (*m*-$NO_2C_6H_4CH_2OH$)
OMe	methoxy (OCH_3)
OEt	ethoxy (OCH_2CH_3)
Pc	caged phosphite {$P(OCH_2)_3CMe$}
Ph	phenyl (C_6H_5)
R	alkyl
RT	retention time
THF	tetrahydrofuran (C_4H_8O)
Tolyl	$C_6H_4CH_3$
Tp	pyrazolylborate ligand [$HB(C_3H_3N_2)_3$]
X	halogen

LIST OF COMPLEXES

(2.1)	$\mathrm{Cp^*Re(CO)_2\{P(OMe)_3\}}$
(2.2)	$\mathrm{Cp^*Re(CO)_2\{P(OEt)_3\}}$
(2.3•SbCl$_6$)	$\mathrm{[Cp^*Re(CO)_2\{P(OMe)_3\}Cl][SbCl_6]}$
(2.4•Br$_3$)	$\mathrm{[Cp^*Re(CO)_2\{P(OMe)_3\}Br][Br_3]}$
(2.5•I$_3$)	$\mathrm{[Cp^*Re(CO)_2\{P(OMe)_3\}I][I_3]}$
(2.6)	$\mathrm{Cp^*Re(CO)_2\{P(O)(OMe)_2\}Cl}$
(2.7)	$\mathrm{Cp^*Re(CO)_2\{P(O)(OMe)_2\}Br}$
(2.8)	$\mathrm{Cp^*Re(CO)_2\{P(O)(OMe)_2\}I}$
(2.9•SbCl$_6$)	$\mathrm{[Cp^*Re(CO)_2\{P(OEt)_3\}Cl][SbCl_6]}$
(2.10•Br$_3$)	$\mathrm{[Cp^*Re(CO)_2\{P(OEt)_3\}Br][Br_3]}$
(2.11•I$_3$)	$\mathrm{[Cp^*Re(CO)_2\{P(OEt)_3\}I][I_3]}$
(2.12)	$\mathrm{Cp^*Re(CO)_2\{P(O)(OEt)_2\}Cl}$
(2.13)	$\mathrm{Cp^*Re(CO)_2\{P(O)(OEt)_2\}Br}$
(2.14)	$\mathrm{Cp^*Re(CO)_2\{P(O)(OEt)_2\}I}$
(3.1)	$\mathrm{Cp^*Re(CO)\{P(OEt)_3\}(N_2)}$
(3.2)	$\mathrm{Cp^*Re(CO)\{P(OPh)_3\}(N_2)}$
(3.3)	$\mathrm{Cp^*Re(CO)(Pc)(N_2)}$
(3.4)	$\mathrm{Cp^*Re(CO)\{P(OMe)_3\}(N_2)}$
(3.5)	$\mathrm{Cp^*Re(CO)(PPh_3)(N_2)}$
(3.6)	$\mathrm{Cp^*Re(CO)(PMe_2Ph)(N_2)}$
(3.7)	$\mathrm{Cp^*Re(CO)\{\eta^2\text{-}P(OCH_2CH_2)(OEt)_2\}H}$
(3.8)	$\mathrm{Cp^*Re(CO)\{P(OEt)_3\}(C_6H_5)H}$
(3.9)	$\mathrm{Cp^*Re(CO)\{\eta^2\text{-}P(OC_6H_4)(OPh)_2\}H}$
(3.10)	$\mathrm{Cp^*Re(CO)(Pc)(C_6H_5)H}$
(3.11)	$\mathrm{[Cp^*Re(CO)\{PO(OMe)_2\}Me]_2}$
(3.12)	$\mathrm{Cp^*Re(CO)\{\eta^2\text{-}P(C_6H_4)Ph_2\}H}$
(3.13)	$\mathrm{Cp^*Re(CO)\{\eta^2\text{-}P(C_6H_4)Ph_2\}Cl}$

(4.1)	$\mathrm{Cp^*Re(CO)\{P(OEt)_3\}PhCl}$
(4.2)	$\mathrm{Cp^*Re(CO)(PMe_2Ph)PhCl}$
(4.3)	$\mathrm{Cp^*Re(CO)(Pc)PhCl}$
(4.4)	$\mathrm{Cp^*Re(CO)\{P(OMe)_3\}PhCl}$
(5.1)	*trans*-$\mathrm{Cp^*Re(CO)_2Me}$(*p*-Tolyl)
(5.2)	*trans*-$\mathrm{Cp^*Re(CO)_2MePh}$
(5.3)	*trans*-$\mathrm{Cp^*Re(CO)_2Me_2}$
(6.1)	$\mathrm{TpRe(CO)_3}$
(6.2)	$\mathrm{TpRe(CO)_2(THF)}$
(6.3)	$\mathrm{[TpRe(CO)_2(NO)][BF_4]}$
(6.4)	$\mathrm{TpRe(CO)(NO)(CO_2Me)}$
(6.5)	$\mathrm{TpRe(CO)(NO)(NCO)}$
(6.6)	$\mathrm{TpRe(CO)(NO)Cl}$

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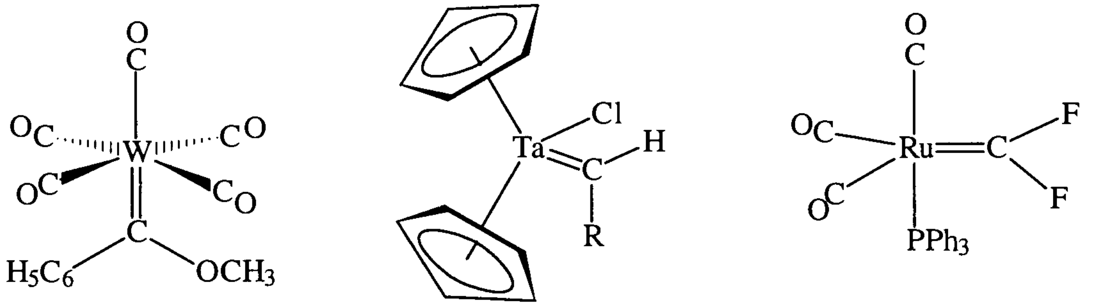
CHAPTER 1

1.1 Introduction

Why would I study *rhenium* chemistry? I think my first motivation was that Chile is one of the countries to recover *rhenium* as $(NH_4)ReO_4$ from the flue ash of molybdenum smelters and we would like to develop new synthetic routes to produce starting materials more economically. I was interested in investigating a new type of reaction and comparing these results with the chemistry that we already knew. However, during the course of this journey through the field of rhenium chemistry, unexpected results and interesting new chemistry has materialised and was explored.

This introduction is going to cover recent advances in *rhenium* chemistry. Organometallic chemistry of rhenium was not explored until the mid-1980's, in part, because common starting materials for rhenium chemistry were moderately expensive, and in part because rhenium has found only limited use in catalysis.[1] The recent advances in rhenium chemistry can be attributed to the following *three* reasons: (*i*) High rhenium-to-element bond strengths which stabilise reactive species and made possible the isolation of normally unstable structural types. (*ii*) The wide range of available oxidation states of rhenium made it possible to isolate organometallic complexes from Re -III in $Re(CO)_4^{3-}$ to Re +VII in $Cp'ReO_3$ ($Cp' = \eta^5$-C_5H_5 (Cp), η^5-C_5Me_5 (Cp*)). (*iii*) The combination of the high bond strengths and the pronounced reluctance of rhenium to form coordinatively unsaturated complexes permits the observation of intermediates which may have a shorter life time in the related reactions of other metals.[2]

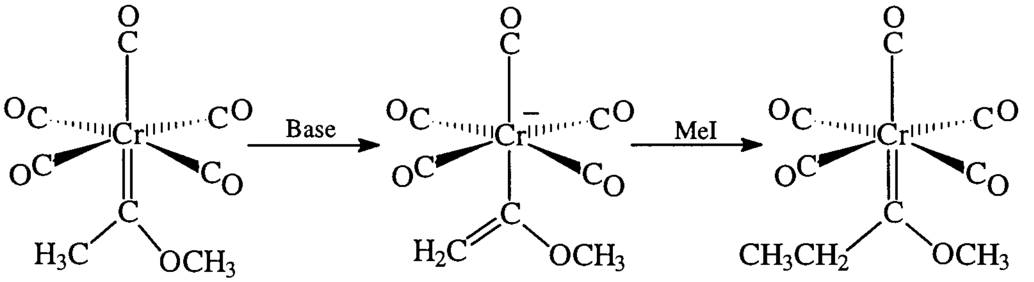
Metal carbene complexes have been playing an important role in the synthesis of organic compounds.[3] It is well known that there are metal carbene complexes that react with nucleophiles *i.e.* "Schrock's carbene" and those which react with electrophiles *i.e.* "Fischer's carbene".[4] The first metal carbene complex that has been shown to have amphiphilic reactivity at the carbene carbon is "Roper's carbene" $(CO)_2(Ph_3P)Ru{=}CF_2$ (Figure 1.1).[5] Casey *et al.*[6] have studied the reactivity of $CpRe(CO)_2({=}CHR)$ ($R = CH_2CH_2CMe_3$) and found that the carbene carbon in $CpRe(CO)_2({=}CHR)$ is susceptible to attack by both electrophiles and nucleophiles. This was the second example where a metal carbene complex has shown an amphiphilic properties. They believe that the high polarizability of the Re=C double bond is responsible for the amphiphilic reactivity of this complex.[6]



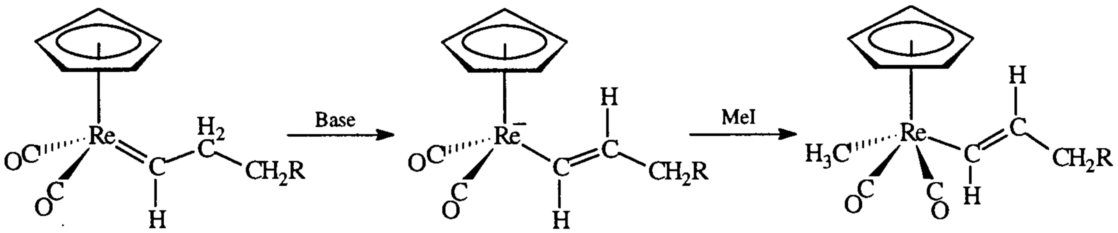
Fischer's Carbene Schrock's Carbene Roper's Carbene

Figure 1.1 Examples of metal carbene complexes.

It has been observed that in general metal carbene complexes with low oxidation states are not stable at room temperature. They generally require an electron-donating methoxy or amino substituent for kinetic stabilization *i.e.* $(CO)_5Cr{=}C(OCH_3)CH_3$. On the other hand the alkyl-substituted rhenium carbene complexes are stable even above room temperature.[6] Deprotonation of the Cr metal carbene complex ($(CO)_5Cr=C(OCH_3)CH_3$) generates vinyl anions that can be alkylated at the vinyl carbon to form a longer alkyl chain (Equation 1.1).[7] In contrast, the vinyl anion complex generated by deprotonation of the rhenium carbene complex $CpRe(CO)_2(=CHR)$ (R = $CH_2CH_2C(Me)_3$) underwent alkylation at rhenium to generate alkyl vinyl complexes (Equation 1.2).[8] This difference in regiochemistry of alkylation is a reflection of the ability of rhenium complexes to stabilize both the Re (I) (d^6) in the starting material and the formally oxidised Re (III) (d^4).



Eq 1.1



R = CMe_3

Eq 1.2

Another example of the capability of a rhenium complex to stabilize different oxidation states is seen in the reaction of the rhenium(I) propene complex with the hydrogen abstraction agent $(C_6H_5)_3C^+$, which leads to the formation of the rhenium(III) π-allyl complex.[9] Like most cationic π-allyl complexes it reacts with nucleophiles at the terminal allyl carbon to produce the rhenium alkene complex shown in Figure 1.2.[10]

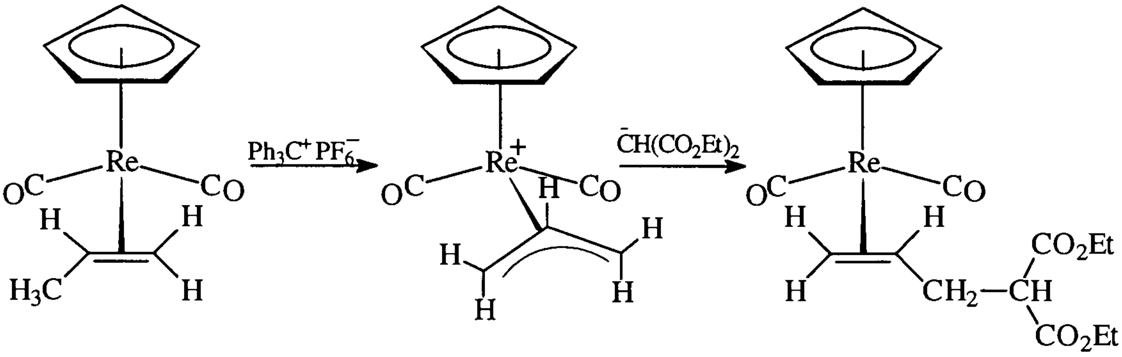


Figure 1.2 Reactivity of rhenium alkene complex $CpRe(CO)_2(\eta^2\text{-}CH_3CH{=}CH_2)$.

1.1.1 σ- and π- Rhenium Nitrosyl Complexes of Aldehydes and Ketones

Chiral transition metal reagents and catalysts are now extensively utilized for the elaboration of achiral monofuntional aldehydes and ketones to optically active organic molecules.[11]

Gladysz and co-workers have exploited pseudotetrahedral "chiral" rhenium $[CpRe(NO)(PPh_3)L]^+$ complexes to develop enantioselective syntheses and to probe the intimate details of the mechanisms of organometallic reactions. A key starting material for the synthesis of complexes of the formula $[CpRe(NO)(PPh_3)L]^+$ is $CpRe(NO)(PPh)_3(CH_2Cl_2)$ which is a very labile CH_2Cl_2 adduct, formed by the low-temperature reaction of $CpRe(NO)(PPh_3)CH_3$ with $HBF_4 \bullet Et_2O$ in CH_2Cl_2 (Figure 1.3).[12]

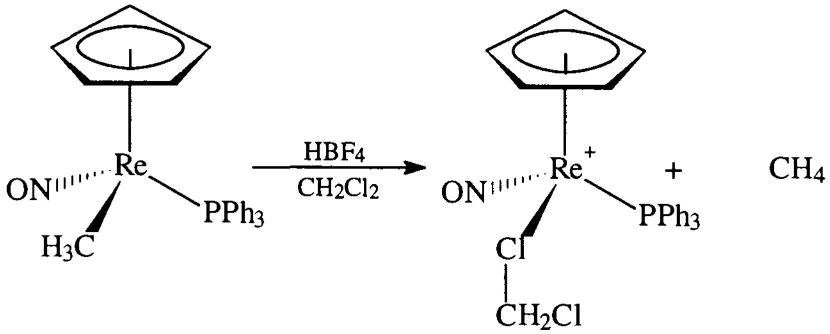


Figure 1.3 Reaction of $CpRe(CO)(NO)CH_3$ with $HBF_4{\bullet}Et_2O$ in CH_2Cl_2.

Unsaturated organic molecules are often activated towards nucleophilic addition upon coordination to a transition metal. Gladysz *et al.* have carried out extensive studies on the binding of aldehydes and ketones to the $[CpRe(NO)(PPh_3)]$ fragment. They observed that aliphatic aldehydes react with $CpRe(NO)(PPh_3)(CH_2Cl_2)$ to give π–complexes of the general structure **A** (Figure 1.4).[13] The aldehyde ligands adopt a Re–(O$\overline{\cdots\cdots}$C) conformation that places the larger =CHR terminus *anti* to the sterically bulky PPh_3 ligand. Two configurational diastereomers are then possible. These differ in the position of the alkyl and hydrogen substituent, or which enantioface of O=C is bound to the rhenium.

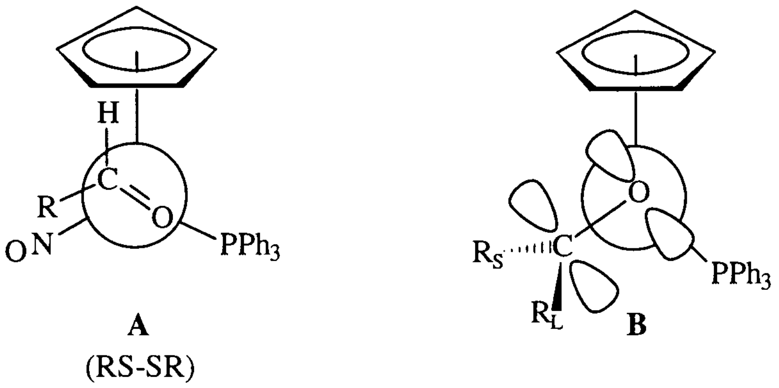


Figure 1.4 Idealized structure for π–aldehyde complexes (**A**) and for σ–ketone complexes (**B**).[13,14]

In contrast, most aliphatic and aromatic ketones give σ complexes with the idealized Re–O conformation shown in **B** (see Figure 1.4).[14] Methyl alkyl and aryl ketones are believed to give predominantly *E* isomers. Aromatic aldehydes give a mixture of π and σ complexes. The isomers formed are strongly influenced by the properties of the aryl substituent, the solvent, and the temperature.[15]

1.1.2 σ- and π- Rhenium Complexes of Alkenes

Chiral transition metal catalysts are now extensively used in the conversion of achiral alkenes into chiral organic molecules.[16] When alkenes are coordinated to chiral fragments, two π-diastereoisomers, that differ in the alkene enantioface bound to the metal, can be formed. The interconversion of these π-diastereoisomers plays a key role in asymmetric transformations and often occurs via alkene dissociation.

In recent studies of chiral rhenium alkene complexes, Gladysz and Peng have proposed an unprecedented pathway for the interconversion of diastereoisomers.[17] The reaction of alkenes with $[CpRe(NO)(PPh_3)(CH_2Cl_2)]^+$ initially produces a 2:1 mixture of diastereoisomeric alkene complexes (Figure 1.5). The alkene C=C bond is aligned parallel to the Re-P bond, which provides optimum overlapping of the donor *d* orbital on the rhenium with the acceptor π^* alkene orbital. Upon heating to 373 K, the ratio of the two isomers changed to 9:1. No exchange with deuterated alkenes or with $P(C_6D_5)_3$ was observed up to 423 K. Retention of configuration at rhenium and the absence of scrambling of *E*/*Z* deuterium labels ruled out a number of intramolecular mechanisms.

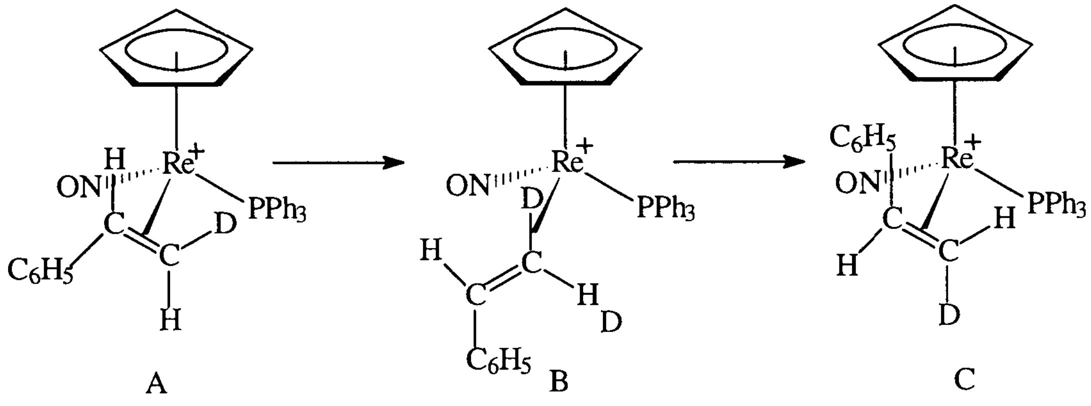


Figure 1.5 Proposed mechanism in the interconversion of alkene diastereoisomers.[17]

The mechanism proposed by Gladysz and Peng for stereoisomerization of alkenes on the $[CpRe(NO)(PPh_3)]$ fragment involves movement of rhenium through the π-nodal plane of the alkene via the carbon-hydrogen "σ-bond complex" (see Figure 1.5, species B).[17] The C-H bond's interaction with the metal is very weak (< 10 kcal mol^{-1}). This interaction is sometimes referred to as an *agostic* interaction. The intervention of a carbon-hydrogen ‘σ-bond complex” prevents the formation of the high-energy coordinatively unsaturated intermediate $[CpRe(NO)(PPh_3)]^{\#}$. An alternative mechanism involving a vinyl hydride oxidative-addition product has not been excluded.

A carbon-hydrogen “σ-bond complex” has also been proposed as an intermediate in the acid-catalysed isomerisation and deuterium exchange reactions of rhenium alkene complexes (Figure 1.6).[18]

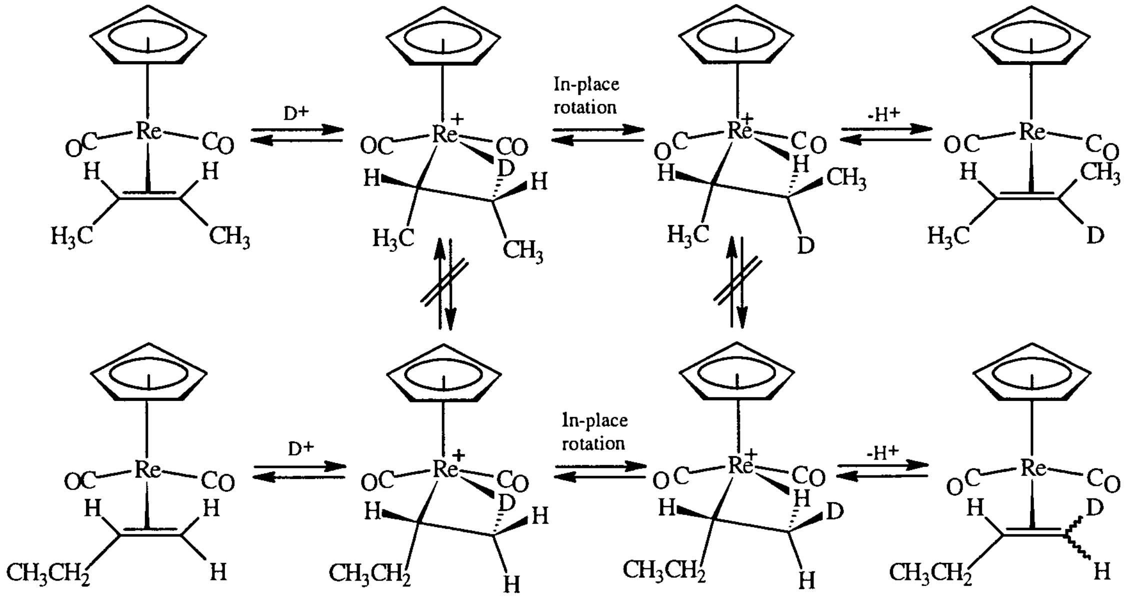


Figure 1.6 Proposed mechanism of the interconversion of *cis* to *trans*-2-butene rhenium complex.

The reaction of the *cis*-2-butene rhenium complex $CpRe(CO)_2(CH_3CH{=}CHCH_3)$ (**A**) with CF_3COOH generated an equilibrium mixture of 45:55 of *cis*-2-butene and *trans*-2-butene rhenium complexes. Isomerisation of the *cis*-2-butene rhenium complex by CF_3CO_2D produced only the *trans*-2-butene rhenium complex monodeuterated at the vinyl position (**B**). Treatment of the 1-butene rhenium complex (**C**) with excess

CF_3CO_2D led only to rapid exchange of deuterium into the terminal vinyl position and slower exchange into a secondary vinyl position (**D**). To explain this process, they proposed that the two intermediates fail to interconvert because of an unusually strong agostic interaction between the C-H bond and rhenium. An "in place rotation" of an agostic alkyl group can account for the cis- trans isomerization and deuterium exchange.[19]

1.1.3 Rhenium-Rhenium Double Bonds

Rhenium has played a central role in the understanding of metal-metal multiple bonds. In 1965, Cotton recognised for the first time the existence of a quadruple metal-metal bond in the $Re_2Cl_8^{2-}$ ion.[20]. The eclipsed geometry and short Re-Re bond length (2.24 Å) were explained in terms of one σ, two π, and one δ bond. In the past few years, several compounds with Re-Re double or multiple bonds have been discovered.

Casey *et al.* reported a Re=Re double bond in $\{Cp^*Re(CO)_2\}_2$ formed quantitatively from $Cp^*Re(CO)_2(THF)$ (Figure 1.7).[21] Previously, photolysis of $Cp^*Re(CO)_3$ in THF has been used as a first step for synthesis of new rhenium complexes but pure $\{Cp^*Re(CO)_2\}_2$ had never been isolated.[22]

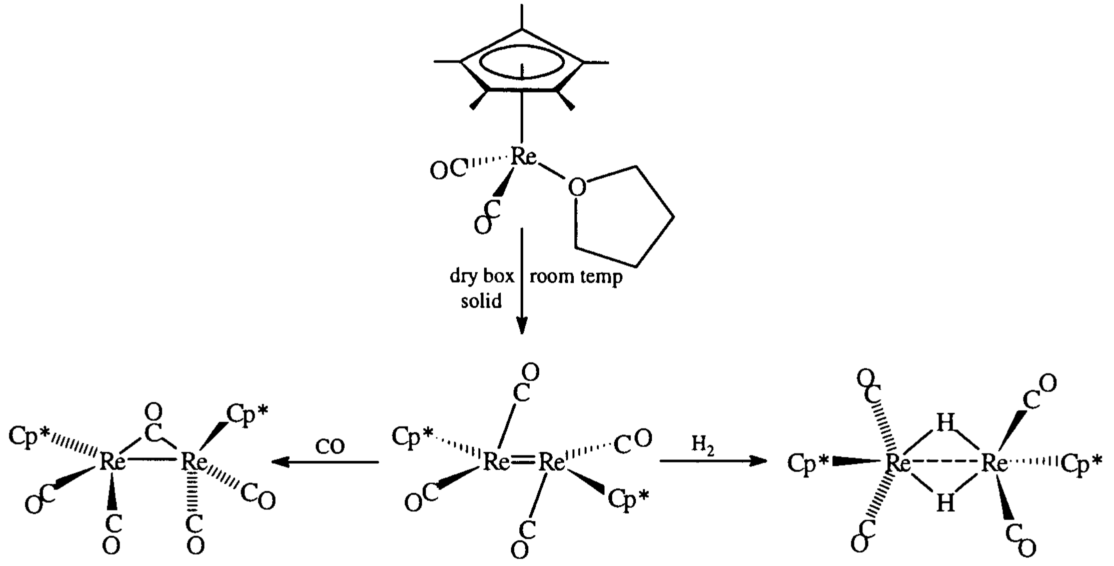


Figure 1.7 Synthesis and reactivity of the complex $[Cp^*Re(CO)_2]_2$.

The X-ray crystal structure of $\{Cp^*Re(CO)_2\}_2$ shows that the 2.72 Å Re=Re double bond is supported only by a semibridging carbonyl ligand. This complex is a rare example of a formal dimer having a 16-electron d^6 metal fragment. This complex is thermally stable and extremely reactive. Addition of CO produces $Cp^*_2Re_2(CO)_4(\mu\text{-}CO)$ and addition of H_2 produces the new dirhenium dihydride complex $Cp^*_2Re_2(CO)_4(\mu\text{-}H)_2$ (see Figure 1.7).[21]

Schrock and co-workers recently characterised another rhenium complex $\{Re(C\text{-}{}^tBu)(O\text{-}{}^tBu)_2\}_2$ which contains a very rare "unsupported" metal-metal double bond (Figure 1.8).[23] Complexes with metal-metal multiple bonds often have bridging ligands that "support" the metal-metal interaction; $\{Re(C\text{-}{}^tBu)(O\text{-}{}^tBu)_2\}_2$ is a formal dimer of 12-electron d^2 metal fragments.

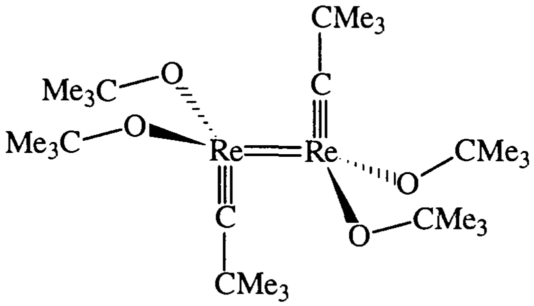


Figure 1.8 Structure of $\{Re(C\text{-}^tBu)(O\text{-}^tBu)_2\}_2$.

1.2 Thesis

There were three distinct goals of the research undertaken for this thesis. The first goal was to compare the reactivity of rhenium phosphite complexes with the corresponding phosphine analogues. The second goal, was to investigate the photochemistry of Cp*Re$(CO)_2$MeL in solution at room temperature. The third objective was to synthesise new aryldiazenido rhenium complexes with a pyrazolylborate ligand (Tp). Chapter 2 describes the synthesis, characterisation and reactivity of rhenium phosphite complexes with halogens. In Chapters 3 and 4, the results of the study of C-H and C-Cl activation by rhenium phosphite complexes are presented. Chapter 5 deals with the identification and characterisation of products of the photolysis of Cp*Re$(CO)_2$MeR and the mechanisms for the formation of these products. Chapter 6 describes the reaction of TpRe$(CO)_2$(THF) with an arene diazonium ion $[N_2C_6H_4R]^+$ and also describes the synthesis and characterisation of a new pyrazolylborate rhenium nitrosyl complex and its reactivity with different nucheophiles.

Previously in our laboratory, the reaction of the trimethylphosphine complex $Cp^{*}Re(CO)_2(PMe_3)$ with halogens X_2 (X = Cl, Br, I) to produce salts of the cations $[Cp^{*}Re(CO)_2(PMe_3)X]^+$ was investigated. The isomers observed for these four-legged piano-stool complex cations depended upon the halogen and the synthetic route used.[24] In Chapter 2, the results of an investigation of the corresponding reactions with the trialkylphosphite complexes $Cp^{*}Re(CO)_2\{P(OR)_3\}$ (R = Me, Et) are presented. In these cases, the chemistry is complicated by the possibility of a Michaelis-Arbuzov-like dealkylation reaction. The nucleophilic anion attacks the phosphite ligand in the cationic complex to give rise to a neutral phosphonate complex $Cp^{*}ReX(CO)_2\{PO(OR)_2\}$. The X-ray structural determination of $Cp^{*}Re(CO)_2\{P(O)(OMe)_2\}I$ (**2.8**) is also included.

In the field of C-H activation, rhodium and iridium complexes have been intensively studied. In Chapter 3, an investigation of the potential ability of rhenium dinitrogen *phosphite* complexes to activate C-H bonds in saturated and unsaturated hydrocarbons under photochemical conditions is reported. The emphasis of this study is to compare the phosphite ligand with PMe_3 to determine the selectivity and the ability of these rhenium complexes to activate hydrocarbons. In this study, cis and trans isomers were observed and the isomerization processes were monitored by ^1H and ^{31}P NMR spectroscopy for the complex $Cp^{*}Re(CO)\{\eta^2\text{-}P(OCH_2CH_2)(OEt)_2\}H$ (**3.7**).

In general, the stabilisation of hydride complexes can be carried out by exchanging hydride for halide by reactions with halogenated solvents. In Chapter 3, it was found that the treatment of the photolysis product with a halogenated solvent did not produce the corresponding phenyl halide complex. As a result, it was of interest to attempt to prepare the expected phenyl halide complexes Cp*Re(CO)(L)PhX by an alternative route in order to assess the relative stability of the complexes.

Therefore, in an attempt to prepare Cp*Re(CO)(L)PhCl, the photochemical reactions of the rhenium dinitrogen complexes Cp*Re(CO)(L)(N_2) (**3.1**-**3.6**) in chlorobenzene were investigated, where L are formally 2-electron donor ligands such as PR_3 or $P(OR)_3$. The reactivity of the product formed in chlorinated solvents is also described in Chapter 4.

In Chapter 5, the photochemical study of the complexes Cp*Re(CO)MeR (R = Me, Ph, *p*-Tolyl) (**5.1**-**5.3**) in hydrocarbons and chlorinated solvent are presented.

Attempts to synthesise pyrazolylborate rhenium aryldiazenido complexes with the general formula $[\{HB(C_3H_3N_2)_3\}Re(CO)(L)(N_2R)]^+$ ($HB(C_3H_3N_2)_3$ = Tp), where L is a 2-electron donor ligand such as CO or PR_3 are described in Chapter 6. In addition, the reaction of $TpRe(CO)_2THF$ (**6.2**) with [NO][BF_4] generated the pyrazolylborate rhenium nitrosyl complex $[TpRe(CO)_2(NO)]^+$ (**6.3**)). This complex is an important precursor for further studies of neutral rhenium nitrosyl complexes. A series of pyrazolylborate rhenium nitrosyl complexes have been synthesised from **6.3**, and the synthesis and characterisation of these complexes is also described in Chapter 6.

CHAPTER 2

Synthesis and Characterization of Cationic Rhenium Halide Phosphite Complexes

2.1. Introduction

In a preceding paper[24] it was demonstrated that the trimethylphosphine complex $Cp^*Re(CO)_2(PMe_3)$ reacts with halogens X_2 (X = Cl, Br, I) in diethyl ether or with $SbCl_5$ in CH_2Cl_2 to produce salts of the cations $[Cp^*Re(CO)_2(PMe_3)X]^+$. The particular isomers observed for these four-legged piano-stool complex cations depended upon the halogen and the synthetic method. Reactions with X_2 directly gave the trans isomers for X = Cl, and Br, but the cis isomer for X = I; for X = Br isomerization from trans to cis occurred in CH_2Cl_2 solution, and the cis isomer for X = Cl was obtained directly by using $SbCl_5$. Here, we report the results of an investigation of corresponding reactions with the trialkylphosphite complexes $Cp^*Re(CO)_2\{P(OR)_3\}$ (R = Me, Et) (Figure 2.1).

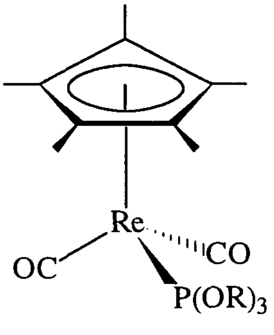


Figure 2.1 Structure of $Cp^*Re(CO)_2P(OR)_3$ (R = Me (**2.1**), Et (**2.2**)).

In these cases the chemistry is complicated by the possibility of a Michaelis-Arbuzov-like dealkylation reaction, whereby the nucleophilic anion attacks the phosphite ligand in the cationic complex to give rise to a neutral phosphonate complex Cp*Re $(CO)_2\{PO(OR)_2\}X$ (R = Me, Et; X = Cl, Br, or I).

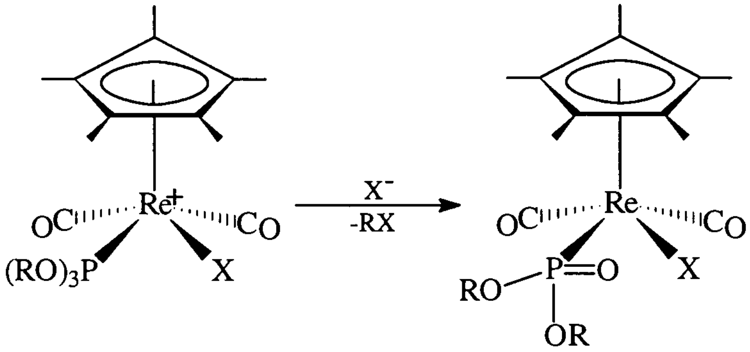


Figure 2.2 Interconversion of $[Cp^*Re(CO)_2\{P(OR)_3\}X]^+$ to $Cp^*Re(CO)_2\{P(O)(OR)_2\}X$ (R = Me, Et; X = Cl, Br, or I).

Cationic halide complexes of the unsubstituted carbonyls $CpRe(CO)_3$ or $Cp^*Re(CO)_3$, e.g., $[Cp^*Re(CO)_3X]^+$, have been known for some time[25-27], and the triphenylphosphite complex $[Cp^*Re(CO)_2\{P(OPh)_3\}I][I_3]$ was recently reported.[28a] A vibrational analysis of the chloro, bromo and iodo dimethylphosphonate complexes $Cp^*Re(CO)_2\{PO(OMe)_2\}X$ (X = Cl, Br, I) described in this paper has already appeared.[28b]

2.2 Results

2.2.1 Synthesis of the Cationic Complexes $[Cp^*Re(CO)_2\{P(OR)_3\}X]^+$

The reaction of a solution of $SbCl_5$ in CH_2Cl_2 with $Cp^*Re(CO)_2\{P(OMe)_3\}$ (**2.1**) in hexane at room temperature gave a yellow precipitate of $[Cp^*Re(CO)_2\{P(OMe)_3\}Cl][SbCl_6]$ (**2.3•SbCl₆**) which was recrystallized from CH_2Cl_2. The $\nu_{(CO)}$ absorptions at 2064, and 2004 s cm^{-1} for **2.3•SbCl₆** in CH_2Cl_2 exhibited an intensity pattern indicative of a trans four-legged piano stool geometry (Figure 2.3) which was supported by the observation of a single $^{13}C\{^1H\}$ NMR carbonyl resonance at δ 192.8 coupled to the cis phosphorus atom with $^2J_{P\text{-}C} = 33.1$ Hz. The ^1H NMR spectrum in acetone-d_6 exhibited the expected resonances at δ 2.19 (Cp*) and 4.18 ($P(OMe)_3$); these were accompanied by much weaker resonances at δ 2.22 (Cp*) and 4.00 ($P(OMe)_3$) attributed to a small amount (less than 15 %) of the cis isomer (Figure 2.4).

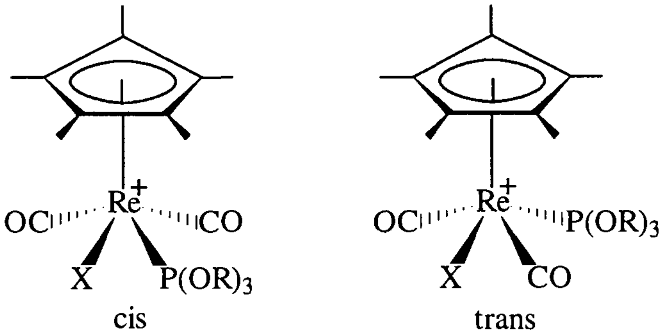


Figure 2.3 Structure of cis and trans isomer of $[Cp^*Re\ (CO)_2\{P(OR)_3\}X]^+$ where R = Me, and Et, X = Cl, Br, and I.

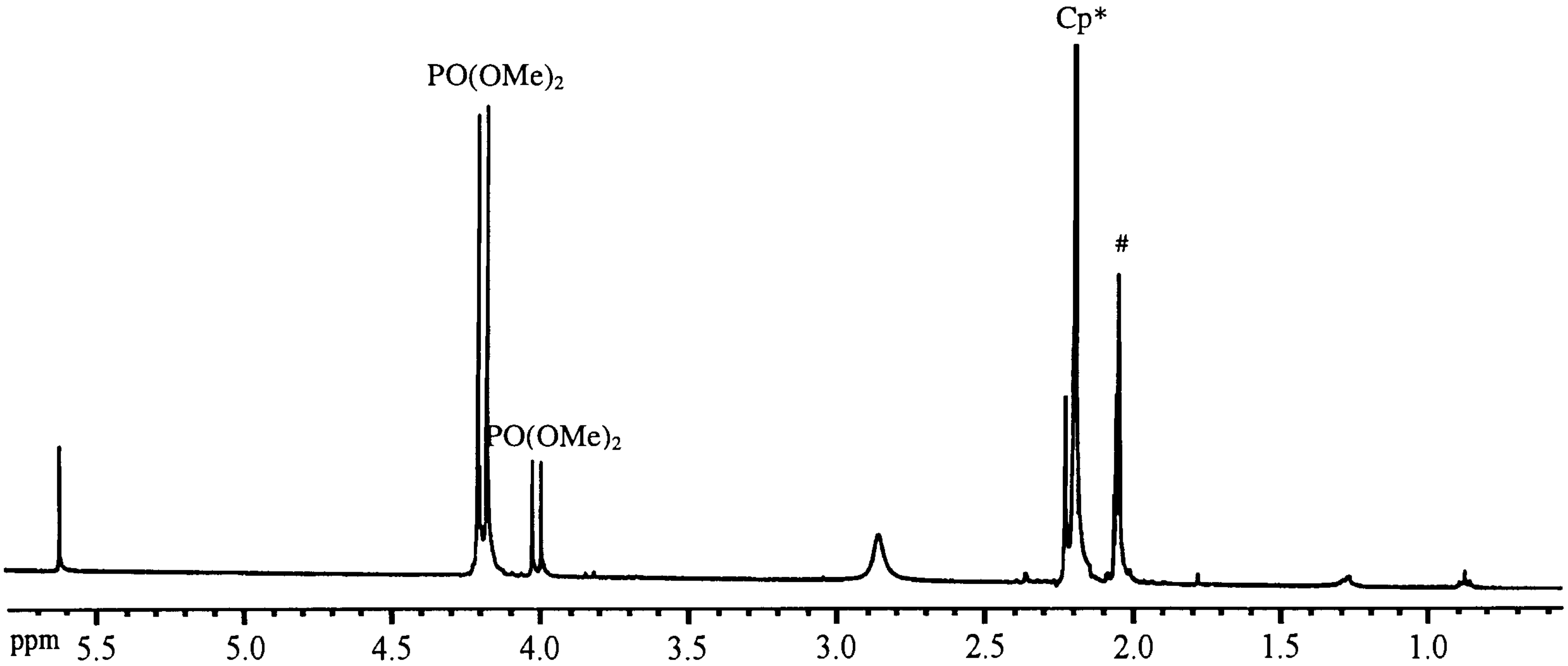


Figure 2.4 ^{1}H NMR spectrum of [Cp*Re(CO)$_2${P(OMe)$_3$}Cl][SbCl$_6$] (**2.3**) in acetone-d_6. # acetone as an impurity

The $^{13}C\{^1H\}$ NMR spectrum exhibited signals for the Cp* and $P(OMe)_3$ carbons for both isomers, but the cis isomer concentration was insufficient for the carbonyl resonances to be detected. The ^{31}P NMR spectrum exhibited a major resonance at δ 92.4 for the trans isomer and a less intense resonance at δ 85.9 for the cis isomer. All of the cationic complexes $[Cp^*Re(CO)_2\{P(OMe)_3\}X]^+$ (X = Cl (**2.3**), Br (**2.4**), I (**2.5**)) and $[Cp^*Re(CO)_2\{P(OEt)_3\}X]^+$ (X = Cl (**2.9**), Br (**2.10**), I (**2.11**)) measured in this study consistently show the ^{31}P NMR resonance of the trans isomer at slightly greater δ value than the cis isomer. Solutions of **2.3•SbCl$_6$** in CH_2Cl_2 or CD_2Cl_2 slowly converted to the phosphonate complex $Cp^*Re(CO)_2\{PO(OMe)_2\}Cl$ (**2.6**) as evidenced by growth of resonances at δ 2.02 (Cp*) and δ 3.72 ($PO(OMe)_2$) in the ^1H NMR spectrum. An overnight $^{13}C\{^1H\}$ NMR spectrum run in CD_2Cl_2 resulted in about equal amounts of the phosphonate **2.6** and the cation **2.3•SbCl$_6$**. However, no conversion of **2.3•SbCl$_6$** to **2.6** was detected by IR in THF even when refluxed for 2 h. Addition of aqueous NaI to a stirred CH_2Cl_2 solution of **2.3•SbCl$_6$** immediately and quantitatively converted it to **2.6**. Notably, the reaction of **2.1** with Cl_2 did not afford the cation **2.3** but resulted in the phosphonate complex **2.6** instead (see below).

The reaction of excess Br_2 or I_2 in THF with **2.1** at 195 K followed by precipitation with hexane resulted in the corresponding salts $[Cp^*Re(CO)_2\{P(OMe)_3\}Br][Br_3]$ (**2.4•Br$_3$**) and $[Cp^*Re(CO)_2\{P(OMe)_3\}I][I_3]$ (**2.5•I$_3$**) as yellow-orange and orange solids respectively. Compound **2.4•Br$_3$** was observed to have $\nu_{(CO)}$ bands at 2052 (m), 1990 (s) cm^{-1} in THF, with intensities indicative of the ***trans*-2.4** isomer,[25] again supported by the single ^{13}CO resonance at δ 190.5 ($^2J_{P-C}$ = 33.7 Hz). In this case only very weak (ca. 4 %) resonances attributable to the ***cis*-2.4** isomer could be detected in the ^{1}H NMR spectrum at δ 2.26 (Cp*) and 3.90 (P(OMe)$_3$). For the iodo compound (**2.5•I$_3$**), however, the IR spectrum exhibited $\nu_{(CO)}$ absorptions at 2047 (s), 1989 (s) cm^{-1} having near equal intensities suggesting a mixture of both isomers ***cis*-** and ***trans*-2.5**. The Cp* methyl ^{1}H NMR resonances for these two isomers were almost coincident at δ 2.38 but there were two well separated doublets for the P(OMe)$_3$ protons of each isomer at δ 3.88 ($^3J_{P\text{-}H}$ = 12.1 Hz) and 4.05 ($^3J_{P\text{-}H}$ = 12.1 Hz) assigned to the cis and trans isomers respectively in 4:1 ratio. The ^{31}P NMR spectrum exhibited a resonance at δ 81.8 assigned to the cis isomer which was more intense that the one at δ 91.3 for the trans isomer (Figure 2.5). The ^{1}H NMR spectrum of the mixture of isomers of (**2.5•I$_3$**) in acetone-d_6 was measured over the temperature range 313-233 K and the reverse to test for thermodynamic equilibrium. At 298 K the ratio cis:trans was 1:4, and the proportion of trans isomer decreased further with decrease in temperature (e.g., cis:trans = 1:1.8 at 233 K) and returned to 1:4 at 298 K showing the system to be at equilibrium at this temperature. The rate of isomerization was not measured, but was too slow to give any observable spin saturation transfer between the P(OEt)$_3$ methyl signals for the two isomers at 298 K (Table 2.1).

The related triethylphosphite complexes [Cp*Re(CO)$_2${P(OEt)$_3$}X][X$_3$] for X = Br (**2.10•Br$_3$**) and X = I (**2.11•I$_3$**) were synthesized in a similar fashion as orange and dark red crystalline solids respectively. In these cases both trans and cis isomers are present in the isolated products, and the proportions can be easily determined from an inspection of

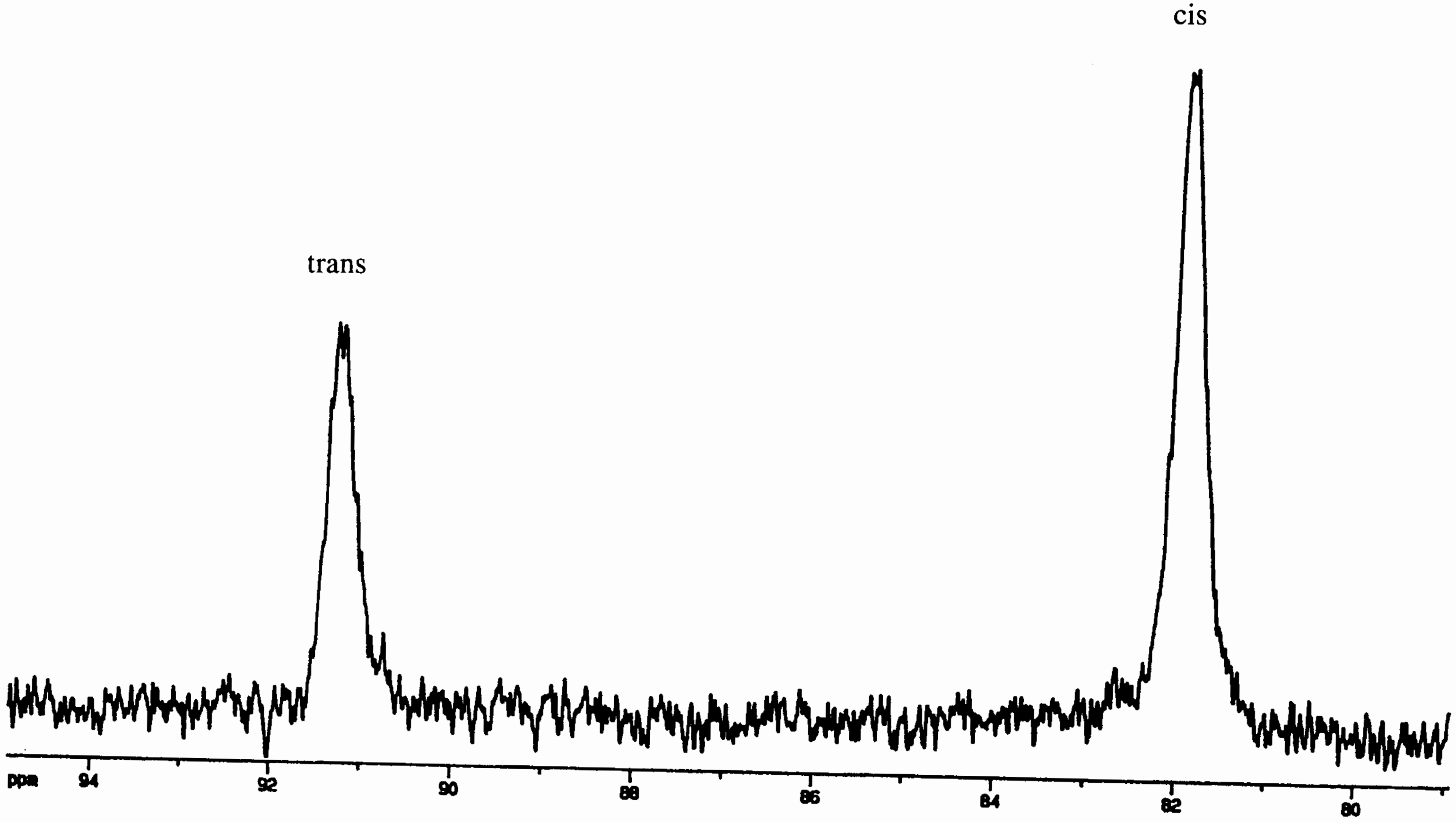


Figure 2.5 ^{31}P NMR of [Cp*Re(CO)$_2${P(OMe)$_3$}I][I$_3$] (**2.5**) in acetone-acetone-d_6.

Table 2.1 Variable temperature ^{1}H NMR data for the isomers produced from the reaction of Cp*Re(CO)$_2${P(OEt)$_3$} (**2.2**) with I$_2$.

T (K)	**^{1}H NMR** [a] **δ CH$_3$** (***cis*-2.5**)	%	δ CH$_3$ (***trans*-2.5**)	%
298	4.04	20	3.88	80
313	4.05	20	3.89	80
298	4.04	20	3.88	80
273	4.04	30	3.87	70
253	4.03	33	3.87	67
233	4.02	35	3.86	63

(a) The ^{1}H NMR spectrum was recorded in CDCl$_3$. The percentages of the isomers were obtained from the intensities of the phosphite resonances.

the methylene proton resonances in the ^{1}H NMR spectrum (Figure 2.6). This is because the methylene protons are equivalent in the trans isomer and give rise to a simple quintet pattern by coupling to the CH$_3$ protons and to phosphorus with identical J = 7.0 Hz, but the methylene protons in the cis isomer are diastereotopic and the pattern at 400.13 MHz appears as a multiplet (an apparent quintet of doublets). The assignment was confirmed in detail for (**2.11•I$_3$**) by appropriate decoupling procedures (Figure 2.6a, 2.6b).

Phosphorus decoupling reduced the δ 4.17 signal to a simple quartet (***trans*-2.11**). Irradiation at δ 4.17 left the δ 4.34 pattern unaffected, confirming that these resonances arise from separate isomers, and it reduced the methyl triplet at δ 1.42 (i.e., the major one) to a singlet, thus confirming the major isomer to be ***cis*-2.11**. Correspondingly irradiation of the methylene signal at δ 4.34 reduced the minor methyl triplet at δ 1.50 (from trans) to a singlet but left the resonances of the cis isomer unaffected. The ratio of cis:trans for **2.11•I$_3$** was determined from the ^{1}H NMR spectrum to be 3:1. The ^{1}H NMR spectrum of the bromo complex **2.10•Br$_3$** exhibits similar features except that here the resonance pattern for the diastereotopic methylene protons is weaker than the methylene resonance for the other isomer, and therefore the cis isomer is the minor one in this case. The ratio of cis:trans for **2.10•Br$_3$** was estimated from ^{1}H NMR intensities to be 1:4. The ^{31}P NMR spectra were in accord with these cis:trans ratios; for example for **2.11•I$_3$** a less intense resonance occurred at δ 83.7 (trans isomer) downfield of a more intense peak at δ 75.9 (cis isomer).

In an interesting contrast with $Cp^*Re(CO)_2\{P(OMe)_3\}$ (**2.1**) the reaction of the triethylphosphite complex $Cp^*Re(CO)_2\{P(OEt)_3\}$ with either $SbCl_5$ or Cl_2 gave in both cases the cation $[Cp^*Re(CO)_2\{P(OEt)_3\}Cl]^+$ (**2.9**) whereas the reaction of Cl_2 with **2.1** afforded only the phosphonate complex **2.3**.

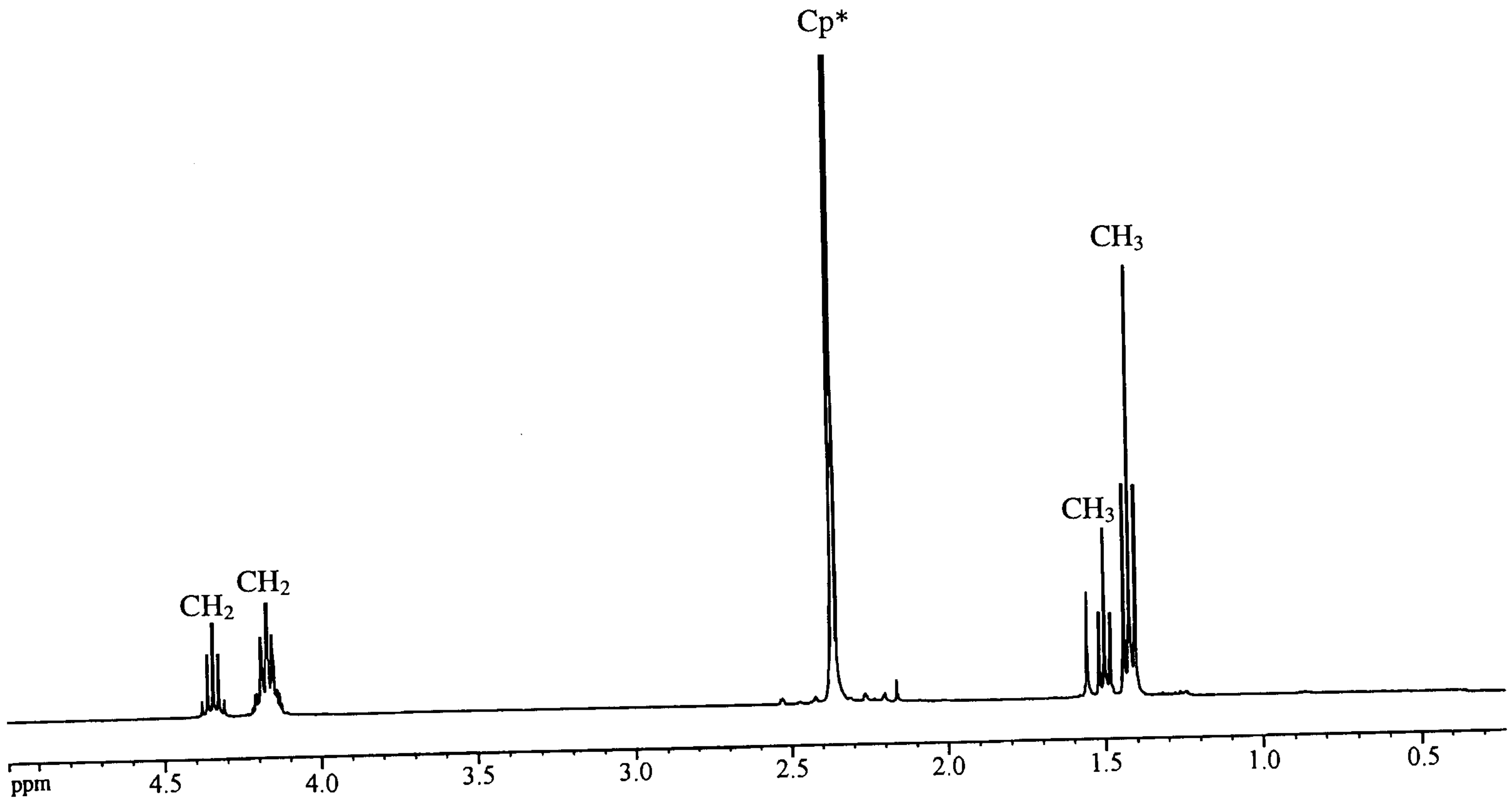


Figure 2.6 ^{1}H NMR spectrum of [Cp*Re(CO)$_2${P(OEt)$_3$}I][I$_3$] (**2.11**) in CDCl$_3$.

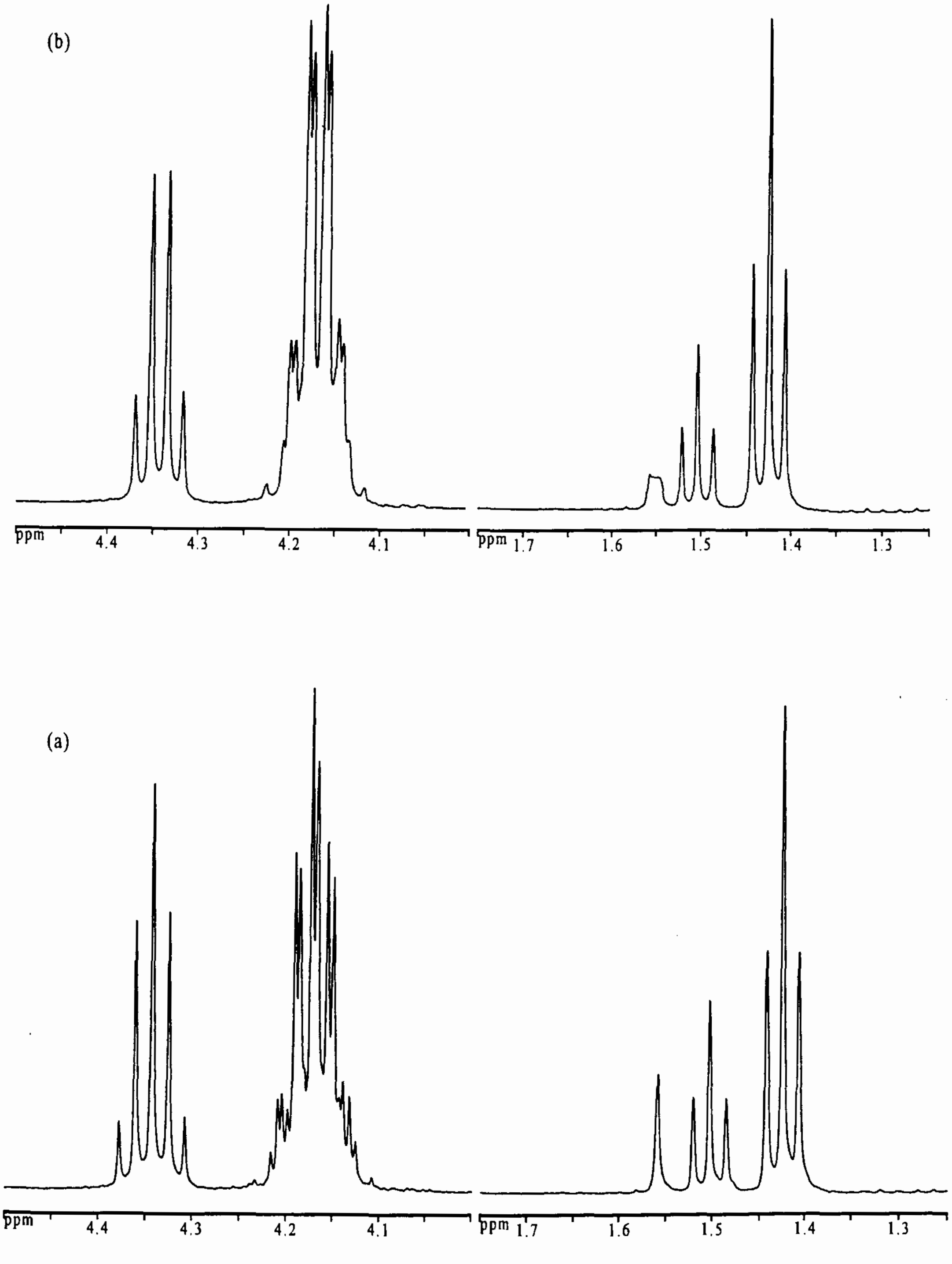


Figure 2.6a Expanded region of the Figure 2.6 (a) ^{1}H NMR spectra of the methyl and methylene region (b) ^{1}H NMR spectrum with ^{31}P decoupled.

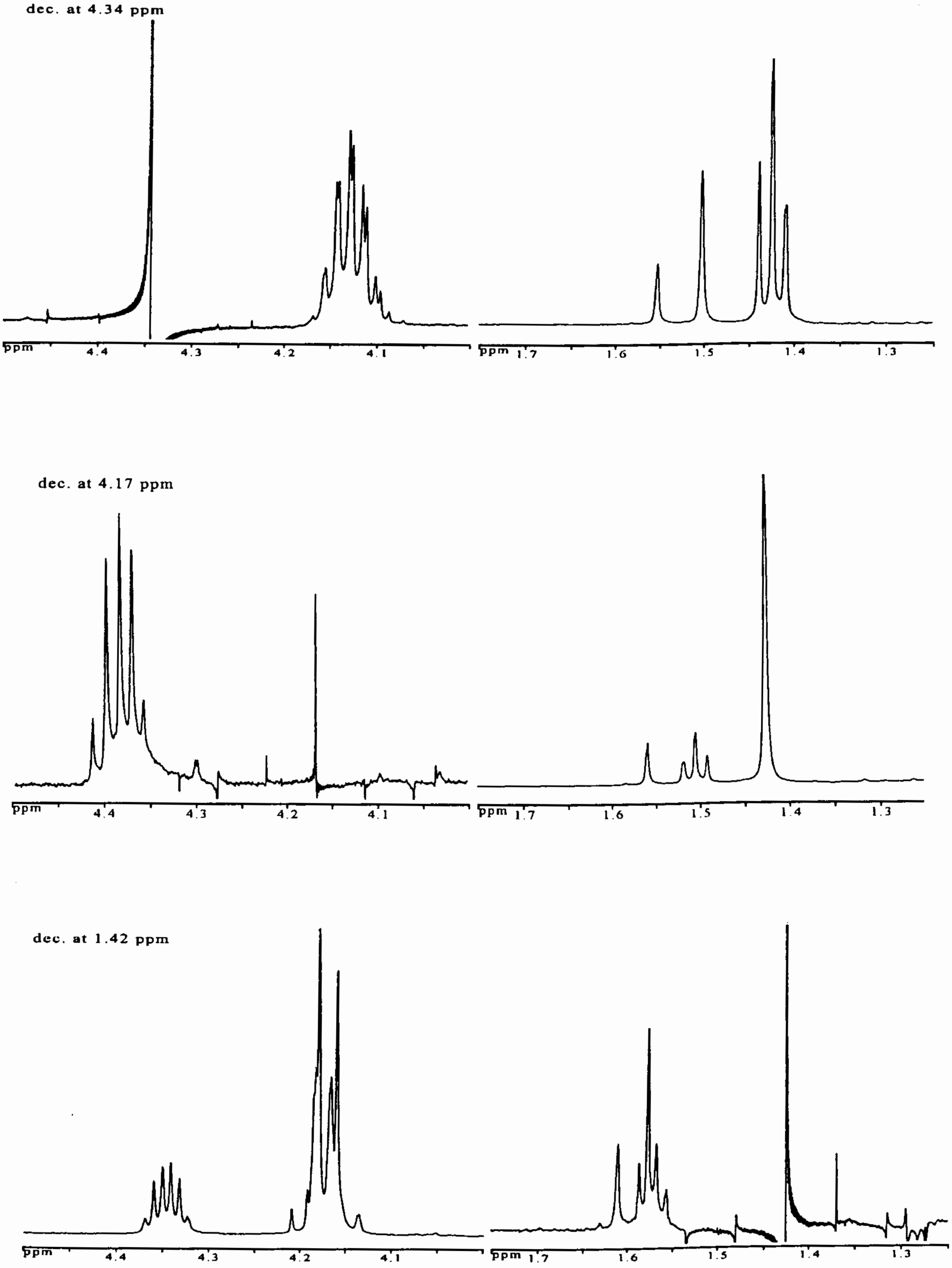


Figure 2.6b Decoupled experiment for the Complex **3.11** in $CDCl_3$

2.2.2 Synthesis of Dialkylphosphonate Complexes Cp*Re(CO)$_2${PO(OR)$_2$}X.

The reaction of Cp*Re(CO)$_2${P(OMe)$_3$} (**2.1**) with Cl_2 in THF at 195 K gave upon work-up a high yield of the trans isomer of the dimethylphosphonate complex Cp*Re(CO)$_2${PO(OMe)$_2$}Cl (**2.6**) as a yellow solid (Figure 2.7). The assignment of the stereochemistry of **2.6** was straightforward from the $\nu_{(CO)}$ intensities and the single CO resonance at δ 195.1 ($^2J_{P\text{-}C}$ = 31 Hz). The corresponding bromo and iodo analogues **2.7** and **2.8** were synthesized as pale yellow crystals by the thermolysis of **2.4•Br$_3$** and (**2.5•I$_3$**) respectively in THF at 333 K for 3h followed by extraction into CH_2Cl_2, chromatography, and recrystallization from hexane. These also were obtained exclusively as the trans isomers. The corresponding diethylphosphonate complexes Cp*Re(CO)$_2${PO(OEt)$_2$}X (X = Br (**2.13**), I (**2.14**)) were obtained as pale yellow solids by treating the triethylphosphite complexes **2.10•Br$_3$** or **2.11•I$_3$** with NaI. Thermolysis at 60°C in THF for 4 h was also carried out for **2.10•Br$_3$** and gave **2.13** as expected by analogy with the trimethylphosphite examples. Again, only the trans isomers were

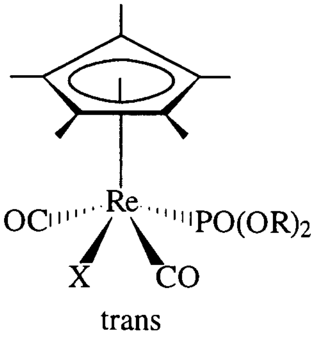


Figure 2.7 Structure for Cp*Re (CO)$_2${PO(OR)$_2$}Cl where R= Me and Et; X = Cl, Br, and I.

obtained for **2.13** and **2.14**. The chloride $Cp^*Re(CO)_2\{PO(OEt)_2\}Cl$ (**2.12**) was prepared similarly, by thermolysis of $[Cp^*Re(CO)_2\{P(OEt)_3\}Cl]^+$ (**2.9**) (prepared from $Cp^*Re(CO)_2\{P(OEt)_3\}$ and Cl_2) at 333 K in THF for 5 h. The ^{31}P NMR spectra of the dialkylphosphonate complexes all exhibit a single resonance consistent with the presence of only the trans isomer in each case. The chemical shift region, ca. 43-51 ppm, is characteristic and readily distinguishes the phosphonate from the relatively more deshielded resonances of the parent cationic trialkylphosphite complexes.

2.2.3 X-Ray Structure Determination of $Cp^*Re(CO)_2\{PO(OMe)_2\}I$ (2.8)

The structure determination of complex $Cp^*Re(CO)_2\{PO(OMe)_2\}I$ (**2.8**) was kindly carried out by Dr. F. W. B. Einstein and Dr. C. E. F. Rickard, and confirmed the composition indicated by the spectroscopic data and demonstrated that the complex **2.8** showed a trans stereochemistry

The molecular structure of $Cp^*Re(CO)_2\{PO(OMe)_2\}I$ (***trans*-2.8**) is illustrated in Figure 2.8, and the selected intramolecular distances and angles are listed in Table 2.2.

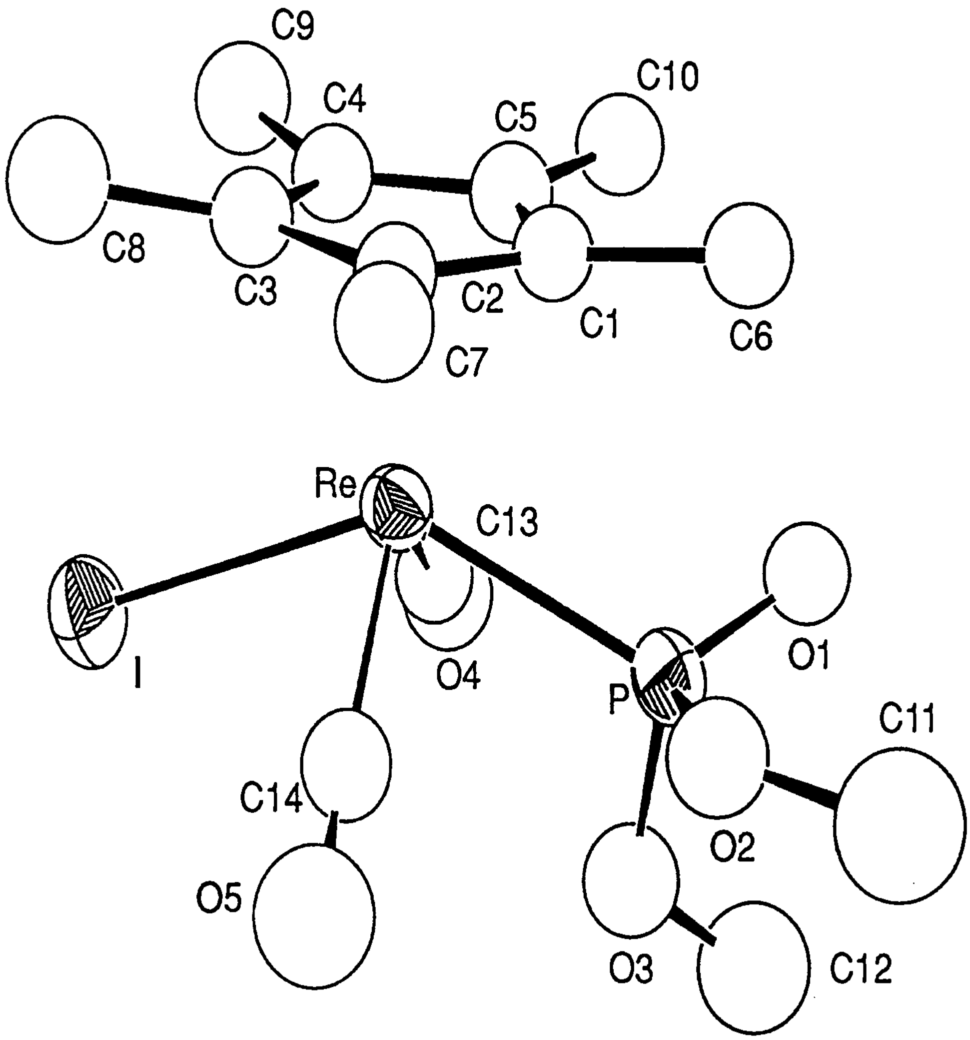


Figure 2.8 The structure of Cp*Re(CO)$_2${PO(OMe)$_2$}I (**2.8**).

Table 2.2 Selected intramolecular distance (Å) and angles (°) for $Cp^*Re(CO)_2\{PO(OMe)_2\}I$.

Distances(Å)		Distances (Å)	
Re - I	2.7942(17)	P - O(3)	1.607(15)
Re - P	2.417(5)	C(13) - O(4)	1.17(3)
Re - C(13)	1.899(21)	C(14) - O(5)	1.13(3)
Re - C(14)	1.936(22)	O(2) - C(11)	1.40(3)
P - O(1)	1.471(14)	O(3) - C(12)	1.42(3)
P - O(2)	1.600(15)		
Angles (°)		**Angles (°)**	
I - Re - P	134.29(13)	I - Re- C(13)	77.1(6)
C(13) - Re - C(14)	106.9(8)	I -Re - C(14)	75.7(6)
P - Re - C(13)	75.9(6)		
P - Re - C(14)	77.6(6)		

2.2.4 Reversible Formation of the Cationic Phosphite and Neutral Phosphonate Complexes.

When Cp*Re(CO)$_2${P(OMe)$_3$} (**2.1**) was reacted with *one* equivalent of Br$_2$ at 198 K in THF the solution obtained did not contain the trimethylphosphite complex cation [Cp*Re(CO)$_2${P(OMe)$_3$}Br]$^+$ (**2.4**), but was a mixture of the phosphonate complex Cp*Re(CO)$_2${P(O)(OMe)$_2$}Br (**2.7**) and unreacted **2.1**. Addition of a *second* equivalent of Br$_2$ converted the remaining **2.1** to the phosphonate complex **2.7** and the spectrum now indicated also the presence of a small amount of the trimethylphosphite complex cation **2.4**. Addition of a *third* equivalent of Br$_2$ resulted in disappearance of most of the phosphonate complex **2.7** in favor of the cationic trimethylphosphite complex **2.4** (Figure 2.9). In order to probe in more detail the competing reactions that give rise to this behavior some further reactions were carried out. When the phosphonate **2.7** was treated with CH$_3$Br gas in THF there was no evidence of a change in the IR spectrum. However, addition of MeBr and Br$_2$ to **2.7** resulted in formation of the trimethylphosphite complex cation **2.4** as the only rhenium product. When the isolated Br salt of the trimethylphosphite complex **2.4** i.e., (**2.4•Br$_3$**) was dissolved in CH$_2$Cl$_2$ at room temperature the IR spectrum showed, within 15 min, the appearance of absorptions resulting from the phosphonate complex **2.7** and this could be completely reversed by the addition of Br$_2$ to the solution (Figure 2.10). Exactly similar behavior was observed for the bromo diethylphosphonate complex Cp*Re(CO)$_2${P(O)(OEt)$_2$}Br (**2.13**). Addition of EtBr and Br$_2$ converted this quantitatively to the cationic complex [Cp*Re(CO)$_2${P(OEt)$_3$}Br]$^+$ (**2.10**).

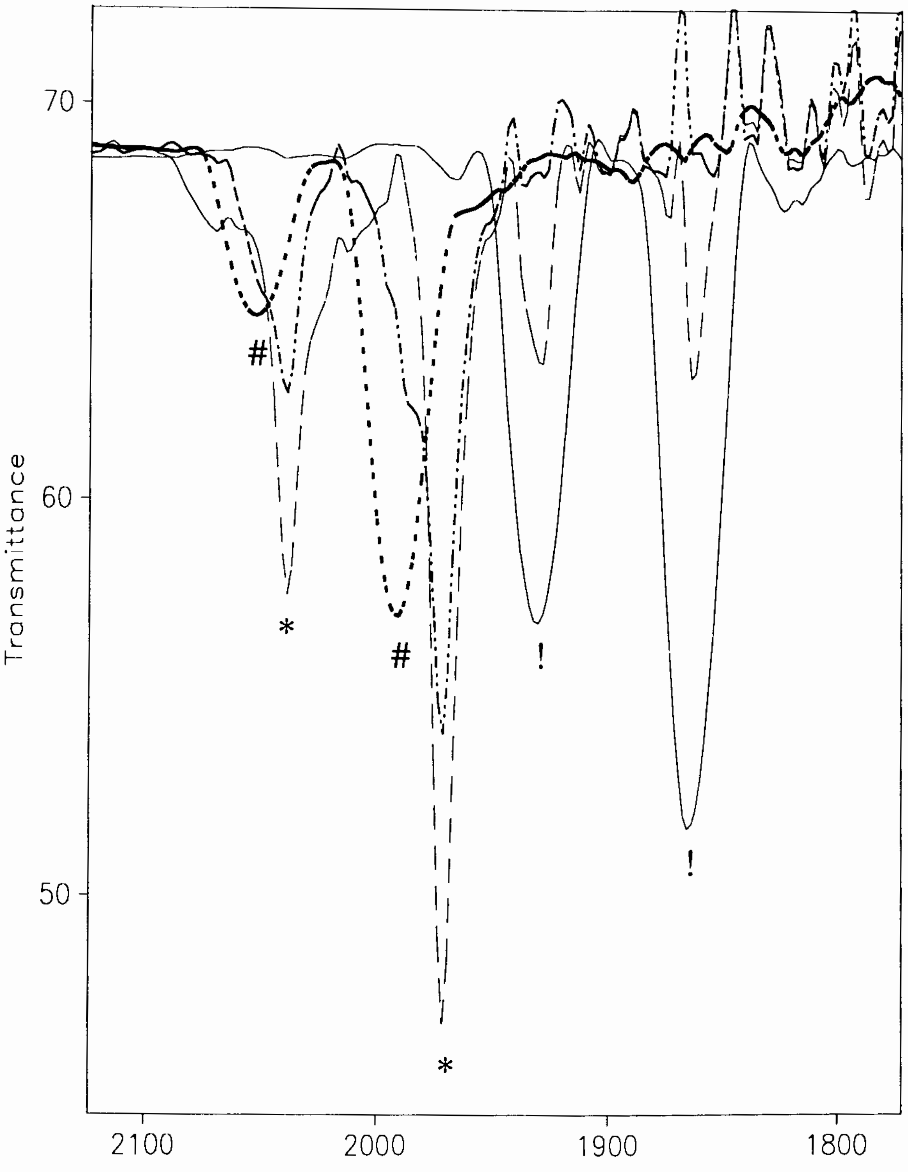


Figure 2.9 IR spectra of the reaction of Cp*Re(CO)$_2${P(OMe)$_3$} (**2.1**) with Br_2 at 194 K in THF. ! Cp*Re(CO)$_2${P(OMe)$_3$} (**2.1**); # [Cp*Re(CO)$_2${P(OMe)$_3$}Br]$^+$ (**2.4**); * Cp*Re(CO)$_2${PO(OMe)$_2$}Br (**2.7**). — **2.1** in THF; –1 equiv of Br_2; - - - 2 equiv Br_2; ···· 3 equiv of Br_2.

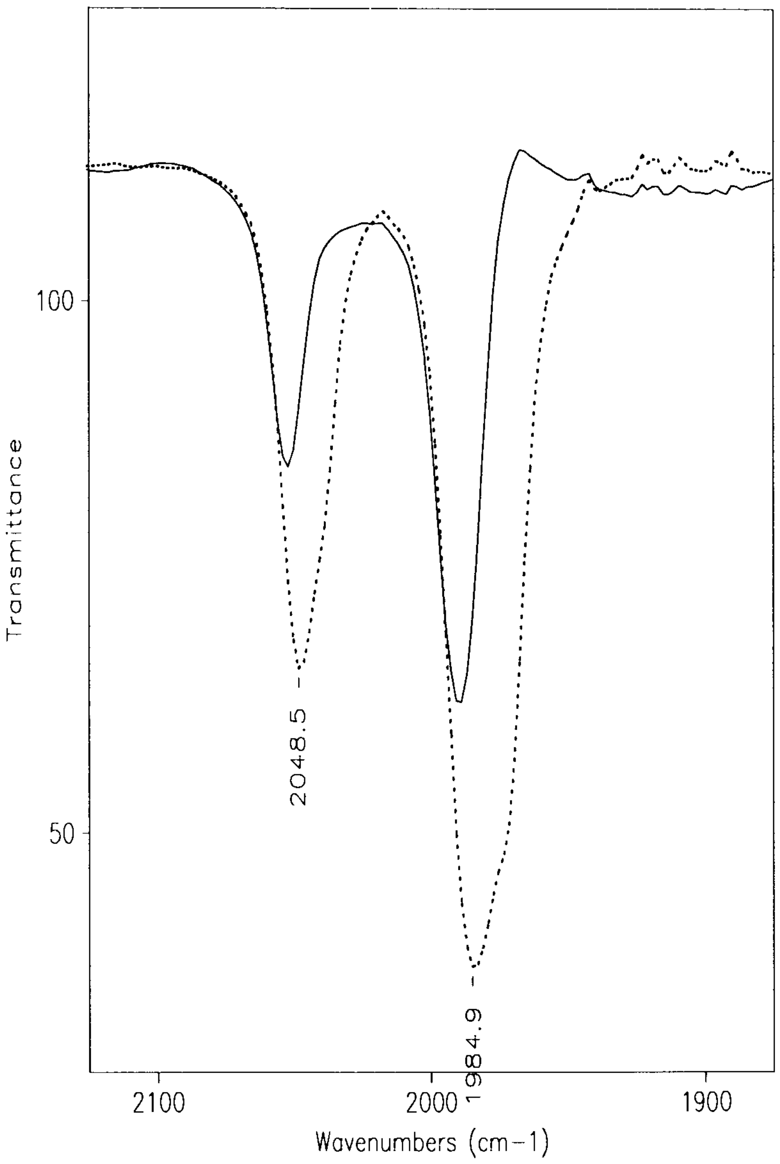


Figure 2.10 — IR spectra of [Cp*Re(CO)$_2${P(OMe)$_3$}Br][Br$_3$] (**2.4**) in CH$_2$Cl$_2$,
···· after 15 min at room temperature

2.3 Discussion

2.3.1 Synthesis and Interconversions of Cationic Phosphite Complexes and Neutral Phosphonate Complexes.

The trialkylphosphite complexes $Cp^*Re(CO)_2\{P(OR)_3\}$ (R = Me, Et) behave similarly to $CpRe(CO)_3$[26,27], $Cp^*Re(CO)_3$[25], $Cp^*Re(CO)_2(PMe)_3)$[24], $Cp^*Re(CO)_2\{P(OPh)_3\}$[28] and $Cp^*Re(CO)_2(PPh_3)$[29] in forming a cationic electrophilic addition product, in this case $[Cp^*Re(CO)_2\{P(OR)_3\}X]^+$, in reactions with X_2 (X = Br, I) or $SbCl_5$. Because of the possibility of subsequent nucleophilic attack by the anion on the trialkylphosphite ligand in a Michaelis-Arbuzov type of reaction[30] to give a dialkylphosphonate ligand (vide infra), the success in isolating these cationic trialkylphosphite complexes is very dependent on the reaction conditions. The use of $SbCl_5$ is very straightforward and both **2.3** and **2.9** precipitate readily and can be recrystallized from CH_2Cl_2 without further reaction because of the low nucleophilicity of the $[SbCl_6]$ counter anion. (Equation 2.1).

$$Cp^*Re(CO)_2\{P(OR)_3\} + 2SbCl_5 \longrightarrow [Cp^*Re(CO)_2\{P(OR)_3\}Cl][SbCl_6] + SbCl_3 \qquad \text{Eq 2.1}$$

By way of comparison, the use of Cl_2 directly, even at 195 K, gives on subsequent isolation a high yield of the dialkylphosphonate complex (i.e., (**2.6**)) in the case of trimethylphosphite (but not triethylphosphite). This we attribute to initial formation of cations **2.3** or **2.9** (Equation 2.2a) and **2.3** then immediately reacts according to the reaction in Equation 2.2b (whereas $Cp^*Re(CO)_2\{PO(OEt)_2\}Cl$ (**2.9**) requires heating) due to the much higher nucleophilicity of the chloride anion (or possibly other anionic chlorine species such as Cl_3^-) now present compared with $[SbCl_6]^-$. It has previously been observed that triethylphosphite ligands are more resistant than trimethylphosphite to dealkylation [30a,31a]

$$\text{(a) } Cp^*Re(CO)_2\{P(OR)_3\} \;+\; Cl_2 \longrightarrow [Cp^*Re(CO)_2\{P(OR)_3\}Cl][Cl]$$

$$\text{(b) } [Cp^*Re(CO)_2\{P(OR)_3\}Cl][Cl] \longrightarrow Cp^*Re(CO)_2\{PO(OR)_2\}Cl] \;+\; RCl \qquad \text{Eq 2.2}$$

In the cases of Br_2 and I_2, however, an excess of these reagents in THF at 195 K followed by precipitation with hexane produced excellent yields of the solid bromo and iodo cationic trialkylphosphite complexes (**2.4**), (**2.10**),(**2.5**) and (**2.11**) as the $[Br_3]^-$ or $[I_3]^-$ salts (Equation 2.3).

$$Cp^*Re(CO)_2\{P(OR)_3\} \xrightarrow[(X = Br \text{ or } I)]{\text{excess } X_2} [Cp^*Re(CO)_2\{P(OR)_3\}X][X_3] \qquad \text{Eq 2.3}$$

Each of these salts is sufficiently stable in THF or $CDCl_3$ solution during short periods of time to enable the IR and ^1H and ^{13}C NMR spectra to be obtained. Over longer periods in solution there is significant conversion to the neutral dialkylphosphonate complexes **2.7**, **2.13**, **2.8** and **2.14**. For example a solution of **2.4•Br₃** in $CDCl_3$ after 1 h exhibited a ^1H NMR spectrum indicating a 1:1:9 approximate ratio of ***trans-***, ***cis*-2.4** and phosphonate **2.7**. This occurs more rapidly at higher temperatures, as expected, giving good yields of these phosphonate complexes as the trans isomers in each case.

Although the reactions with excess X_2 yield the trialkylphosphite complex cations $[Cp^*Re(CO)_2\{P(OMe)_3\}X]^+$ (X = Br (**2.4**), I (**2.5**)), $[Cp^*Re(CO)_2\{P(OEt)_3\}X]^+$ (X = Br

(**2.10**) and I (**2.11**)) it is interesting that following the reaction of **2.1** with Br_2 in 1:1 ratio at room temperature none of the cationic complex **2.4** is observed spectroscopically; rather, there is formed a mixture of unreacted **2.1** with the phosphonate complex **2.7**. Then, addition of a further equivalent of Br_2 consumes all of **2.1** but the product is still substantially **2.7** (with a small amount of the cation **2.4** now observable). Only after a third equivalent of Br_2 is added, is complex **2.4** the major product. This result, and the results of the reactions described above in which the phosphonate **2.7** can be reconverted to the cationic phosphite complex **2.4** only with MeBr and Br_2 together but not by MeBr alone can be understood in terms of the equilibrium between Br^- and $[Br_3]^-$ as given in Equation 2.4,

$$Br^- + Br_2 \rightleftharpoons [Br_3]^- \qquad \text{Eq 2.4}$$

with the assumption that Br^- is sufficiently nucleophilic to rapidly dealkylate the $P(OR)_3$ ligand, but that in $[Br_3]^-$ this tendency is much reduced. Thus, we propose that the first step is formation of the cation **2.4** (Equation 2.5).

$$Cp^*Re(CO)_2\{P(OMe)_3\} + Br_2 \rightleftharpoons [Cp^*Re(CO)_2\{P(OMe)_3\}Br]Br \qquad \text{Eq 2.5}$$

However, in the presence of 1 equiv of Br_2 this does not go to completion and much of **2.1** remains because much of the Br_2 is unavailable for reaction with **2.1** owing to its involvement in complexing with Br^- to give $[Br_3]^-$ as shown in Equation 2.4. We now propose that cation **2.4** is rapidly dealkylated by nucleophilic attack of Br^- (but not by

$[Br_3]^-$) to give the phosphonate **2.7** and MeBr (Equation 2.6) so that at 1:1 ratio of reactants only **2.1** and **2.7** are observed.

$$[Cp^*Re(CO)_2\{P(OMe)_3\}Br]^+ \quad + \quad Br^- \quad \rightleftharpoons \quad Cp^*Re(CO)_2\{PO(OMe)_2\}Br \quad + \quad MeBr \qquad \text{Eq 2.6}$$

Addition of excess Br_2 displaces the equilibrium position in favor of the poorly nucleophilic $[Br_3]^-$ ion and shifts the reaction in favor of the cationic complex **2.4** which can be isolated as the $[Br_3]^-$ salt (Equation 2.3). The addition of MeBr by itself to **2.7** in solution is ineffective in converting **2.7** to **2.4** because of the overwhelming forward reaction due to the strong nucleophilicity of Br^-; but when assisted by Br_2 addition (which consumes Br^- as the weakly nucleophilic $[Br_3]^-$) transformation of **2.7** to **2.4** is observed to be essentially quantitative (see Equation 2.6).

In the case of I_2, addition to $Cp^*Re(CO)_2\{P(OMe)_3\}$ (**2.1**) in 1:1 ratio at 195 K again only consumes about half of **2.1** but the product at this stage is mainly the cation $[Cp^*Re(CO)_2\{P(OMe)_3\}I]^+$ (**2.5**) rather than the phosphonate $Cp^*Re(CO)_2\{P(O)(OMe)_2\}I$ (**2.8**). This is presumably because I^- is virtually completely complexed with further I_2 as $[I_3]^-$ which is not nucleophilic enough to convert **2.5** to the phosphonate **2.8** at a sufficient rate at this temperature. At room temperature eventually all of **2.1** is consumed and the cationic complex disappears in favor of the phosphonate complex **2.8** presumably as a result of the increased rate of dealkylation by $[I_3]^-$ (or I^-) at the higher temperature.

3.3.2 Stereochemistry of Phosphite and Phosphonate Complexes.

The complexes (**2.3-2.14**) are all presumed to adopt the four-legged piano-stool geometry that has been well-established for $CpML_4$ types of complexes[31b]. In the particular case of the phosphonate complex $Cp^*Re(CO)_2\{PO(OMe)_2\}I$ (**2.8**) this has been confirmed by an X-ray crystal structure determination[32]. Furthermore, the structure determination unequivocally showed **2.8** to adopt the trans geometry and this is in agreement with the relative intensities of the $\nu_{(CO)}$ bands in the IR spectrum, where the intensity of the higher wavenumber symmetric stretching mode (ν_{sym}) is weaker than the lower wavenumber antisymmetric stretching mode (ν_{asym}). A similar pattern of intensities is observed for all of the phosphonate complexes (**2.6-2.8** and **2.12-2.14**) and all exhibit a ^{13}CO resonance for equivalent CO groups in the $^{13}C\{^1H\}$ NMR spectrum. Accordingly we are confident that all adopt the trans geometry, and this is the geometry which places the bulky phosphonate and halogens in the least mutually sterically hindered positions.[31a]

In agreement with the compilation of Brill and Landon [30a], we find that the ^{31}P resonances for the phosphonate complexes, in the range 43-51 ppm, are all shifted to smaller δ values compared to the parent cationic trialkylphosphite complexes. However, both occur rather upfield of the tabulated ranges of phosphonate and phosphite complexes quoted in that review.[30a]

The crystal structure of several other phosphonate complexes have been reported, including $CpFe(CO)_2\{PO(OEt)_2\}$[33], $Hg\{PO(OEt)_2\}_2$[34], $HgCl\{PO(OEt)_2\}$[34], $CpCo\{P(OMe)_3\}\{PO(OMe)_2\}_2$[35],$[CpCo(dppe)\{PO(OMe)_2\}]^{+}$[36],$CpCoI\{PPh_2NHCH(Me)Ph\}\{PO(OMe)_2$,[37] $CpCo(C_3F_7)\{PPh_2NHCH(Me)Ph\}\{PO(OMe)_2\}$,[38]

$Cp^*CoI\{PPh_2NHCH(Me)Ph\}\{PO(OMe)_2\}$,[39] $CpCr(CO)_2\{P(OMe)_3\}\{PO(OMe)_2\}$,[40] $Pt\{P(OH)(OMe)_2\}_2\{PO(OMe)_2\}_2$,[41] $ReOCl(OMe)\{PO(OMe)_2\}(PPh_3)_2$,[42] $[(C_6H_6)OsI\{PO(OMe)_2\}_2]^-$, $(C_6H_6)OsI\{PO(OMe)_2\}H$[43] and $[Pt\{P(OMe)_3\}_3\{PO(OMe)_2\}]PF_6$.[44]

While all the phosphonates (**2.6**-**2.8** and **2.12**-**2.14**) are observed to be trans complexes, the stereochemistry of the cationic trialkylphosphite complexes **2.3**-**2.5** and **2.9**-**2.11**) depends on the halogen and particular alkyl group. Complex **2.3•SbCl$_6$** was obtained mainly as the trans isomer, though spectroscopy indicated the presence of about 15 % of the cis isomer also; however **2.3•Cl$_3$** was obtained exclusively as the cis isomer. This contrasts with $Cp^*Re(CO)_2(PMe_3)$, where reaction with $SbCl_5$ was reported to give the cis isomer of $[Cp^*Re(CO)_2(PMe_3)Cl][SbCl_6]$ whereas Cl_2 produced the cation as the trans isomer.[24] In reactions with excess Br_2 , $Cp^*Re(CO)_2\{P(OMe)_3\}$ gave predominantly the trans isomer of **2.10•Br$_3$**, while $Cp^*Re(CO)_2\{P(OEt)_3\}$ gave a mixture of both isomers of **2.10•Cl$_3$**, with the trans:cis ratio about 4:1 in favour of trans. For the iodide **2.5•I$_3$** the ratio is about 4:1 in favour of the cis isomer and for **2.11•I$_3$** it is about 3:1 in favour of cis isomer. Although the results as a whole show no parallel with those for $Cp^*Re(CO)_2(PMe_3)$,[24] it can be noted that, in this case also, formation of the cis isomer was predominant for iodide.

Because of the tendency of these complexes to convert to the phosphonate in solution, we have not undertaken an exhaustive study of the conditions that favour the formation of the particular isomers and have not attempted to isolate pure isomers. It has, however, been established for **2.5•I_3** and **2.11•I_3** that the observed ratio of the isomers in solution at ambient temperature is the thermodynamic equilibrium ratio.

2.4 Conclusion

In this study, we have demonstrated that the rhenium trialkylphosphite complexes $Cp^*Re(CO)_2\{P(OR)_3\}$ readily form the cationic halide derivatives $Cp^*Re(CO)_2\{P(OR)_3\}X]^+$ which are unstable with respect to a Michaelis-Arbuzov-like dealkylation by a sufficiently nucleophilic anion. We have further demonstrated that in this system this is a reversible process, and the resulting neutral dialkylphosphonate complex $Cp^*Re(CO)_2\{PO(OR)_2\}Br$ may be completely reconverted to the cationic complex by the addition of, for example, alkyl bromide and Br_2 together, because the $[Br_3]^-$ anion thus generated is too weakly nucleophilic to effect the dealkylation reaction.

2.5 Experimental Section

2.5.1 General Methods

All reactions were carried out under an atmosphere of nitrogen using Schlenk tube techniques. Solvents were dried by conventional methods, distilled under nitrogen and used immediately. Infrared spectra were measured using a Bomem Model Michelson-120 FTIR instrument, usually for solutions in CaF_2 cells. ^1H, ^{13}C and ^{31}P NMR spectra were measured by M. M. Tracey on a Bruker WM-400 instrument at 400.13, 100.16 and 162.0 MHz respectively, and are referenced to $SiMe_4$ (^1H, ^{13}C) and 85 % H_3PO_4 (^{31}P). Mass spectra were obtained by G. Owen using a Hewlett-Packard Model 5985 mass spectrometer utilizing electron-impact (EI) or Xenon fast-atom-bombardment (FAB) techniques. For the latter, the sample was dissolved in *m*-nitrobenzyl alcohol (NOBA). The masses are reported for ^{35}Cl, ^{79}Br and ^{187}Re. Microanalyses were performed by the Simon Fraser University Microanalytical Laboratory. The preparation of $Cp^*Re(CO)_2\{P(OEt)_3\}$(**2.2**) has been reported.[28a]

2.5.2 Syntheses

Preparation of $Cp^*Re(CO)_2\{P(OMe)_3\}$ (2.1). A solution of $Cp^*Re(CO)_3$ (0.30 g, 0.74 mmol.) and $P(OMe)_3$ (0.11 g, 0.89 mmol) in 200 mL of tetrahydrofuran was irradiated in a quartz tube at 273 K for 90 min. During the photolysis a slow flux of N_2 was maintained. After this time, the IR spectrum of the solution showed a 70 % conversion to the trimethyl phosphite complex. Solvent was removed under vacuum and the residual yellow solid was dissolved in hexane and chromatographed on a neutral alumina column prepared in hexane. Elution with hexane-diethyl ether (3:1) eluted only the trimethyl phosphite complex. It was recrystallized from hexane at 279 K to yield the product as white crystals m.p. 114.0 °C (0.25 g, 73%). IR(CH_2Cl_2): $\nu_{(CO)}$ 1929, 1856 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.08 (s, 15H, Cp*), 3.50 (d, 9H, $^3J_{P\text{-}H}$ = 12.2 Hz, $P(OMe)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.6 (s, $C_5\underline{Me_5}$), 51.6 (s, $O\underline{Me}$), 96.6 (s, $\underline{C_5}Me_5$), 203.9 (s, $\underline{C}O$). ^{31}P NMR (acetone/acetone-d_6): δ 142.6. MS (EI): *m/z* 502 (M^+), 471 (M^+-CO-2H). Anal. Calc^d. for $C_{15}H_{24}O_5PRe$: C, 35.85; H, 4.81. Found: C, 35.62; H, 4.70.

Preparation of $[Cp^*Re(CO)_2\{P(OMe)_3\}Cl][SbCl_6]$ ($2.3\bullet SbCl_6$). A solution of $SbCl_5$ (in CH_2Cl_2) was added dropwise to (**2.1**), 0.15g, 0.30 mmol.) in hexane (6 mL), resulting in the immediate formation of a yellow precipitate. The solvent was removed and the solid was washed with hexane (2 x 5 mL). The yellow solid residue was recrystallized from dichloromethane:hexane to yield yellow crystals of the product (0.256g, 98%). IR (CH_2Cl_2): $\nu_{(CO)}$ 2064 (m), 2004 (s) cm^{-1}. ^1H NMR (acetone-d_6): (ratio 6:1 trans:cis), δ (trans isomer) 2.19 (s, 15H, Cp*), 4.18 (d, 9H, $^3J_{P-H}$ = 12.2 Hz, $P(OMe)_3$); δ (cis- isomer) 2.22 (d, 15H, J_{P-H} = 1.3 Hz, Cp*), 4.00 (d, 9H, $^3J_{P-H}$ = 12.0 Hz, $P(OMe)_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ (trans isomer) 10.0 (s, $C_5\underline{Me}_5$), 58.3 (d, $^2J_{P-C}$ = 10 Hz, $O\underline{Me}$), 110.5 (s, $\underline{C}_5Me_5$), 192.8 (d, $^2J_{P-C}$ = 33.1 Hz, $\underline{C}O$). ^{31}P NMR (acetone/acetone-d_6): δ 92.4 (trans isomer), 85.9 (cis isomer). MS (FAB): *m/z* 537 (M^+), 509 (M^+-CO), 477 (M^+-CO-OCH_3). Anal. Calc^d. for $C_{15}H_{24}Cl_7O_5PReSb$: C, 20.67; H, 2.76. Found: C, 22.41; H, 3.01.

Preparation of $[Cp^*Re(CO)_2\{P(OMe)_3\}Br][Br_3]$ ($2.4\bullet Br_3$). A solution of **2.1** (0.20g, 0.40 mmol) in tetrahydrofuran (2 mL) was added dropwise to Br_2 (0.19g, 0.80 mmol) in tetrahydrofuran (1 mL) at -78 °C. The resulting mixture was stirred for 5 min to produce an orange solution. The product was precipitated with hexane. The solvent was removed and the yellow-orange solid was washed with hexane (2 x 5 mL) and then dried under vacuum (0.314g, 96%). IR (THF): $\nu_{(CO)}$ 2052 (m), 1990 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.28 (s, 15H, Cp*), 4.08 (d, 9H, $^3J_{P-H}$ = 12.2 Hz, $P(OMe)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.71 (s, $C_5\underline{Me}_5$), 57.9 (d, $^2J_{P-C}$ = 10 Hz, $O\underline{Me}$), 109.5 (s, $\underline{C}_5Me_5$), 190.5 (d,

${}^{2}J_{P\text{-}C}$ = 33.7 Hz, <u>C</u>O). ^{31}P NMR (acetone/acetone-*d*$_6$): δ 77.6. MS (FAB): *m/z* 581 (M$^+$), 553 (M$^+$-CO), 521 (M$^+$-CO-OCH$_3$). Anal. Calc^d. for $C_{15}H_{24}Br_4O_5PRe$: C, 21.94; H, 2.95. Found: C, 21.39 ; H, 2.96.

Preparation of [Cp*Re(CO)$_2${P(OMe)$_3$}I][I$_3$] (2.5•I$_3$). A solution of (**2.1**) (0.100g, 0.20 mmol) in tetrahydrofuran (2 mL) was added dropwise to I_2 (0.101g, 0.40 mmol) in tetrahydrofuran (1 mL) at -78 °C. The resulting mixture was stirred for 10 minutes to produce a red solution. The product was precipitated with hexane. The solvent was removed and the orange solid was washed with hexane (2 x 4 mL) and then dried under vacuum (0.202g, 99%). IR (CH$_2$Cl$_2$): $\nu_{(CO)}$ 2047 (s), 1989 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$):(ratio 1:4 trans:cis) δ (trans isomer) 2.38 (s, 15H, Cp*), 4.05 (d, 9H, ${}^{2}J_{P\text{-}H}$ = 12.1 Hz, P(OMe)$_3$); δ (cis isomer) 2.37 (s, 15H, Cp*), 3.88 (d, 9H, ${}^{3}J_{H\text{-}H}$ = 12.1 Hz, P(OMe)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ (trans isomer) 11.7 (s, C$_5$<u>Me$_5$</u>), 57.8 (d, ${}^{2}J_{P\text{-}C}$ = 9.6 Hz, OMe), 107.5 (s, <u>C$_5$</u>Me$_5$), 186.7 (d, ${}^{2}J_{P\text{-}C}$ = 33.1 Hz, CO); (cis isomer) 11.6 (s, C$_5$<u>Me$_5$</u>), 58.3 (d, ${}^{2}J_{P\text{-}C}$ = 8.4 Hz, O<u>Me</u>), 107.8 (s, <u>C$_5$</u>Me$_5$), 198.1 (d, ${}^{2}J_{P\text{-}C}$ = 33.1 Hz, <u>C</u>O cis to P), 186.2 (d, ${}^{2}J_{P\text{-}C}$ = 20.7 Hz, <u>C</u>O trans to P). ^{31}P NMR (acetone/acetone-*d*$_6$): δ 91.3 (trans isomer), 81.8 (cis isomer). MS (FAB): *m/z* 629 (M$^+$), 601 (M$^+$-CO), 569 (M$^+$-CO-OCH$_3$). Anal. Calc^d. for $C_{15}H_{24}I_4O_5PRe$: C, 17.85; H, 2.40. Found: C, 17.62; H, 2.67.

Preparation of Cp*Re(CO)$_2${PO(OMe)$_2$}Cl (2.6). A solution of (**2.3**) (0.15g, 0.30 mmol) in tetrahydrofuran (3 mL) was treated with Cl$_2$ gas at -78 °C and the resulting mixture was stirred for 15 minutes. The mixture was allowed to warm to room temperature and the solvent and volatiles were removed under vacuum. The remainder was dissolved in hexane (1 mL) and filtered through a short neutral alumina column. The column was first eluted with hexane (10 mL), then diethyl ether (5 mL) and finally acetone (10 mL); the latter fraction contained the product. After the acetone was removed under vacuum, the yellow solid (2.6) was obtained in 98 % yield. IR (CH_2Cl_2): $\nu_{(CO)}$ 2045, 1973 (s), $\nu_{(P=O)}$ 1182 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.02 (s, 15H, Cp*), 3.72 (d, 6H, $^3J_{P\text{-}H}$ = 11.6 Hz, $PO(OMe)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.6 (s, $C_5\underline{Me}_5$), 52.7 (d, $^2J_{P\text{-}C}$ = 9.0 Hz, OMe), 105.4 (s, $\underline{C}_5Me_5$), 195.1 (d, $^2J_{P\text{-}C}$ = 31 Hz, $\underline{C}O$). ^{31}P NMR (acetone/acetone-d_6): δ 50.7. MS (EI): *m/z* 522 (M^+), 494 (M^+-CO), 466 (M^+-2CO), 388 (M^+-2CO-PO_2CH_3). Anal. Calc^d. for $C_{14}H_{21}ClO_5PRe$: C, 32.18; H, 4.02. Found: C, 32.05; H, 4.10.

Preparation of Cp*Re(CO)$_2${PO(OMe)$_2$}Br (2.7). A solution of **2.4•Br$_3$** (0.10g, 0.12 mmol) in tetrahydrofuran (6 mL) was heated at 60 °C for 3 hours. The solvent was removed under vacuum and the residue was extracted with dichloromethane (2 mL). The product was chromatographed on a neutral alumina column made up in hexane and eluted with acetone. The fraction containing the product was evaporated and the residue was recrystallized from hexane at -4 °C to afford pale yellow crystals (0.06g, 78 %). IR (CH_2Cl_2): $\nu_{(CO)}$ 2041(m), 1971(s), $\nu_{(P=O)}$ 1177 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.09 (s, 15H, Cp*), 3.73 (d, 6H, $^3J_{P\text{-}H}$ = 11.6 Hz, $PO(OMe)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.9 (s, $C_5\underline{Me}_5$), 52.6 (d, $^2J_{P\text{-}C}$ = 9.3 Hz, OMe), 105.4 (s, $\underline{C}_5Me_5$), 193.3 (d, $^2J_{P\text{-}C}$ = 31 Hz, $\underline{C}O$). ^{31}P NMR (acetone/acetone-d_6): δ 48.7. MS (EI), *m/z* 566 (M^+), 538 (M^+-CO), 510 (M^+-2CO), 432 (M^+-2CO-PO_2CH_3). Anal. Calc^d. for $C_{14}H_{21}BrO_5PRe$: C, 29.62; H, 3.71. Found: C, 29.48; H, 3.90.

Preparation of Cp*Re(CO)$_2${PO(OMe)$_2$}I (2.8). This complex was synthesized analogously to **2.7** as a pale yellow crystalline solid in 80 % yield. IR (CH_2Cl_2): $\nu_{(CO)}$ 2031(m), 1964(s), $\nu_{(P=O)}$ 1180 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.20 (s, 15H, Cp*), 3.73 (d, 6H, $^3J_{P\text{-}H}$ = 14.0 Hz, PO(OMe)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.5 (s, $C_5\underline{Me_5}$), 52.5 ($\underline{d}$, $^2J_{P\text{-}C}$ = 9 Hz, OMe), 104.2 (s, $\underline{C_5}Me_5$), 190.7 (d, $^2J_{C\text{-}P}$ 30 Hz, $\underline{C}$O). ^{31}P NMR (acetone/acetone-d_6): δ 47.6. MS (EI): *m/z* 614 (M$^+$), 586 (M$^+$-CO), 558 (M$^+$-2CO), 480 (M$^+$-2CO-PO_2CH_3). Anal. Calc^d. for $C_{14}H_{21}IO_5PRe$: C, 27.36; H, 3.42. Found: C, 27.18; H, 3.59.

Preparation of [Cp*Re(CO)$_2${P(OEt)$_3$}Cl][SbCl$_6$] (2.9•SbCl$_6$) A solution of $SbCl_5$ (in CH_2Cl_2) was added dropwise to Cp*Re(CO)$_2${P(OEt)$_3$} (**2.2**) (0.20 g, 0.37 mmol) in hexane (4 mL), resulting in the immediate formation of a yellow precipitate. The solvent was removed and the solid was washed with hexane (2 x 4 mL). The yellow solid residue was recrystallized from acetone:ether to yield yellow crystals of the product (0.17 g,78%). IR (CH_2Cl_2): $\nu_{(CO)}$ 2062(m), 2006(s) cm^{-1}. ^{1}H NMR ($CDCl_3$): (ratio 2:1 trans:cis) δ (cis isomer) 1.50 (t, 9H, $^3J_{H\text{-}H}$ = 7.0 Hz, CH_3), 2.15 (s, 15H, Cp*), 4.18 (multiplet, 6 H, CH_2), δ (trans isomer) 1.40 (t, 9H, $^3J_{H\text{-}H}$ = 7.0 Hz, CH_3), 2.10 (s, 15H, Cp*), 4.35 (quintet, 6H, $^3J_{P\text{-}H}$ = $^3J_{H\text{-}H}$ = 7.0 Hz, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ (trans isomer) 10.2 (s, $C_5\underline{Me_5}$), 15.9 (s, $POCH_2\underline{C}H_3$), 67.6 (s, $\underline{C}H_2$), 109.0 (s, $\underline{C_5}Me_5$), 192.3 (d, $^2J_{P\text{-}C}$ 31.0 Hz, $\underline{C}$O). ^{31}P NMR (acetone/acetone-d_6): δ 84.8 (trans isomer), 80.7 (cis isomer). MS (FAB): *m/z* 579 (M$^+$), 551 (M$^+$-CO). Anal. Calc^d. for $C_{18}H_{30}Cl_7O_5PReSb$: C, 29.72; H, 4.16. Found: C, 25.32; H, 3.44.

Preparation of [Cp*Re(CO)$_2${P(OEt)$_3$}Cl][Cl$_3$] (2.9•Cl$_3$) A solution of Cp*Re(CO)$_2${P(OEt)$_3$} (**2.2**) (0.05g, 0.09 mmol) in hexane (4 mL) was treated with Cl_2 gas at -78 ^{O}C. There was immediate precipitate. The supernatant was removed and the solid was washed with hexane (2 x 5 mL). The product was dried under vacuum (0.04g, 68%). ^{1}H NMR (CDCl$_3$): δ 1.34 (t, 9H, $^3J_{H\text{-}H}$ 7.0 Hz, CH$_3$), 2.05 (s, 15H, Cp*), 4.24 (multiplet, 6 H, CH$_2$). Anal. Calc^d. for $C_{18}H_{30}Cl_4O_5PRe$: C, 31.50; H, 4.38. Found: C, 31.53; H, 4.84.

Preparation of [Cp*Re(CO)$_2${P(OEt)$_3$}Br][Br$_3$] (2.10•Br$_3$). A solution of Cp*Re(CO)$_2${P(OEt)$_3$}(**2.2**) (0.05g, 0.09 mmol) in hexane (30 mL) was added dropwise to Br_2 (0.09g, 0.54 mmol) in hexane (4 mL). There was an immediate precipitate. The supernatant was removed, and the product was washed with hexane (2 x 5 mL). After the hexane was removed the yellow-red residue was recrystallized from dichloromethane:hexane to yield the product as orange crystals (0.07g, 90%). IR(CH$_2$Cl$_2$): $\nu_{(CO)}$ 2056(m), 1993(s) cm^{-1}. ^{1}H NMR (CDCl$_3$): (ratio 4:1 trans:cis) δ (trans isomer) 1.50 (t, 9H, $^3J_{H\text{-}H}$ 7.0 Hz, CH$_3$), 2.23 (s, 15H, Cp*), 4.48 (quintet, 6H, $^3J_{H\text{-}H} = {}^3J_{P\text{-}H} = 7.0$ Hz, CH$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ (trans isomer) 10.6 (s, $C_5\underline{Me}_5$), 16.0 (s, $POCH_2\underline{C}H_3$), 67.4 (s, $\underline{C}H_2$), 108.7 (s, $\underline{C}_5Me_5$), 190.5 (d, $^2J_{C\text{-}P} = 34.1$ Hz, $\underline{C}O$). ^{31}P NMR (acetone/acetone-*d*$_6$): δ 83.5 (trans isomer), 78.4 (cis isomer). MS (FAB): *m/z* 623 (M$^+$), 595 (M$^+$-CO). Anal. Calc^d. for $C_{18}H_{30}Br_4O_5PRe$: C, 25.04; H, 3.47. Found: C, 25.30; H, 3.38.

Preparation of [Cp*Re(CO)$_2${P(OEt)$_3$}I][I$_3$] (2.11•I$_3$). This complex was prepared in a similar manner to (**2.10•Br$_3$**) using I_2 and 0.10 g of Cp*Re(CO)$_2${P(OEt)$_3$}

(**2.2**). The product was obtained as a dark red solid (97 %). IR (CH_2Cl_2): $\nu_{(CO)}$ 2045(s), 1987(s) cm^{-1}. ^{1}H NMR ($CDCl_3$): (ratio 1:3 trans:cis) δ (trans isomer) 1.45 (t, 9H, $^3J_{H-H}$ = 7.0 Hz, CH_3), 2.36 (s, 15H, Cp*), 4.34 (quintet, 6H, $^3J_{H-H}$ = $^3J_{P-H}$ = 7.0 Hz, CH_2); δ (cis isomer) 1.42 (t, 9H, $^3J_{H-H}$ = 7.0 Hz, CH_3), 2.36 (s, 15H, Cp*), 4.17 (multiplet, 6H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (trans isomer) 11.5 (d, $C_5\underline{Me}_5$), 16.28 (s, $POCH_2\underline{C}H_3$), 67.7 (s, $\underline{C}H_2$), 107.2 (s, $\underline{C}_5Me_5$), 187.8 (d, $^2J_{P-C}$ = 34.2 Hz, $\underline{C}O$); δ (cis isomer) 11.5 (s, $C_5\underline{Me}_5$), 15.8 (s, $POCH_2\underline{C}H_3$), 67.6 (s, $\underline{C}H_2$), 107.6 (s, $\underline{C}_5Me_5$), 186.8 (d, $^2J_{P-C}$ 21.0 Hz, $\underline{C}O$); 198.9 (d, $^2J_{P-C}$ = 32.1 Hz, $\underline{C}O$). ^{31}P NMR (acetone/acetone-d_6): δ 83.7 (trans isomer), 75.9 (cis isomer). MS (FAB): *m/z* 671 (M^+), 643 (M^+-CO). Anal. Calc^d. for $C_{18}H_{30}I_4O_5PRe$: C, 20.57; H, 2.86. Found: C, 20.64; H, 2.84.

Preparation of Cp*Re(CO)$_2${PO(OEt)$_2$}Cl (2.12). A solution of (2.9 Cl$_3$) (0.12 g. 0.18 mmol) in THF (6 mL) was heated at 60 ^oC for 5 hours. The solvent was removed under vacuum, and the remainder was extracted in hexane (3 mL). This hexane extract was placed on a neutral alumina column. Elution with acetone removed the product. Evaporation of the solvent resulted in a pale yellow solid (0.05g, 50%).

IR (CH_2Cl_2): $\nu_{(CO)}$ 2045(m), 1973(s), $\nu_{(P=O)}$ 1179 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.29 (t, 6H, $^3J_{H-H}$ = 7.0 Hz, CH_3), 2.02 (s, 15H, Cp*), 4.12 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.6 (s, $C_5\underline{Me}_5$), 16.3 (s, $\underline{C}H_3$), 61.1 (s, $\underline{C}H_2$), 105.8 (s, $\underline{C}_5Me_5$), 197.6 (d, $^2J_{P-C}$ = 31 Hz, $\underline{C}O$). ^{31}P NMR (acetone/acetone-d_6): δ 47.3. MS (EI): *m/z* 550 (M^+), 522 (M^+-CO), 494 (M^+-2CO), 402 (M^+-2CO-PO_2Et). Anal. Calc^d. for $C_{16}H_{25}ClO_5PRe$: C, 34.93; H, 4.55. Found: C, 35.03; H, 4.46.

Preparation of Cp*Re(CO)$_2${PO(OEt)$_2$}Br (2.13). A solution of (2.10 Br$_3$) (0.11g, 0.20mmol) in acetone (20 mL) was treated with NaI (in excess), and the resulting mixture was stirred for 12 h. The solvent was removed under vacuum, and the remainder was dissolved in dichloromethane (2 mL) and filtered through a short Celite column. This dichloromethane extract was placed on a neutral alumina column. Elution with acetone removed the product. Evaporation of the solvent resulted in a pale yellow solid (0.07g, 60%). IR (CH$_2$Cl$_2$): $\nu_{(CO)}$ 2040(m), 1969(s), $\nu_{(P=O)}$ 1181 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.29 (t, 6H, $^3J_{H\text{-}H}$ 7.0 Hz, CH$_3$), 2.08 (s, 15H, Cp*), 4.12 (m, 4H, CH$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 9.9 (s, C$_5\underline{Me_5}$), 16.0 (s, $\underline{C}$H$_3$), 61.6 (s, $\underline{C}$H$_2$), 105.5 (s, $\underline{C_5}$Me$_5$), 193.7 (d, $^2J_{P\text{-}C}$ = 31 Hz, $\underline{C}$O). ^{31}P NMR (acetone/acetone-d_6): δ 45.2. MS (EI): *m/z* 594 (M$^+$), 566 (M$^+$-CO), 538 (M$^+$-2CO), 446 (M$^+$-2CO-PO$_2$Et). Anal. Calc^d. for C$_{16}$H$_{25}$BrO$_5$PRe: C, 32.32; H, 4.21. Found: C, 32.31; H, 4.21.

Preparation of Cp*Re(CO)$_2${PO(OEt)$_2$}I (2.14). This complex was prepared following the same procedure as above, but the solvent was methanol and the complex (2.11 I$_3$) was stirred and refluxed for 22 h. The product was pale yellow and obtained in a 30 % yield. IR (CH$_2$Cl$_2$): $\nu_{(CO)}$ 2031 (m), 1964 (s), $\nu_{(P=O)}$ 1155 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.29 (t, 6H, $^3J_{H\text{-}H}$ 7.0 Hz CH$_3$), 2.20 (s, 15H,Cp*), 4.10 (m, 4H, CH$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 9.9 (s, C$_5\underline{Me_5}$), 16.0 (s, CH$_3$), 61.6 (s, CH$_2$), 105.1 (s, $\underline{C_5}$Me$_5$), 193.7 (d, $^2J_{P\text{-}C}$ = 31 Hz, CO). ^{31}P NMR (acetone/acetone-d_6): δ 43.9. MS (EI): *m/z* 642(M$^+$), 614 (M$^+$-CO), 586 (M$^+$-2CO), 494 (M$^+$-2CO-PO$_2$Et). Anal. Calc^d. for C$_{16}$H$_{25}$IO$_5$PRe: C, 29.91; H, 3.89;. Found: C, 29.87; H, 3.84.

CHAPTER 3

Photochemical Reaction of $Cp^*Re(CO)(L)(N_2)$, ($L = P(OMe)_3, P(OEt)_3, P(OPh)_3$, Pc, PPh_3) with Saturated and Unsaturated Hydrocarbons.

3.1. Introduction

" One '*Holy Grail*' of C-H activation research... is not simply to find new C-H activation reactions but to obtain an understanding of them that will allow the development of reagents capable of *selective* transformations of C-H bonds into more reactive functionalized molecules".[45] This quotation is taken from a 1995 issue of Accounts of Chemical Research devoted to frontiers of chemistry research.

One of the most intriguing goals of homogeneous organometallic chemistry is the ability to promote chemical transformation or functionalization of unreactive materials such as saturated hydrocarbons.[46,47] The most extensive areas studied have been those involving iridium and rhodium complexes. These are capable of intermolecular oxidative-addition of C-H bonds in saturated hydrocarbons, leading to stable hydrido-alkyl metal complexes (Equation 3.1).

$$[M] \quad + \quad RH \quad \longrightarrow \quad M(H)(R) \qquad \text{Eq. 3.1}$$

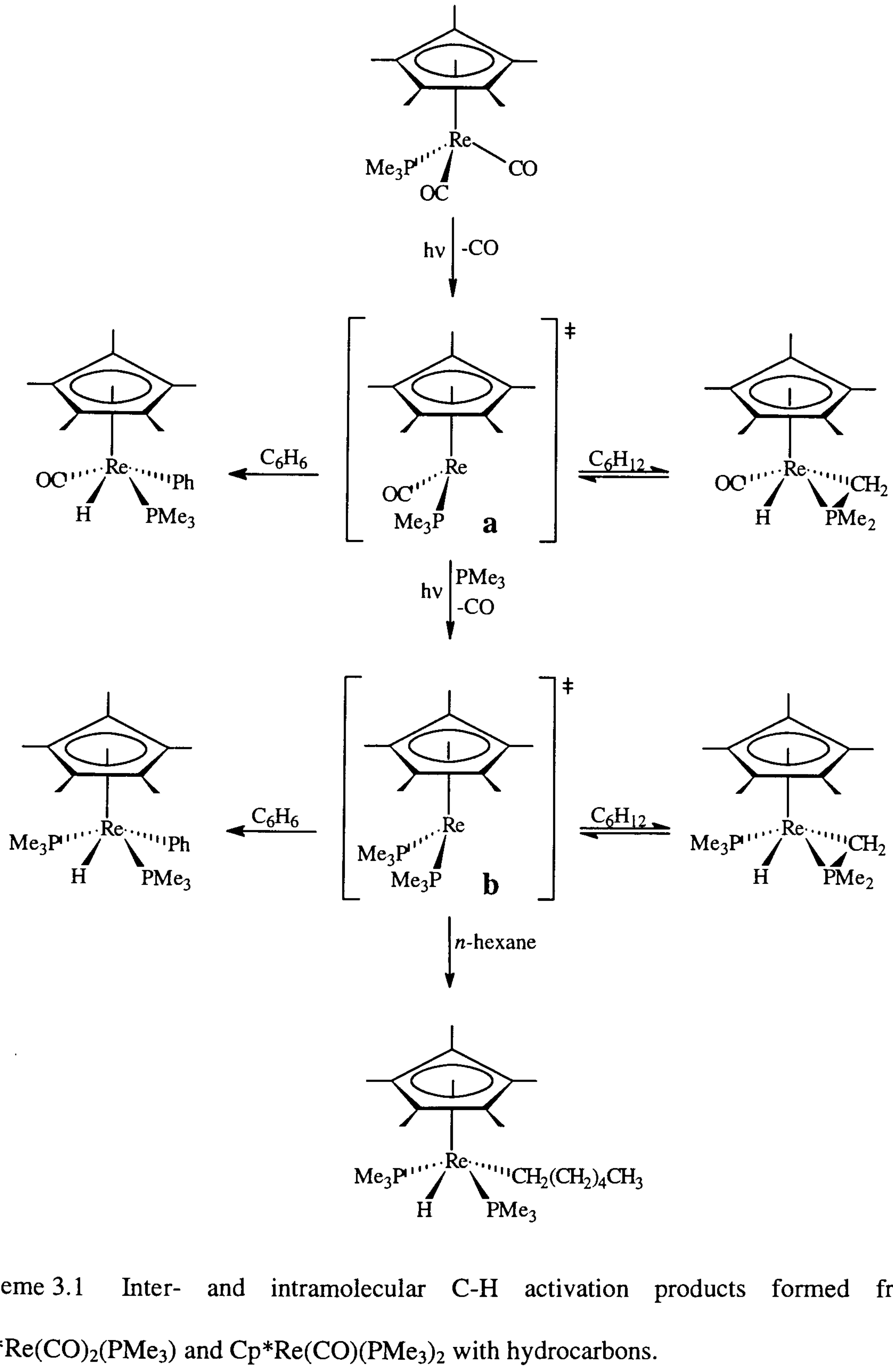
The reactive 16-electron intermediate "[M]" responsible for the activation of the hydrocarbon was created by loss of CO or PMe_3 under photolysis conditions at low temperature.[48,49]

In 1985, Bergman *et al.* reported the first example of oxidative-addition of C-H bonds in the reaction of hydrocarbons with "piano stool" *rhenium* complexes (Scheme 3.1).

It was observed that the unsaturated *bis*-trimethylphosphine intermediate (**b**) was more effective in the intermolecular activation of hydrocarbons than the carbonyl trimethylphosphine analogue (**a**).[50,51]

There is precedence for the N_2 ligand being an attractive alternative as a leaving group for C-H activation studies. The first example of photoextrusion of N_2 from dinitrogen complexes was reported by Darensbourg *et al.* in 1972. They observed that N_2 substitution by CO in Fe, Mo, Re, and Os complexes was facilitated by UV irradiation.[52] Since then, a number of studies have been published involving photochemical reactions of dinitrogen complexes to promote addition[53] or substitution reactions[54] at the metal center. In general, these reactions were carried out in aromatic solvents (e.g., benzene), and the unsaturated fragment generated by the photoextrusion of N_2 apparently either did not react with the solvent,[55] or did not provide an isolable C-H activation product.[56]

Previously, our group has studied the ability of rhenium dinitrogen complexes $Cp^*Re(CO)(L)(N_2)$ (L = PMe_3 and PCy_3) to activate hydrocarbons.[57,58] Under photochemical conditions, it was observed that the rhenium dinitrogen complex loses the N_2 ligand, and the resultant 16-electron intermediate reacts with C-H bonds both in an inter- and intramolecular fashion.



Scheme 3.1 Inter- and intramolecular C-H activation products formed from $Cp^*Re(CO)_2(PMe_3)$ and $Cp^*Re(CO)(PMe_3)_2$ with hydrocarbons.

In that study, it was observed that the irradiation of Cp*Re(CO)(PMe_3)(N_2) in benzene produced the intermolecular C-H activation complex *cis*-Cp*Re(CO)(PMe_3)(Ph)H. However, the reaction of the trimethylphosphine dinitrogen complex in cyclohexane provided only the cyclometalated product *cis*-Cp*Re(CO){η^2-P(CH_2)Me_2}H, while the irradiation of Cp*Re(CO)(PCy_3)(N_2) in cyclohexane *or benzene* gave the orthometalated complex *trans*-Cp*Re(CO){η^2-P(C_6H_{10})Cy_2}H (Figure 3.1) as the only product.[58]

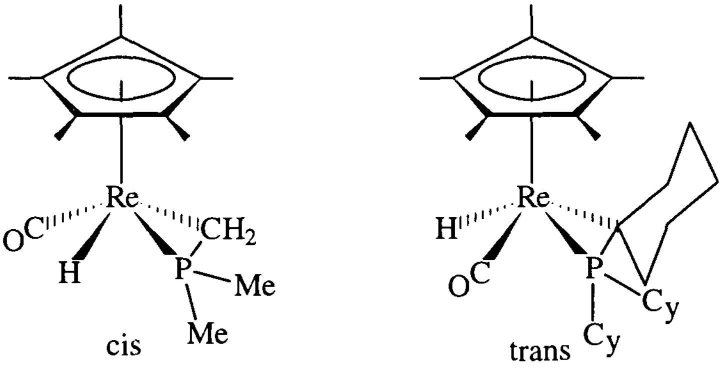


Figure 3.1 Structure of the cyclometalated complexes *cis*-Cp*Re(CO){η^2-P(CH_2)Me_2}H and *trans*-Cp*Re(CO){η^2-P(C_6H_{10})Cy_2}H.

In this chapter, we describe an investigation of the potential ability of rhenium dinitrogen *phosphite* complexes (Figure 3.2) to activate C-H bonds in saturated and unsaturated hydrocarbons under photochemical conditions, with emphasis on comparing the phosphite ligand (a weak σ-donor) with PMe_3 (a strong σ-donor) in determining the selectivity and the ability of these rhenium complexes to activate hydrocarbons.

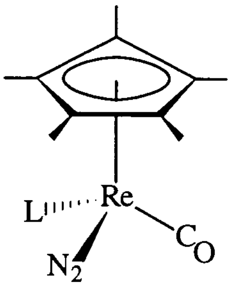


Figure 3.2 Structures of Cp*Re(CO)(L)(N_2) (L =P(OEt)$_3$ (**3.1**), P(OPh)$_3$ (**3.2**), Pc (**3.3**), P(OMe)$_3$ (**3.4**) and PPh$_3$ (**3.5**)).

In this chapter, we will report different isomers present in solution and we would like to clarify the terminology used in this chapter to prevent confusion. The term cis isomer will be used when the *phosphorus* ligand is cis to the *hydride* moiety and the term trans isomer will be used when the *phosphorus* ligand is trans to the *hydride* group (Figure 3.3). Note that this convention is different from that used elsewhere. Generally, the cis stereochemical designation has been used when a carbonyl ligand is cis to the

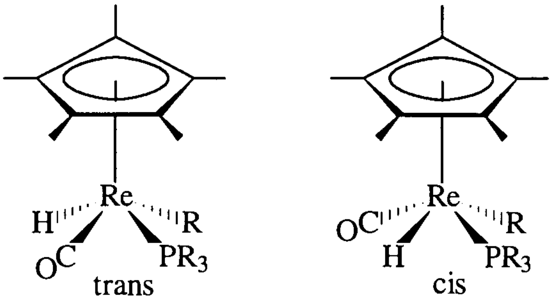


Figure 3.3 Designation of cis and trans stereochemistry in rhenium hydride complexes.

phosphorus group, and trans when the carbonyl is trans to the phosphorus ligand. Now, in our systems both carbonyl and hydride ligands are present, which is why it is important to explain the terminology used.

The term *agostic* will be used in the discussion and this term has been defined by Brookhart *et al.* as a "covalent interaction between carbon-hydrogen groups and transition metal centers in an organometallic compound, in which a hydrogen atom is covalently bonded simultaneously to both a carbon atom and to a transition metal atom".[59]

3.2. Results

3.2.1. Photochemical Reaction of Cp*Re(CO){P(OEt)$_3$}(N$_2$) (3.1) in Hexane.

Photolysis of a hexane solution of Cp*Re(CO){P(OEt)$_3$}(N$_2$) (**3.1**) in a Pyrex vessel for 10 min gave the cyclometalated complexes *trans-* and *cis*-Cp*Re(CO){η^2-P(OCH$_2$CH$_2$)(OEt)$_2$}H (***trans-, cis*-3.7**) resulting from intramolecular C-H activation of an ethyl group in the triethylphosphite ligand (Figure 3.4) plus a third species identified to be the ***agostic*-3.7** (see Figure 3.9).

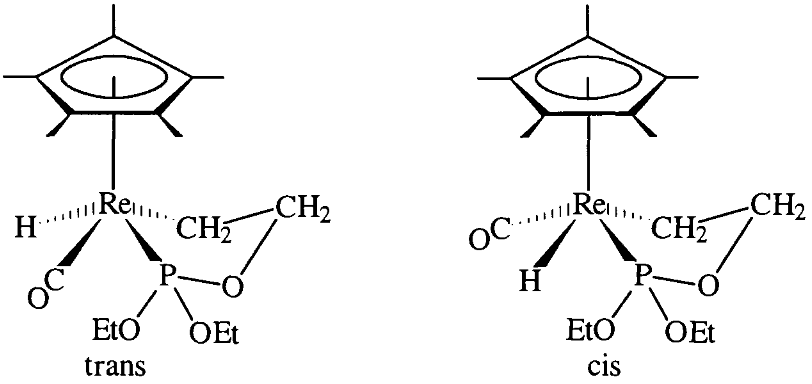


Figure 3.4 Geometry of the trans and cis isomers of **3.7**.

The IR spectrum of the reaction solution after 10 min photolysis showed two carbonyl stretching bands ($\nu_{(CO)}$) at 1898, 1860 cm^{-1}; subsequent work indicated that the band at 1860 cm^{-1} was associated with ***agostic*-3.7** and the one at 1898 cm^{-1} with both ***trans-*** and ***cis*-3.7** (Figure 3.5). The solvent was removed under vacuum with the sample in an ice bath to keep it at 273 K.

The ^1H NMR of the crude photoproduct was then recorded immediately in toluene-d_8 at 273 K. The ^1H NMR spectrum showed the disappearance of **3.1**, and exhibited *three* resonances in the metal hydride region. The major resonance was a doublet at δ -9.82 with a coupling constant of 12.0 Hz. The resonance at δ -10.10 was a doublet with a coupling constant of 28.0 Hz, and further the signal at δ -10.20 was a doublet with a coupling constant of 60.0 Hz. Later, by phosphorus decoupling experiments, these were shown to be $J_{P\text{-}H}$ couplings. Subsequent work indicated that these hydride resonances arise from separate species. The ratio of these species was determined by the relative areas in the hydride region (66:26:7) respectively. The Cp* region showed three resonances at δ 1.93, 1.87 and 1.85. The methyl and methylene regions at δ 1.00-1.50 and δ 2.80-4.30 showed a complicated set of multiplets indicative, at least, of inequivalent triethylphosphite ligands (Figure 3.6).

The presence of metal hydride resonances suggested the formation of C-H activation products. Identification of the major product was done by immediately running a ^1H Homonuclear Chemical-Shift Correlated (COSY) experiment at 273 K on this sample and by variable temperature ^1H NMR (273-313 K), both in toluene-d_8. By following the cross-peak patterns in the COSY spectrum (Figures 3.7-3.8), it was possible

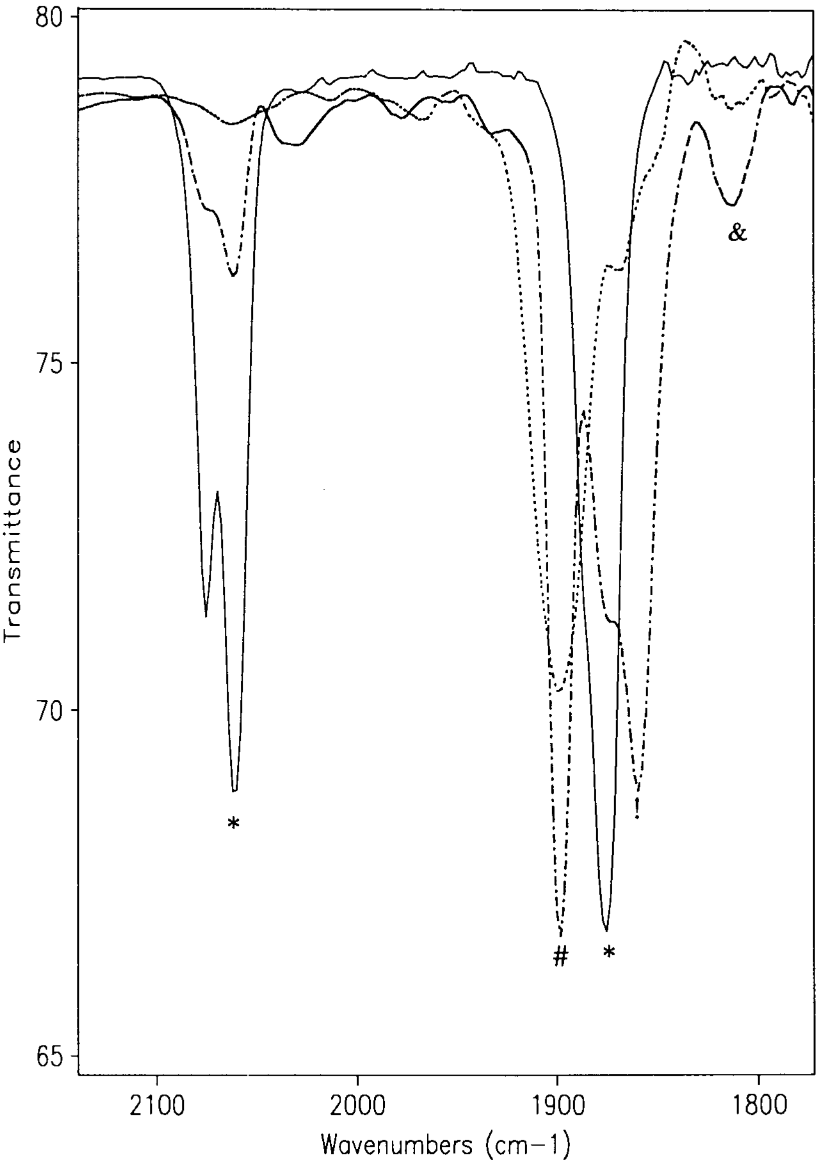


Figure 3.5 IR spectrum (—) before; (– – –) after 6 min; (···) after 12 min, photolysis of **3.1** in hexane. * Cp*Re(CO){P(OEt)$_3$}(N$_2$) (**3.1**); ! ***agostic*-3.7**; # Cp*Re(CO){η^2-P(OCH$_2$CH$_2$)(OEt)$_2$}(H) (**3.7**); & impurity in the cell.

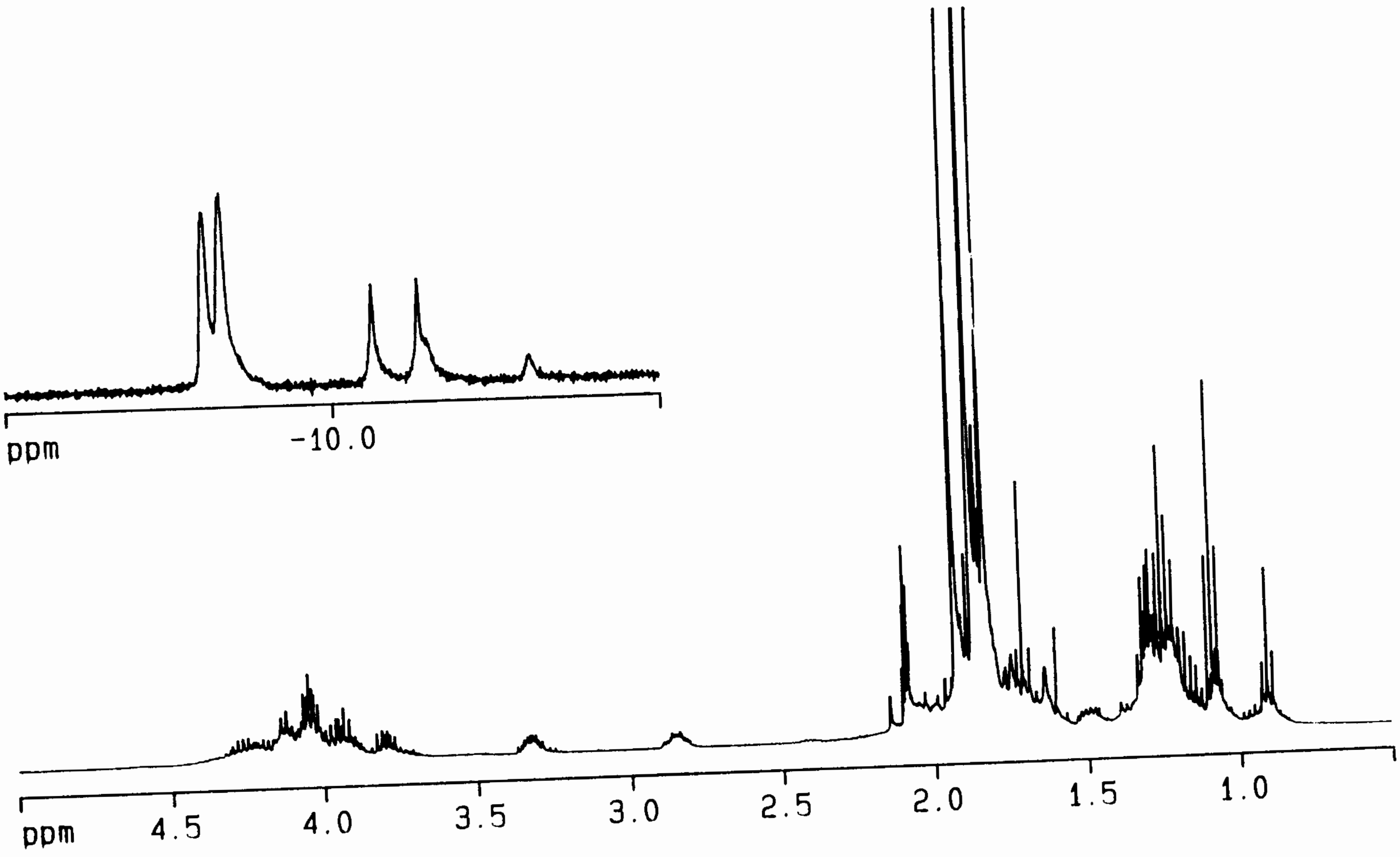


Figure 3.6 ^{1}H NMR spectrum in toluene-d_8 after irradiation of Cp*Re(CO){P(OEt)$_3$}(N$_2$) (**3.1**) in hexane

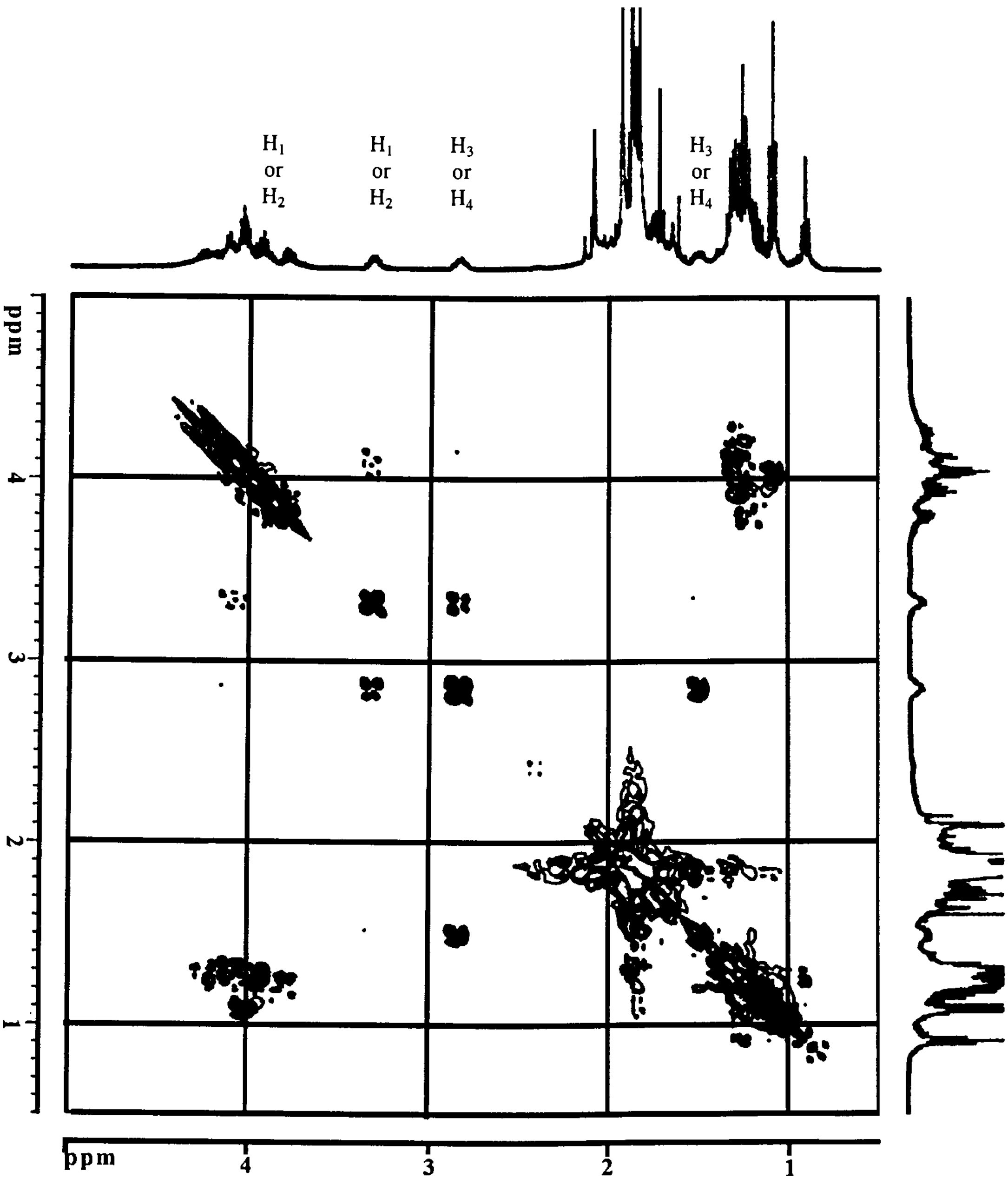


Figure 3.7 COSY spectrum in toluene-d_8 of the crude sample after photolysis of Cp*Re(CO){P(OEt)$_3$}(N_2) (**3.1**) in hexane.

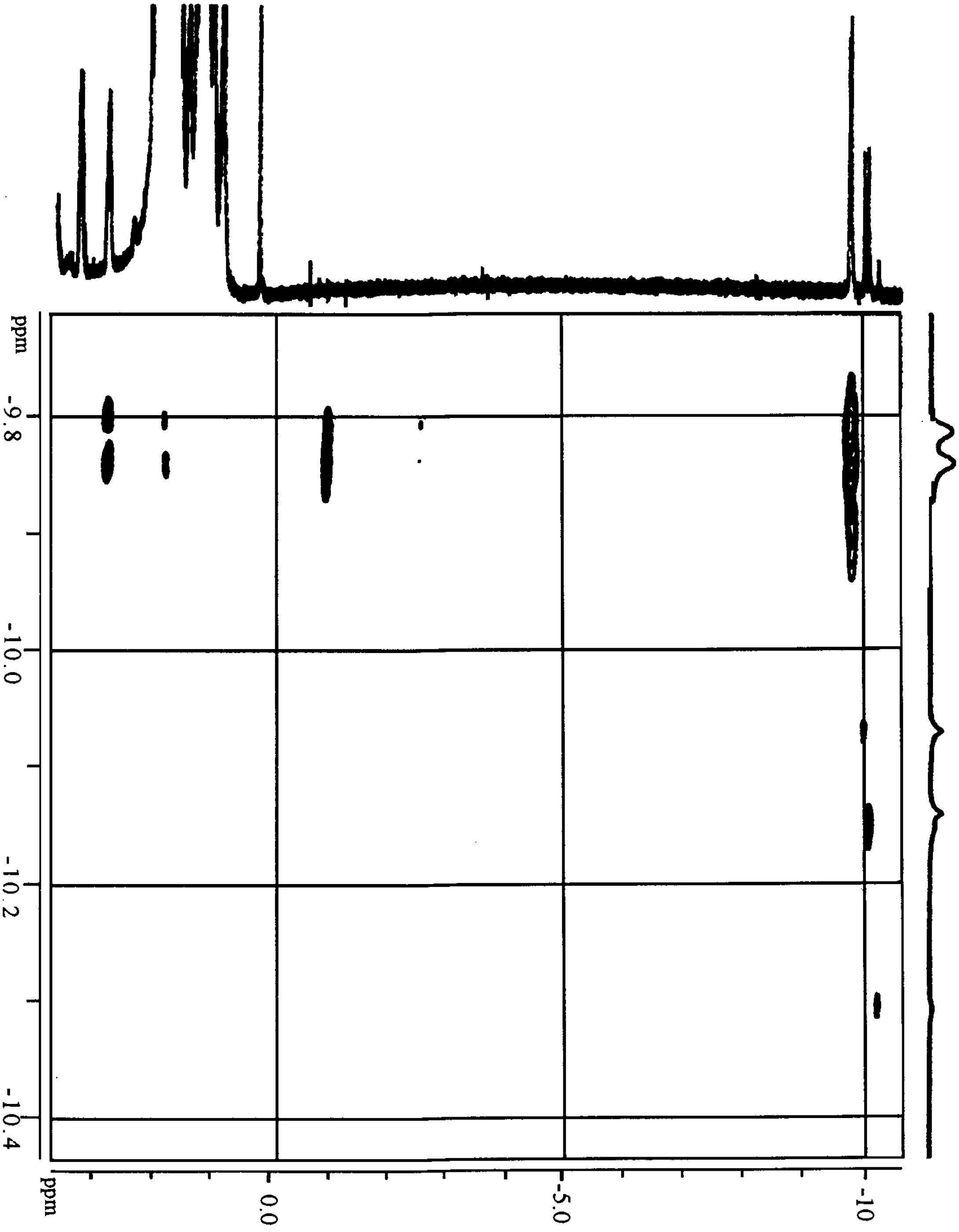


Figure 3.8 Expanded region of the 2D-^{1}H NMR COSY spectrum.

to identify the major species in solution as ***agostic*-3.7**. Fortunately, this complex gave several resonances that were well separated from those of the other isomers. The latter were present in smaller concentration and gave overlapping resonances and were not easily characterized by the COSY at 273 K.

The COSY spectrum exhibited five distinct H atom environments for one of the ethyl groups in the triethylphosphite ligand. This indicates that these protons are chemically inequivalent. The resonances all integrated for one proton respectively and were mutually correlated. One resonance occurs at δ -9.92 and is assigned to the *agostic* hydrogen H_a (Figure 3.9). This is considered to be the same resonance cited in the ^1H NMR spectrum at δ -9.82 in the crude product above. Other resonances at δ 1.49 and δ 2.84 are assigned to H_3 and H_4 (or vice-versa) and those at δ 3.32 and δ 4.05 to H_1 and H_2 (or vice-versa) in this ethyl group. Interestingly, the resonance at δ -9.92 showed cross-peaks to the resonances at δ 1.49 and δ 2.84 (H_3 or H_4); the signal at δ 2.84 showed a stronger interaction compared with the resonance at δ 1.49. The resonances at δ 1.49 and

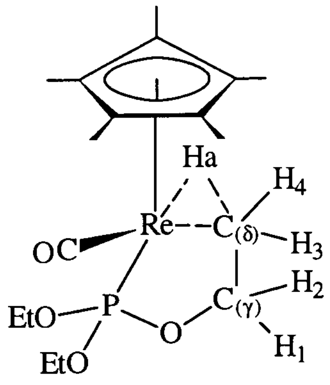


Figure 3.9 Proposed structure for ***agostic*-3.7**.

δ 2.84 are correlated, and δ 2.84 is correlated with the resonance at δ 3.32. Finally, the resonances at δ 3.32 and δ 4.05 (H_1 or H_2) are correlated. Resonances for the remaining two ethoxy groups were assigned as indicated in the Experimental Section. The proposed structure for ***agostic*-3.7**, consistent with all the evidence, is shown in Figure 3.9.

This assignment compares satisfactorily with those made previously for *agostic* ethyl or similar groups in cobalt[60] and molybdenum[61] complexes. As an example, for the complex Cp*Co{P(OMe)$_3$}(C_2H_4)H, the ^{1}H NMR showed a dynamic interconversion of the "ethylene hydride" complex (**a**) and the "*agostic* structure" (**b**) (Figure 3.10). The ^{1}H NMR spectrum at 203 K for the "*agostic* structure" (**b**) showed a multiplet at δ -12.1 (H_b) with $J_{P\text{-}H}$ = 12 Hz; H_1 or H_2 were assigned to multiplets at δ -0.3 and δ -0.2, and H_4 or H_5 were assigned to multiplets at δ 1.9 and δ 2.5.[60c]

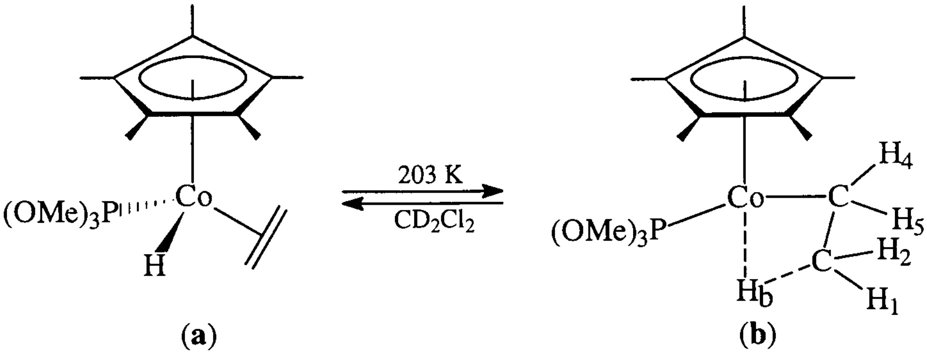


Figure 3.10 Structure for Cp*Co{P(OMe)$_3$}(C_2H_4)H (**a**) in equilibrium with "*agostic* structure" (**b**) at 203 K.

Note that strong evidence for an *agostic* interaction comes from the reduced value of $J_{P\text{-}Ha}$ = 12.0 Hz in the ^{1}H NMR spectrum of ***agostic*-3.7**. This is identical with the value of $J_{P\text{-}H}$ = 12 Hz observed for the *agostic* hydrogen in the above cobalt complex.[60c]

This value can be compared to $J_{P\text{-}H}$ = ~27 Hz when the phosphorus ligand is trans to a true hydride moiety or $J_{P\text{-}H}$ = ~69 Hz when the phosphorus ligand is cis to a true hydride in four legged "piano stool" molybdenum complexes, which serve as a model for $J_{P\text{-}H}$ in *terminal hydride* structures.[62a] Such low $J_{P\text{-}Ha}$ couplings have been observed in other agostic complexes with a phosphine and phosphite ligand and are an indication of a reduced Re-H bond order in the 3-center-2-electron interaction.[60b,63] Note that $J_{P\text{-}H}$ values observed for the hydride resonances at δ -10.10 and δ -10.20 in the present case are 28.0 Hz and 60.0 Hz respectively suggesting these to be the complexes ***trans*-3.7** and ***cis*-3.7**.

The remaining *four* OEt groups in the ***cis*-** and ***trans*-3.7** are inequivalent, leading to the complexity of the methyl and methylene regions in the ^{1}H NMR at 273 K; these resonances appeared as multiplets in the range δ 1.00-1.25 and 3.7-4.3 respectively (see Figure 3.6). Partial assignments were made from relative intensities and coupling patterns where these could be seen.

3.2.1.1 Variable Temperature ^{1}H NMR for *agostic*-3.7 in Toluene-d_8.

The purpose of this experiment was to examine in more detail whether there is isomerization of the *agostic*-, *trans*-, and *cis*-isomers of **3.7**.

First, a ^{1}H NMR spectrum was reacquired at 273 K 1.55 h later (after the COSY experiment) and this showed that a further change in this spectrum had occurred with time while the temperature was constant (Table 3.1). The spectrum was obtained again at 283 K. It showed that the intensity of the resonance at δ -9.83 (H_a) decreased slightly relative to the initial spectrum at 273 K.

The ^{1}H NMR spectra were recorded from 293 K to 303 K over 3.16 h (Figure 3.11), and the ratio of trans and cis isomers continued to change and the ***agostic*-3.7** decreased. When the temperature was increased to 313 K, the signal at δ -9.83 (H_a) disappeared, with the concomitant growth of the cis and trans isomers. The temperature was raised to 323 K and the ratio of the remaining cis and trans isomers was slightly different. The sample was cooled again to 293 K and stored at this temperature and a ^{1}H NMR was recorded after a further 0.63 h. The ratio of both isomers remained the same.

The changes in relative proportions of ***cis*-** and ***trans*-3.7** allowed assignments of the Cp* and ethyl resonances in the phosphite ligand of these isomers. The Cp* resonances for ***trans*-**and ***cis*-3.7** at 293 K were at δ 1.86 and δ 1.85 respectively. The resonances for the methyl groups in the triethylphosphite moiety were at δ 1.08 and δ 1.13 for ***cis*-3.7** and at δ 1.23 and δ 1.27 for ***trans*-3.7,** in each case as a triplet with a coupling constant of 7.0 Hz. The methylene groups in the triethylphosphite moiety were assigned in the region δ 3.65-4.40. Observable resonances corresponding to the cyclometalated ethyl group (η^2-$POCH_2CH_2$) for ***cis*-3.7** were at δ 2.39 (relative integral 1H) and δ 3.40 (relative integral 2H). No specific resonances were distinguishable in the ^{1}H NMR at 293 K for the cyclometalated group in ***trans*-3.7.** The final ratio of the ***trans*-** : ***cis*-3.7** after the variable temperature study was 34:66 (Figure 3.11).

According to the literature, unstable alkyl or aryl hydride complexes can generally be stabilized in the halide form by thermal exchange of the hydride ligand by using halogenated solvents (such as: CH_3Cl, CCl_4, $CHBr_3$) to generate the more stable alkyl or aryl halide complex.[48c,49a] However, we found that the treatment of **3.7** with a

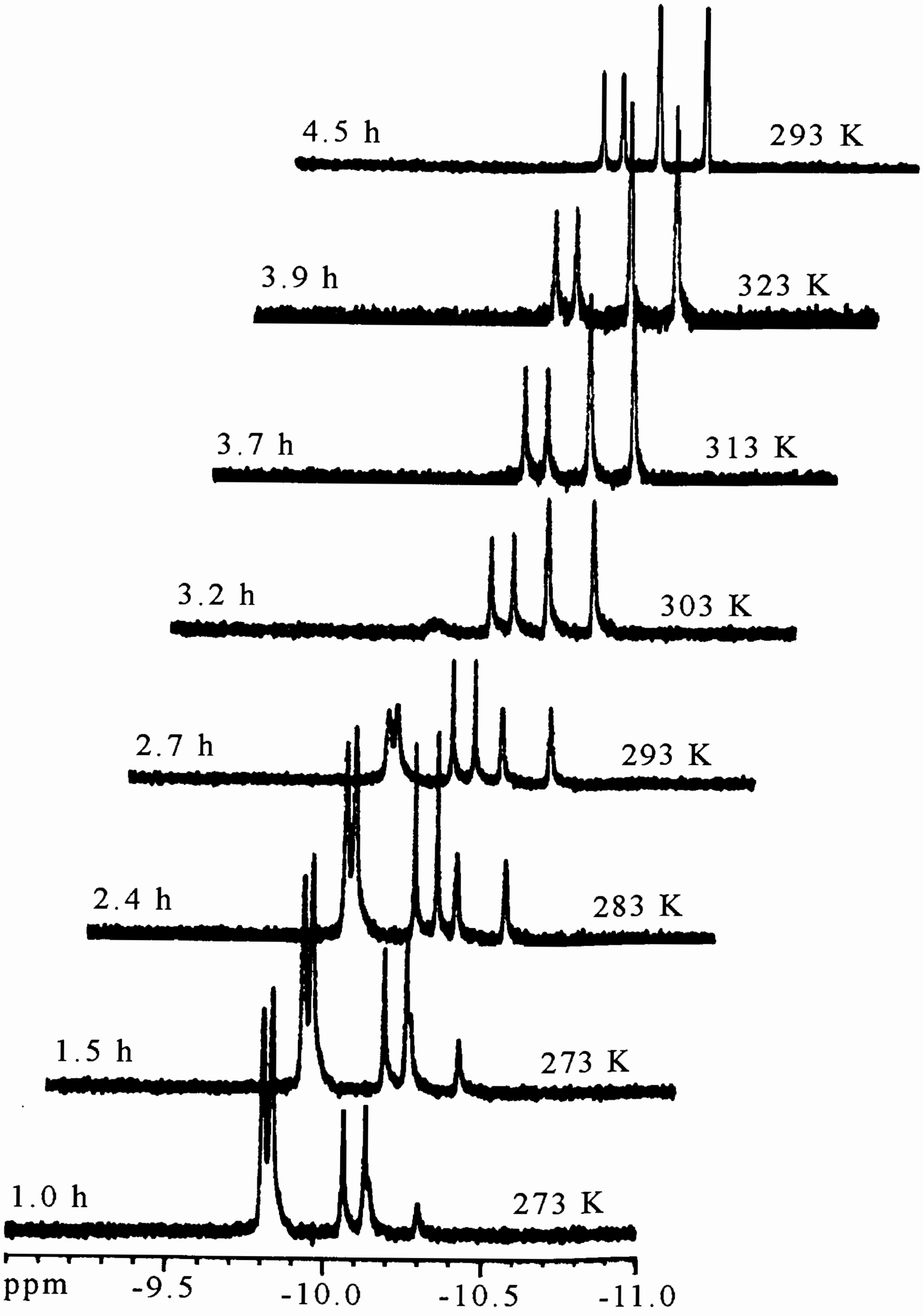


Figure 3.11 Variable temperature ^{1}H NMR spectra of **3.7** in toluene-d_8.

halogenated solvent did not afford the corresponding cyclometalated Cp*Re(CO){η^2-$P(OCH_2CH_2)(OEt)_2$}(Cl) complex. Instead, the only species detectable was the rhenium dihalide complex *trans*-Cp*Re(CO){$P(OEt)_3$}Cl_2.[64a,b] The identification of this species was based on the position of $\nu_{(CO)}$ in the IR spectrum and the MS.

3.2.1.2 Isomerization of *agostic*-3.7 to *trans*- and *cis*- 3.7 Complexes at Room Temperature.

The crude product from the photolysis of Cp*Re(CO){$P(OEt)_3$}(N_2) (**3.1**) in hexane was dried under vacuum and dissolved in benzene-d_6 and the ^1H NMR spectrum was recorded immediately. The spectrum showed resonances at δ 1.88, 1.89 and 1.91 that were assigned to the presence of *three* different Cp* groups. The methyl and methylene groups from the $P(OEt)_3$ moiety appeared as a set of multiplets in the range δ 1.00-1.50 and δ 3.7-4.5, respectively. The ^1H NMR spectrum also exhibited *three* resonances in the metal hydride region. These resonances had relative intensity 19:39:43 respectively. The resonance at δ -10.11 was a doublet with a coupling constant of 62.0 Hz (***cis*-3.7**), while the signal at δ -9.87 was a doublet with a coupling constant of 28.0 Hz (***trans*-3.7**), and the resonance at δ -9.67 had a coupling constant 11.0 Hz (***agostic*-3.7**).

Table 3.1 Variable temperature ^{1}H NMR data for the isomers produced from the photochemical reaction of $Cp^*Re(CO)\{P(OEt)_3\}(N_2)$ (**3.1**) in hexane.

T (K)	Time (h)	**Re-H (ppm)**[a]			**Isomers (%)**		
		agostic-**3.7**		*trans*-**3.7**		*cis*-**3.7**	
		δ	%	δ	%	δ	%
273	1.00	-9.83	66	-10.11	26	-10.20	7
273	1.55	-9.81	61	-10.11	27	-10.20	12
283	2.43	-9.83	55	-10.07	27	-10.24	18
293	2.73	-9.84	41	-10.06	30	-10.26	29
303	3.16	-9.83	9	-10.06	32	-10.27	58
313	3.68			-10.03	36	-10.28	64
323	3.90			- 9.99	34	-10.28	66
293	4.53			- 9.98	34	-10.28	66

(a) The ^{1}H NMR spectrum was recorded in toluene-d_8. The percentages of the isomers were obtained from the intensity of the hydride resonances.

The ^{31}P NMR of this crude photoproduct in benzene-d_6 at ambient temperature showed *three* different resonances for the phosphite ligand. The isomer ***agostic*-3.7** showed a broad singlet at δ 163.9, but the expected 12 Hz coupling was not resolved. The two isomers ***cis*-** and ***trans*-3.7** showed resonances at δ 158.8 and δ 46.6 with coupling constants $J_{P\text{-}H}$ = 58.8 and $J_{P\text{-}H}$ = 27.0 Hz, respectively. The ^{1}H{^{31}P} NMR spectrum showed *three* (singlet) resonances in the hydride region. These results indicated that the *three* hydride resonances exhibit coupling with the phosphorus ligand.

The isomerization of **3.7** was followed by ^{1}H NMR and ^{31}P NMR spectroscopy and the results of the ^{1}H NMR are summarized in Table 3.2.

The ^{1}H NMR spectrum at ambient temperature after 24.0 h was almost the same as the one taken 3 h after the photolysis reaction. The final ratio of the ***trans*-**: ***cis*- 3.7** after ~96 h was 27:73 in benzene-d_6.

This experiment was repeated and the isomerization process was followed by ^{1}H, and ^{31}P NMR. The ^{1}H NMR spectrum in benzene-d_6 exhibited *three* resonances in the hydride region which were assigned to the ***agostic*-3.7**, ***cis*-**, and ***trans*-3.7**. The ^{31}P NMR showed *four* different resonances which were assigned to the ***agostic*-3.7**, ***cis*-**, and ***trans*-3.7**. The fourth resonance was assigned to the unreacted starting material at δ 117.0. In the ^{31}P NMR the resonance assigned to the ***agostic*-3.7** decreased in intensity and the ***cis*-** and ***trans*-3.7** increased over the time. The same process was observed in the ^{1}H NMR spectra over the time. The final products observed were ***trans*-** and ***cis*-3.7** in a ratio 40:60 after 24 h.

Table 3.2 ^{1}H NMR of the isomers produced from the photochemical reaction of $Cp^*Re(CO)\{P(OEt)_3\}(N_2)$ (**3.1**) in hexane at room temperature.

Time (h)	**Re-H (ppm)**[a]			**Isomers (%)**		
	agostic-**3.7**		*trans*-**3.7**		*cis*-**3.7**	
	δ	%	δ	%	δ	%
1.00	-9.67	43	-9.87	38	-10.11	19
1.36	-9.67	23	-9.86	41	-10.11	36
1.94	-9.67	14	-9.86	43	-10.11	42
3.00			-9.86	42	-10.11	60
24.0			-9.86	41	-10.11	59
~96.0			-9.85	27	-10.10	73

(a) The ^{1}H NMR spectrum was recorded in benzene-d_6. The percentages of the isomers were obtained from to the intensities of the hydride resonances.

3.2.2 Photochemical Reaction of $Cp^*Re(CO)\{P(OEt)_3\}(N_2)$ (3.1) in Benzene.

A benzene solution of $Cp^*Re(CO)\{P(OEt)_3\}(N_2)$ (**3.1**) was photolyzed in a Pyrex vessel for 8 min. The reaction was followed by IR spectroscopy and the starting material showed a decrease in intensity of the original $\nu_{(CO)}$ and a new broad band at $\nu_{(CO)}$ 1890 cm^{-1} was the only new $\nu_{(CO)}$ absorption observed.

The ^1H NMR spectrum showed an apparent four resonances in the Cp* region and four doublets in the hydride region (Figure 3.12). The corresponding Cp* resonances could not be unequivocally assigned at this stage because the chemical shift of these resonances is perturbed by their proximity to the benzene solvent resonance that is being irradiated. These Cp* resonances could be assigned later on the basis of the intensities of the species growing or decreasing with time. The hydride resonances at δ -9.50, -9.67, and -9.93 could be immediately assigned to the presence of ***agostic*-3.7**, ***trans*-3.7** and ***cis*-3.7** on the basis of the chemical shift and $J_{P\text{-}H}$ coupling constant by comparison with the results of Section 3.2.1. The *fourth* doublet in the hydride region, with separation 69.2 Hz, is assigned to a product arising from the activation of the solvent benzene. This is thought to be the cis isomer, Cp*Re(CO){P(OEt)$_3$}(Ph)H (***cis*-3.8**), because of the size of the $J_{P\text{-}H}$ coupling constant. This resonance was the most intense hydride signal. Justification for considering this compound to arise from benzene C-H activation is given in the next section 3.2.2. Subsequent observation of the decay of this spectrum indicated that the doublet at δ -9.67 assigned to ***trans*-3.7**, is almost coincident with another similar doublet which occurs at δ -9.66 with $J_{P\text{-}H}$ = 28.0 Hz which we assign to the presence of ***trans*-3.8**. The Cp* and rhenium hydride resonances are summarized in Table 3.3.

The spectrum changed significantly in the following 2 h. The resonances for ***agostic*-3.7** and ***cis*-3.8** disappeared, but that for ***cis*-3.7** increased and there was a change in the situation at *ca* δ -9.67 which was interpreted as a loss of ***trans*-3.8** and increase in ***trans*-3.7**. This interpretation was later substantiated by the results of a time-study in benzene-d_6. The variation in intensities of the hydride signal of ***cis*-3.8** allowed a partial

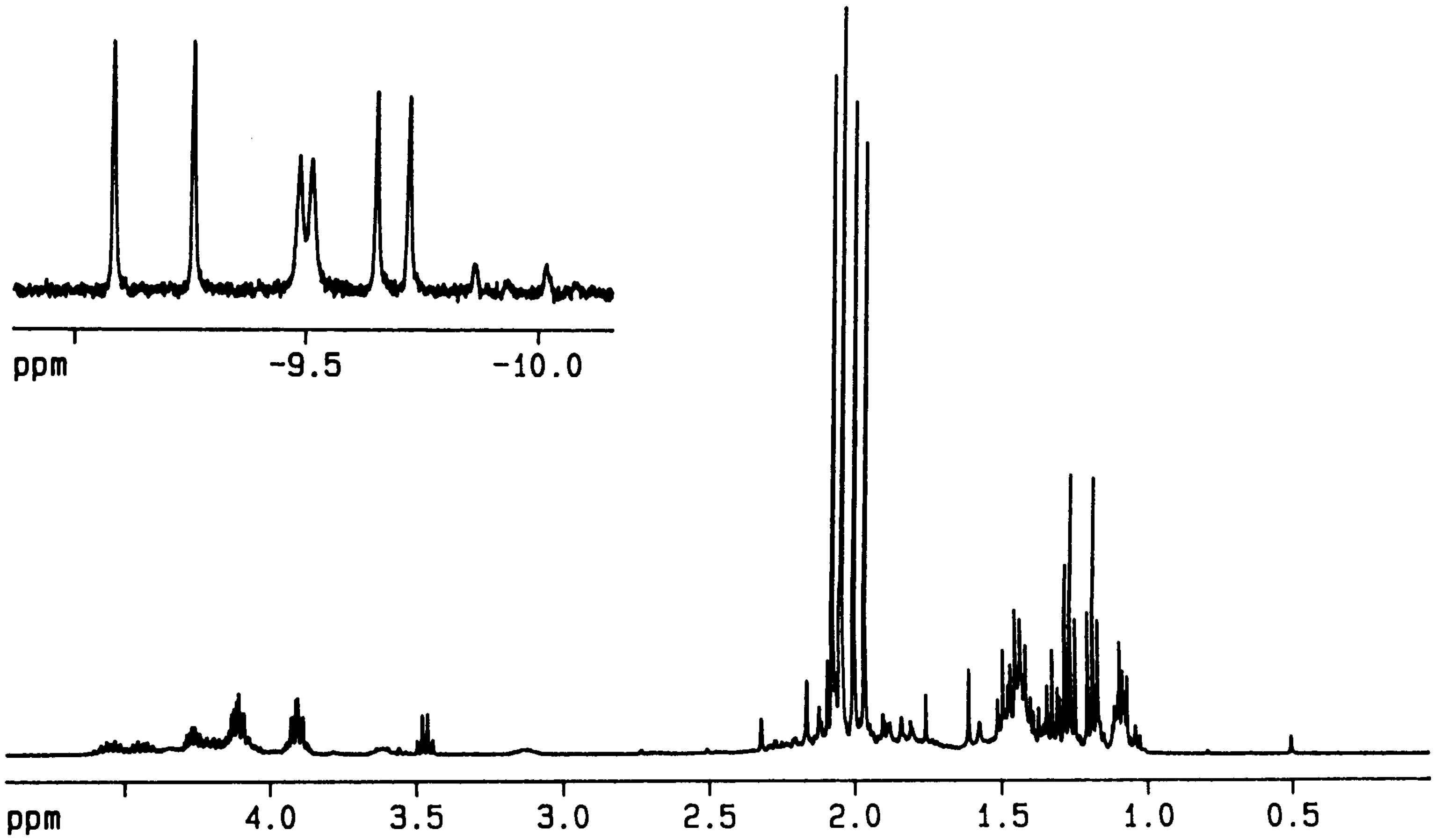


Figure 3.12 ^{1}H NMR spectrum of the crude product after photolysis of **3.1** in C_6H_6. Hydride region is expanded for clarity.

assignment of similarly varying CH_3 resonances at δ 1.19 and δ 1.27 (each a triplet with a coupling constant of 7.0 Hz) and two multiplets at δ 3.90 and δ 4.11 for CH_2 as belonging to the ethoxy groups of this complex. No specific resonances were distinguishable in the ^{1}H NMR for the other isomers in solution.

Table 3.3 ^{1}H NMR data for the isomers produced in the photochemical reaction of **3.1** in benzene.

Complex	**^{1}H NMR δ Cp* (ppm)^a**	**^{1}H NMR δ Re-H (ppm)^{a,b}**
***agostic*- 3.7**	2.00	-9.50 (11.0)
***cis*- 3.7**	2.05	-9.93 (60.0)
***trans*- 3.7**	2.07	-9.67 (28.0)
***cis*- 3.8**	1.96	-9.16 (69.2)
***trans*- 3.8**	2.04	-9.66 (28.0)

(a) The ^{1}H NMR spectrum was recorded in benzene. (b) In parenthesis, $J_{P\text{-}H}$ in Hz.

3.2.2.1 Photochemical Reaction of Cp*Re(CO){P(OEt)$_3$}(N$_2$) (3.1) in Benzene-d_6.

From the results for the irradiation of **3.1** in benzene described in the last section, it was concluded that two of the products (***cis*-** and ***trans*-3.8**) had resulted from the C-H activation of benzene. This could be tested by carrying out the irradiation in benzene-d_6, in which case the corresponding hydride resonances should be absent. Furthermore using benzene-d_6 rather than benzene as the NMR solvent would allow better assignment of the other proton resonances, e.g. Cp* of the individual species.

A benzene-d_6 solution of triethylphosphite complex **3.1** in a Pyrex vessel was irradiated for 12 min. A ^{1}H NMR of the crude sample recorded immediately after the irradiation in benzene-d_6 showed almost complete disappearance of **3.1** and the formation of C-H activation products.

The ^{1}H NMR spectrum showed *five* resonances in the Cp* region and *three* in the metal hydride region. The hydride signals were immediately assignable to the cyclometalated C-H activation products Cp*Re(CO){η^2-P(OCH$_2$CH$_2$)(OEt)$_2$}H (***trans***-, ***cis*-3.7**) and ***agostic*** **3.7** on the basis of the foregoing results. The absence of a fourth hydride (i.e., near δ -9.16) immediately indicates that this species results from the activation of *benzene* in Section 3.2.2. Also the much smaller intensity of the doublet for ***trans*-3.7** observed now, is support for the contention that this doublet has a contribution from ***cis*-3.8** in the spectrum discussed in Section 3.2.2. As will be seen next, this contention receives support when the ^{31}P spectrum is analyzed.

The ^{31}P NMR of this sample, taken immediately after the ^{1}H spectrum showed *five* distinguishable resonances at δ 160.0, 156.8, 122.2, 116.5, and 42.6 (Figure 3.13). The data obtained in the ^{1}H and ^{31}P NMR are summarized in Table 3.4. The ^{31}P NMR resonances at δ 160.0, 156.8 and 42.6 are in agreement with the resonances observed previously for ***agostic*-3.7**, ***cis***-, and ***trans*-3.7** obtained in the photolysis of **3.1** in hexane

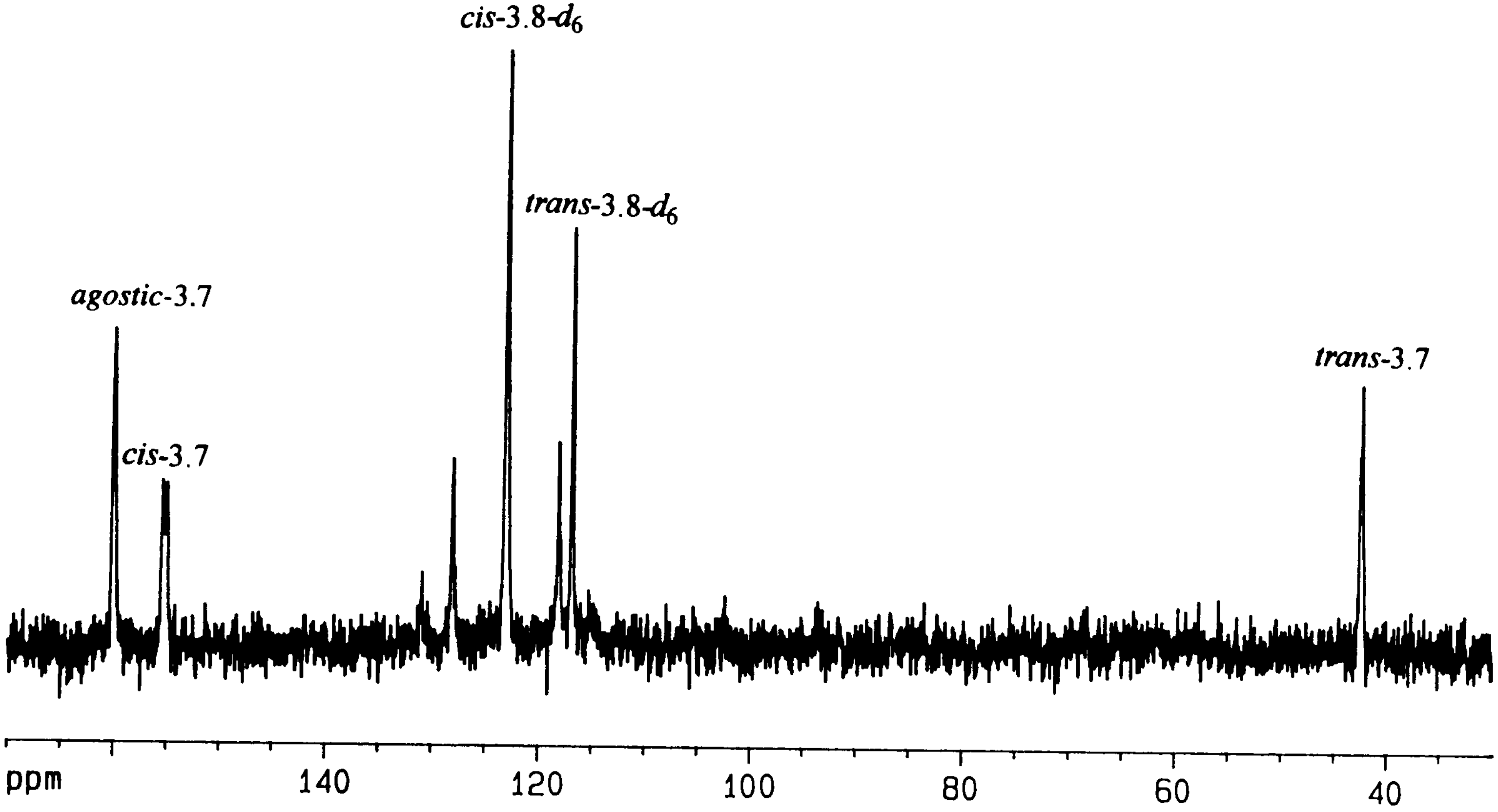
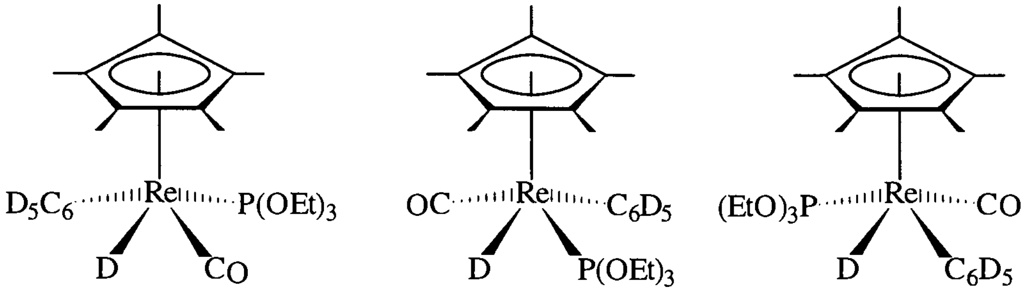


Figure 3.13 ^{31}P NMR spectrum of the crude after photolysis of **3.1** in benzene-d_6 after 1 h.

(See Section 3.2.1). The two other ^{31}P resonances at δ 122.3 and 116.5 are therefore assigned to ***cis***-and ***trans*-3.8-*d*$_6$**, respectively (Figure 3.14).



I **trans** **II** **cis** **III** **cis**

Figure 3.14 Structure of Cp*Re(CO){P(OEt)$_3$}(C$_6$D$_5$)(D) (**3.8-*d*$_6$**).

Table 3.4 ^{1}H and ^{31}P NMR data for **3.7** and **3.8-*d*$_6$** complexes.

Complex	**^{31}P NMR^{a}**	**^{1}H NMR^{a,b}**	
	δ	**δ Cp***	**Re-H**
***agostic*- 3.7**	160.0	(c)	-9.67 (11.0)
***cis*- 3.7**	156.8	1.88	-10.12 (64.0)
***trans*- 3.7**	42.6	1.89	-10.06 (28.0)
***cis*-3.8-*d*$_6$**	122.3	1.83	(d)
***trans*-3.8-*d*$_6$**	116.5	1.86	(d)

(a) The ^{1}H NMR spectrum was recorded in benzene-d_6 and δ in ppm. (b) In parenthesis $J_{P\text{-}H}$ in Hz. (c) It was not possible to obtain this signal due to overlapping resonances. (d) We did not observe a metal hydride resonance due to the activation of C$_6$D$_6$ for these complexes.

The assignment of the downfield shifted resonance at δ 122.3 to the phosphorus which is cis with respect to the deuterium ligand (***cis*-3.8-*d*$_6$**) and the upfield one at δ 116.5 to the phosphorus which is located trans with respect to the deuterium moiety (***trans*-3.8-*d*$_6$**) is based on a comparison with the $^{31}P\{^1H\}$ NMR for $[Cp^*Re(CO)_2LX]^+$ (L= $P(OMe)_3$ or $P(OEt)_3$ and X= Cl, Br, or I) where trans (P-CO) was observed downfield compared with the cis (P-CO) isomer.[65a] The values observed for cis-$[Cp^*Re(CO)_2LX]^+$ were at δ ~82 and at δ ~78 when L was $P(OMe)_3$ and $P(OEt)_3$, respectively. The resonances for the trans isomers were observed downfield compared with the cis isomers which occurred at δ ~92 for trimethylphosphite complexes and at δ ~ 84 for triethylphosphite complexes. It was observed in the ^1H NMR spectrum (Section 3.2.2) that ***cis*-3.8** showed a larger coupling ($J_{P\text{-}H}$) than ***trans*-3.8**. We expected the same difference for the $J_{P\text{-}D}$ coupling. The resonances for **3.8-*d*$_6$** were broad and no resolution of $J_{P\text{-}D}$ coupling was detected, but the resonance at δ 122.3 was wider that the resonance at δ 116.5. We assigned the downfield resonance to ***cis*-3.8-*d*$_6$** and the upfield resonances to ***trans*-3.8-*d*$_6$**. These assignments are consistant with the values reported for cis and trans isomers for the complexes $[Cp^*Re(CO)_2LX]^+$ (L = $P(OMe)_3$, $P(OEt)_3$) (see page 18). An explanation for the unresolved $J_{P\text{-}D}$ could be that the line width was too wide when the experiment was run, and $J_{(P\text{-}D)}$ is 6.51 times smaller than $J_{(P\text{-}H)}$ ($\gamma_H/\gamma_D = 6.51$).[65b]

Although, from the above data, one of the isomers, ***cis*-3.8-*d*$_6$**, is identified to have P and D atoms in a cis arrangement, the available data do not allow us to distinguish which of the two possible configurations II and III in Figure 3.14 is correct. This problem is discussed further in Section 3.3.4.

The ^{31}P NMR intensities further show that the major isomer is ***cis*-3.8-*d*$_6$**. This is consistent with Fig 3.11 where ***cis*-3.8** was the major product. The methyl groups for this complex appeared as triplet at δ 1.02 and at δ 1.10 is $J_{P\text{-}H}$ = 7.0 Hz and the methylenes were multiplets δ 3.74 and δ 3.95.

The evolution of this mixture as a function of time was traced by measuring the ^1H and ^{31}P spectra on the sample at regular intervals (Figure 3.15 and 3.15a). The resonances assigned to ***agostic*-3.7**, and those assigned to ***cis*-** and ***trans*-3.8-*d*$_6$** gradually disappeared (for ***cis*-** and ***trans*-3.8-*d*$_6$** isomers, this observation was obtained from the decrease in intensity of the Cp* signal) and those for ***cis*-** and ***trans*-3.7** increased; the results for the ***agostic*-3.7**, ***cis*-** and ***trans*-3.7** are summarized in Table 3.5. The ratio of ***trans*-** and ***cis*-3.7** appeared to stay reasonably constant from 3.11-21.11 h, and the ratio *ca* 33:67 is similar to that observed in Section 3.2.2 at similar time, but a spectrum after 45 h showed that ***cis*-3.7** had increased relative to ***trans*-3.7**. We cannot be sure that this is the final equilibrium ratio.

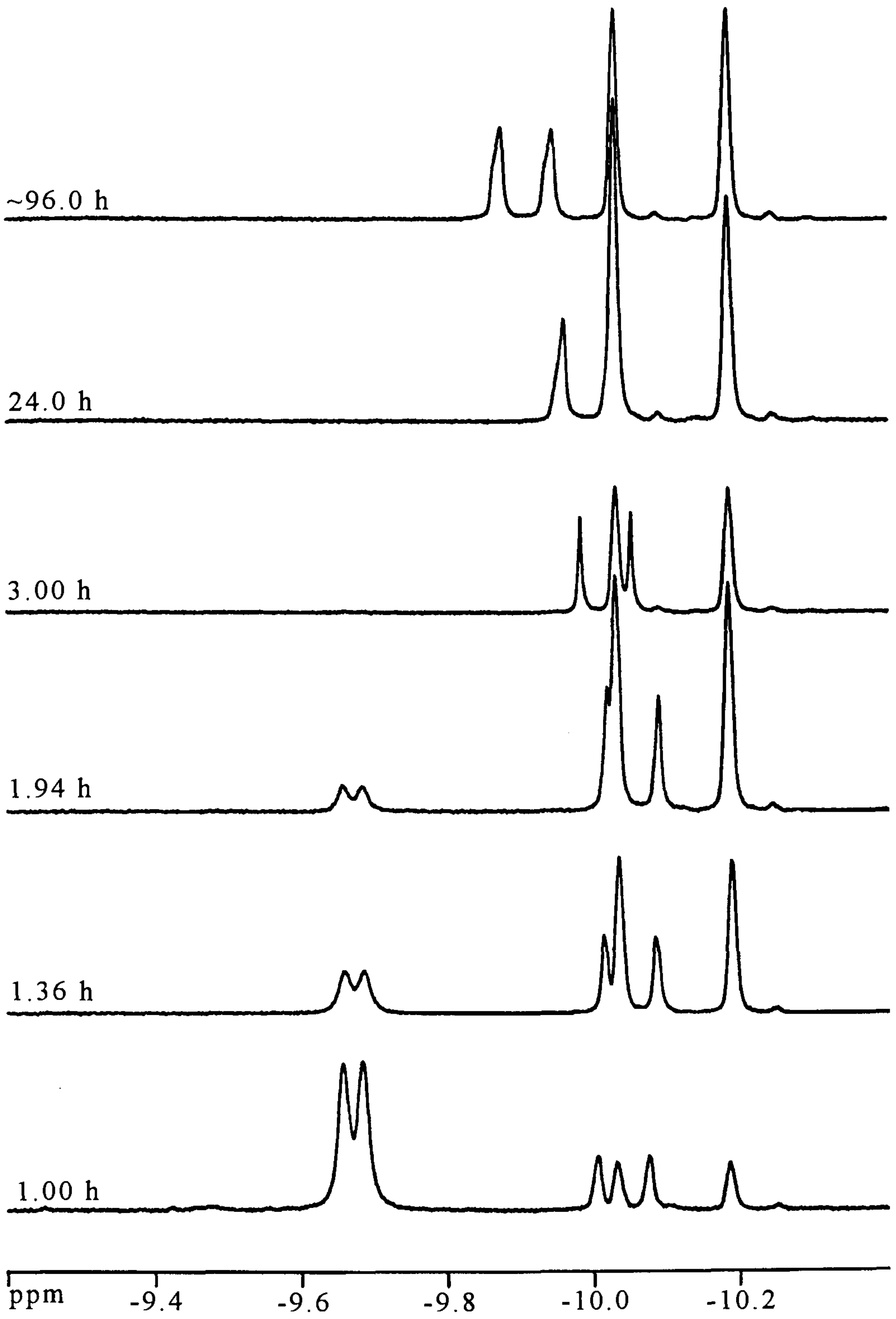


Figure 3.15 Isomerization processes followed by ^{1}H NMR spectra at room temperature in benzene-d_6.

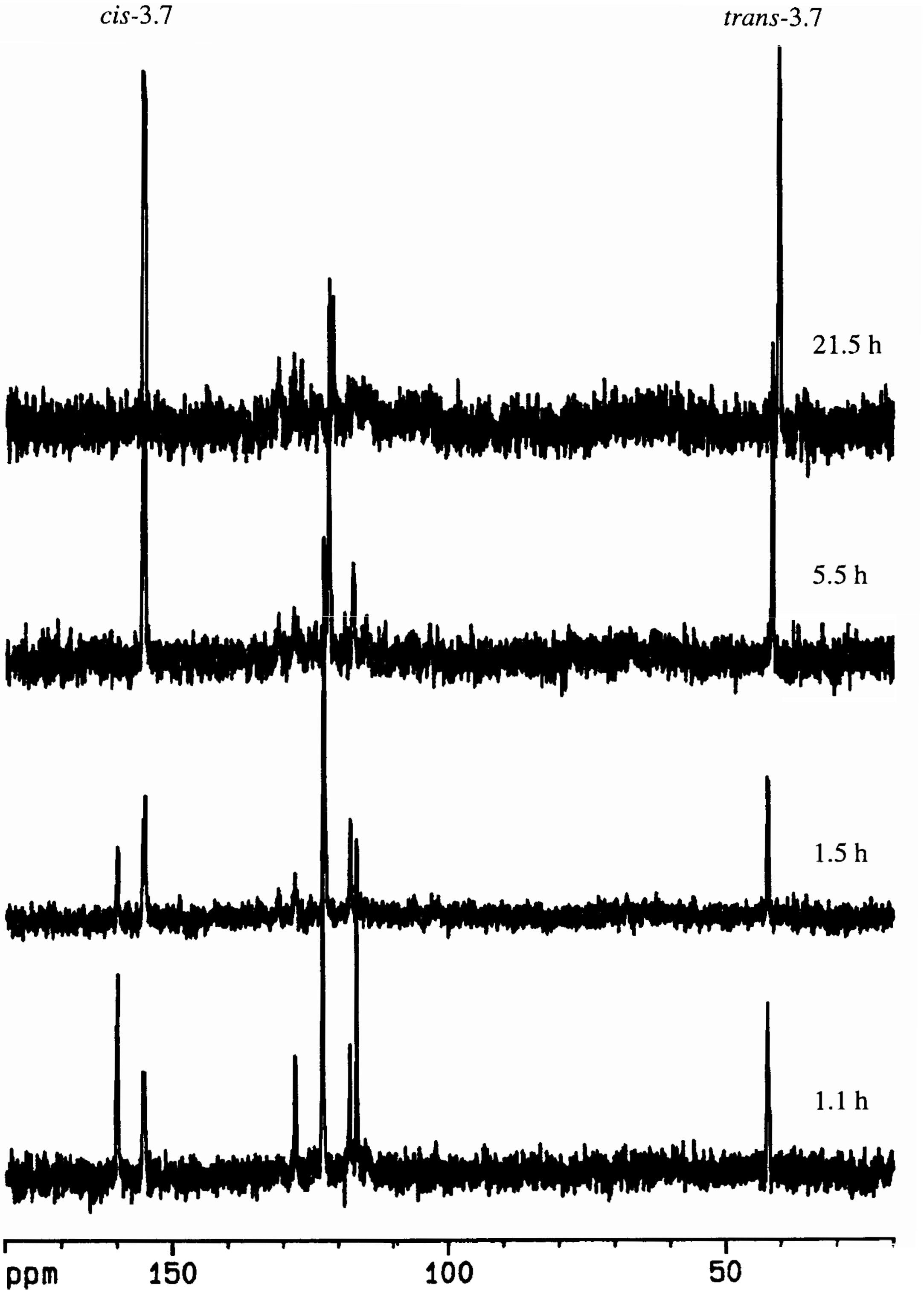


Figure 3.15a Isomerization processes followed by ^{31}P NMR spectra at room temperature in benzene-d_6.

Table 3.5 Interconversion of **3.8-d_6** and ***agostic*-3.7** to ***cis*-** and ***trans*-3.7** in C_6D_6 at room temperature followed by ^1H NMR in the hydride region.

Time (h)	**Re-H (ppm)**[a]			**Isomers (%)**		
	***agostic*-3.7**		***trans*-3.7**		***cis*-3.7**	
	δ	%	δ	%	δ	%
0.00	-9.67	67	-10.04	16	-10.11	17
0.48	-9.67	21	-10.06	25	-10.12	53
1.11	-9.67	10	-10.06	24	-10.11	65
3.11			-10.02	31	-10.11	69
4.11			-9.99	33	-10.11	67
21.11			-9.88	34	-10.11	66
45.11			-9.88	24	-10.11	76

(a) The ^1H NMR spectrum was recorded in benzene-d_6. The percentages of the isomers were obtained from the intensity of the hydride resonances.

3.2.3 Photochemical Reaction of $Cp^*Re(CO)\{P(OPh)_3\}(N_2)$ (3.2) in Benzene, Hexane or Cyclohexane.

Irradiation of the triphenylphosphite dinitrogen complex **3.2** in benzene, cyclohexane or hexane in a Pyrex vessel for 9 min gave the intramolecular C-H activation product $Cp^*Re(CO)\{\eta^2\text{-}P(OC_6H_4)(OPh)_2\}H$ (**3.9**).

The orthometalated complex **3.9** was isolated from benzene-hexane (1:1) at 258 K as a pale yellow solid and was spectroscopically characterized. The complex **3.9** was stable under inert conditions (N_2) and was soluble in benzene, toluene, and cyclohexane and slightly soluble in hexane.

The IR spectrum of **3.9** showed no detectable absorption corresponding to a metal hydride vibration. The carbonyl had a strong $\nu_{(CO)}$ absorption at 1946 cm^{-1} in hexane.

The ^1H NMR spectrum obtained for **3.9** in acetone-d_6 exhibited a resonance corresponding to Cp* (singlet, integral 15H), and the phenyl groups in the phosphite ligand gave a set of multiplets with a relative integrated area of 14H. The identification of the different proton resonances of $\eta^2\text{-}P(OC_6H_4)(OPh)_2$ was difficult due to the inequivalent phenyl rings present in this group. The spectrum also exhibited a doublet in the metal hydride region at δ -10.09 with a relative integrated area of 1H and a coupling constant of 63.0 Hz. This is an indication of cis hydride and phosphorus ligands (see Section 3.2.1).

The $^{13}C\{^1H\}$NMR spectrum of **3.9** in benzene-d_6 showed resonances for the triphenylphosphite moiety in the δ 110 - 163 region but the assignment of the different carbons in the triphenylphosphite ligand was obscured due to overlapping resonances.

The carbonyl carbon resonance was observed at δ 202.4 as a doublet from coupling to phosphorus with $J_{P\text{-}C}$ = 15.0 Hz. The value of this coupling suggests that the carbonyl ligand is trans to the phosphorus moiety.[62b-c] The $^{31}P\{^1H\}$NMR spectrum of **3.9** in acetone-d_6 exhibited a single resonance at δ 83.49.

These results suggest that the isolated product **3.9** has the structure shown in Figure 3.16 with a cis-P-H and trans P-CO configuration

The electron-impact (EI) mass spectrum confirmed the formulation of **3.9**. It showed the molecular ion at *m/z* 630 and a base peak at *m/z* 600 corresponding to the loss of CO and 2H. The loss of two H atoms from the C_5Me_5 ligand in the fragmentation of Cp* complexes is well documented.[66]

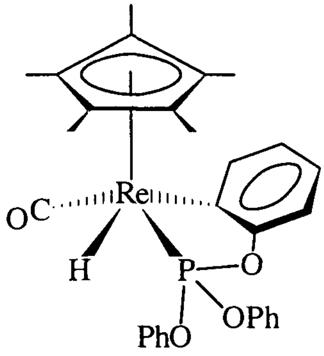


Figure 3.16 Structure of the ***cis*-3.9** complex.

It will be recalled that the hydride complexes just described in Section 3.2.1 were rather unstable typical of many rhenium hydride complexes from C-H activation reactions. However, ***cis*-3.9** was found to be stable in solid state and in solution. Furthermore, treatment of ***cis*-3.9** with chloroform-*d* at room temperature showed no evidence of formation of the analogous chloro-orthometalated complex and, in fact ***cis*-3.9** was unchanged.[49a]

3.2.3.1 Photochemical Reaction of $Cp^*Re(CO)\{P(OPh)_3\}(N_2)$ (3.2) in Benzene- d_6.

From the results for the irradiation of **3.2** in benzene, only ***cis* -3.9** was observed as the isolated final product. The purpose of this experiment, therefore, was to examine in detail by *in situ* ^1H NMR at relatively short times whether there is also activation of benzene or the formation of other isomers of the cyclometalated product.

A benzene-d_6 solution of the triphenylphosphite complex **3.2** in a Pyrex vessel was irradiated for only 5 min. A ^1H NMR spectrum of the crude sample recorded immediately after the irradiation in benzene-d_6 showed almost complete disappearance of **3.2** and the apparent formation of C-H activation products.

The ^1H NMR spectrum exhibited two doublet resonances in the metal hydride region (Figure 3.17). The combined integration was 1/15 the intensity of the single Cp* resonance observed at δ 1.84, and the integration of the phenyl resonances (multiplets) at δ 6.79-7.46 was consistent with the integration observed in the Cp* region. The hydride resonance at δ -9.78 was a doublet with a coupling constant of 62.9 Hz, consistent with a *cis*-$J_{P\text{-}H}$ coupling between hydride and an adjacent phosphite ligand.[62a] This is assigned to ***cis*-3.9**. The signal at δ -7.95 was a doublet with a coupling constant of 11.0 Hz. Because of the small coupling constant, this was assigned to ***agostic*-3.9** by comparison with the results obtained in Section 3.2.1.

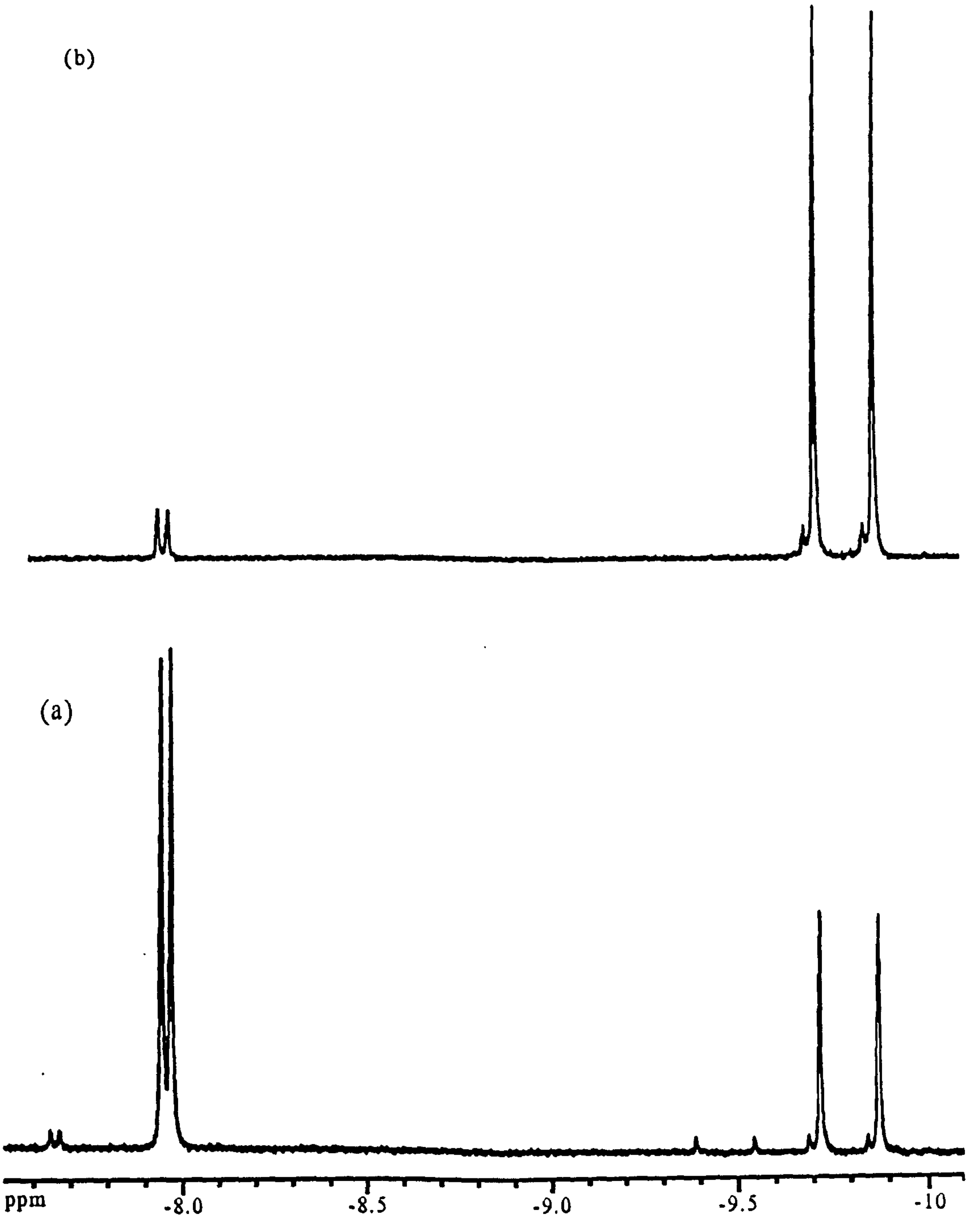


Figure 3.17 ^{1}H NMR spectra of the photolysis of **3.2** in C_6D_6 (a) after irradiation for 5 min, (b) after 3.5 h at room temperature. Upfield resonances have been expanded for clarity.

The ^1H NMR spectrum of the same sample acquired after 3.5 h showed a large decrease in the metal hydride resonance at δ -7.95 and the concomitant growth of ***cis*-3.9** with respect to the unreacted starting material.

3.2.4 Photochemical Reaction of Cp*Re(CO)(Pc)(N_2) (3.3) in Hexane.

In the irradiation of **3.1** in hexane two products (***cis*-** and ***trans*-3.7**) were observed that resulted from the C-H activation of an ethyl group in the triethylphosphite ligand. In order to minimize the possibility of a cyclometalated product, and thus possibly allow an intermolecular C-H activation product to be observed, we investigated the photochemical reaction of Cp*Re(CO)(Pc)(N_2). The Pc ligand (Figure 3.18) has similar electronic properties compared with $P(OEt)_3$ and $P(OMe)_3$ but the possibility of cyclometalation is reduced due to the structure of this ligand.

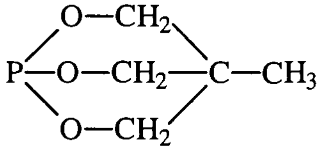


Figure 3.18 Structure of the Pc ligand.

A hexane solution of Cp*Re(CO)(Pc)(N_2) (**3.3**) in a Pyrex vessel was irradiated for 10 min under a N_2 purge until the starting material had disappeared. The reaction was followed by IR spectroscopy every 3 min. No evidence of a new $\nu_{(CO)}$ was detected after the time of photolysis, and the original $\nu_{(CO)}$ and $\nu_{(N2)}$ absorptions had disappeared. The solvent was removed and the residue (without purification) was dissolved in benzene-d_6.

The ^1H NMR spectrum showed no evidence of any C-H activation product (*i.e.*, no hydride resonances), or resonances assignable to the Cp* ligand.

3.2.5 Photochemical Reaction of Cp*Re(CO)(Pc)(N_2) (3.3) in Benzene.

A benzene solution Cp*Re(CO)(Pc)(N_2) (**3.3**) was irradiated in a Pyrex vessel for 10 min. The reaction was followed by IR spectroscopy and the starting material showed a decrease in intensity of the original absorption at $\nu_{(N2)}$ 2079, $\nu_{(CO)}$ 1880 cm^{-1}, and a new $\nu_{(CO)}$ at 1913 cm^{-1} was observed. A ^1H NMR spectrum of the crude solution after the irradiation was recorded. This indicated the complete disappearance of **3.3** and the apparent formation of a C-H activation product. The ^1H NMR spectrum showed a resonance at δ -0.50 integrating to 3H, and a resonance at δ 3.34 integrating to 6H which were assigned to the Pc ligand, and a resonance for Cp* at δ 1.72 integrating to 15 H. There was also a doublet in the metal hydride region at δ -9.20, integrating to 1 H with a coupling constant of 68.8 Hz. The phenyl resonances were not observed because this spectrum was recorded by using a benzene solvent suppression pulse program.

The large hydride coupling constant is consistent with a *cis*-$J_{P\text{-}H}$ coupling between the hydride and an adjacent phosphite as reported previously.[62a] With this spectroscopic evidence we propose that the C-H activation product is *cis*-Cp*Re(CO)(Pc)(C_6H_5)H (***cis*-3.10**) (Figure 3.19).

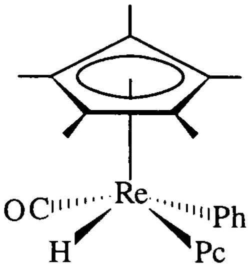


Figure 3.19 Structure of *cis*-**3.10**.

A ^{1}H NMR spectrum of the same sample was acquired after 1 h at room temperature. This showed a decay of the product compared with the first spectrum. This complex proved difficult to characterize spectroscopically due to its thermal instability at room temperature as demonstrated by the ^{1}H NMR spectrum.

An attempt to convert the phenyl hydride complex **3.10** by reaction with CH_3Cl or CCl_4 so as to produce a more stable phenyl halide complex failed. The only species observed was the dihalide complex Cp*Re(CO)(Pc)Cl_2. The identification of this species was based on the carbonyl band observed in the IR spectrum and MS.[64a,c]

3.2.6. Photochemical Reaction of Cp*Re(CO){P(OMe)$_3$}(N_2) (3.4) in Hexane, Cyclohexane or Benzene.

A benzene solution of Cp*Re(CO){P(OMe)$_3$}(N_2) (**3.4**) in a Pyrex vessel was irradiated for 15 min. A ^{1}H NMR spectrum of the crude sample that was recorded in benzene-*d*$_6$ immediately after irradiation showed the complete disappearance of **3.4** and the lack of any hydride resonances suggested there was no formation of any C-H activation products. The new complex **3.11** was purified by chromatography and recrystallized from hexane at 265 K as a pale yellow solid and was spectroscopically characterized. The complex **3.11** is unstable in the presence of air, and acetone under nitrogen to give an uncharacterized product.

The IR spectrum of **3.11** showed *two* absorptions at 1900 and 1879 cm^{-1} both with the same intensity, corresponding to $\nu_{(CO)}$. The ^{1}H NMR spectrum obtained for **3.11** (Figure 3.20) in acetone-d_6 exhibited a resonance corresponding to Cp* as a singlet integrating to 15H and two doublets at δ 3.42 and δ 3.49 (integral area 6H) for the diastereotopic phosphonate OMe protons with a coupling constant of 8.0 Hz. The ^{1}H NMR spectrum showed a resonance at δ 0.74 which was assigned to a methyl group coordinated to the rhenium center (integral area 3H).

The ^{13}C{^{1}H} NMR spectrum of **3.11** in acetone-d_6 also demonstrated the presence of a metal-bound methyl group at δ -0.98 ($J_{C\text{-}P}$ = 11.7 Hz) and *two* inequivalent methyl groups on the phosphonate ligand at δ 51.35, 52.66 with a coupling constant of 11.4 Hz. The carbonyl carbon resonance was observed at δ 221.35 as a doublet with a coupling constant of 28.9 Hz. The ^{31}P{^{1}H} NMR spectrum of **3.11** in acetone-d_6 exhibited a single resonance at δ 80.70. This chemical shift in ^{31}P{^{1}H} NMR spectroscopy is characteristic for a phosphonate group coordinated to a metal center.[67] The proposed structure for **3.11** is shown in Figure 3.21.

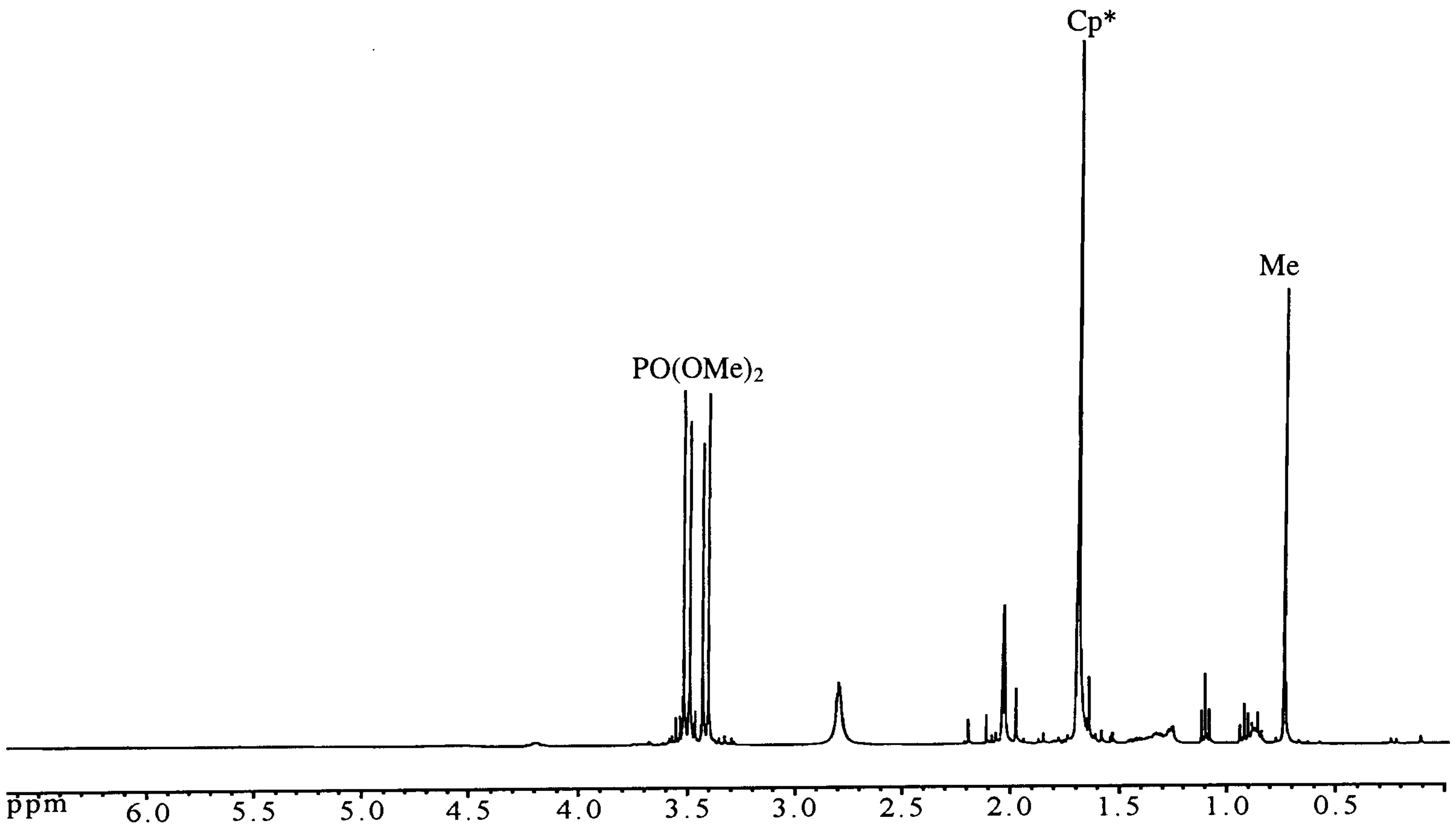


Figure 3.20 ^{1}H NMR spectrum of [Cp*Re(CO){PO(OMe)$_2$}(Me)]$_2$ (**3.11**) in acetone-d_6.

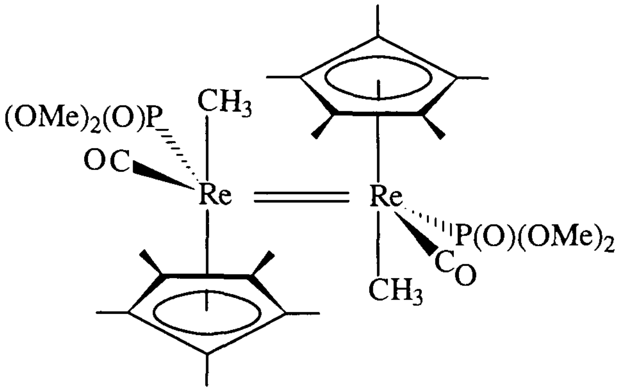


Figure 3.21 Proposed structure for **3.11**

The proposed structure for **3.11** was based upon the observation of a single resonance in the ^{1}H NMR for the Cp* ligands (which must be symmetry-related), and for the methyl groups coordinated in the rhenium center. Similarly, the single resonance observed for the phosphonate ligand in the ^{31}P{^{1}H} NMR and only two diastereotopic OMe groups indicates that the phosphonate ligands are symmetry-related. However, the presence of two $\nu_{(CO)}$ IR absorbances indicates that the CO groups are not centrosymmetric. The configuration shown in Figure 3.21 in which the individual Cp*, CH_3, phosphonate and CO groups are 2-fold related, appears to satisfactorily fit the observed data. The proposed Re=Re double bond is required to fulfill an 18-electron count for each Re. The formulation of **3.11** as a binuclear complex was made on the basis of the electron impact (EI) spectrum (Figure 3.22), which showed a dirhenium isotopic pattern assignable to the the molecular ion at *m/z* 946 and a base peak at *m/z* 918, resulting from the loss of a carbonyl ligand, having a similar pattern.

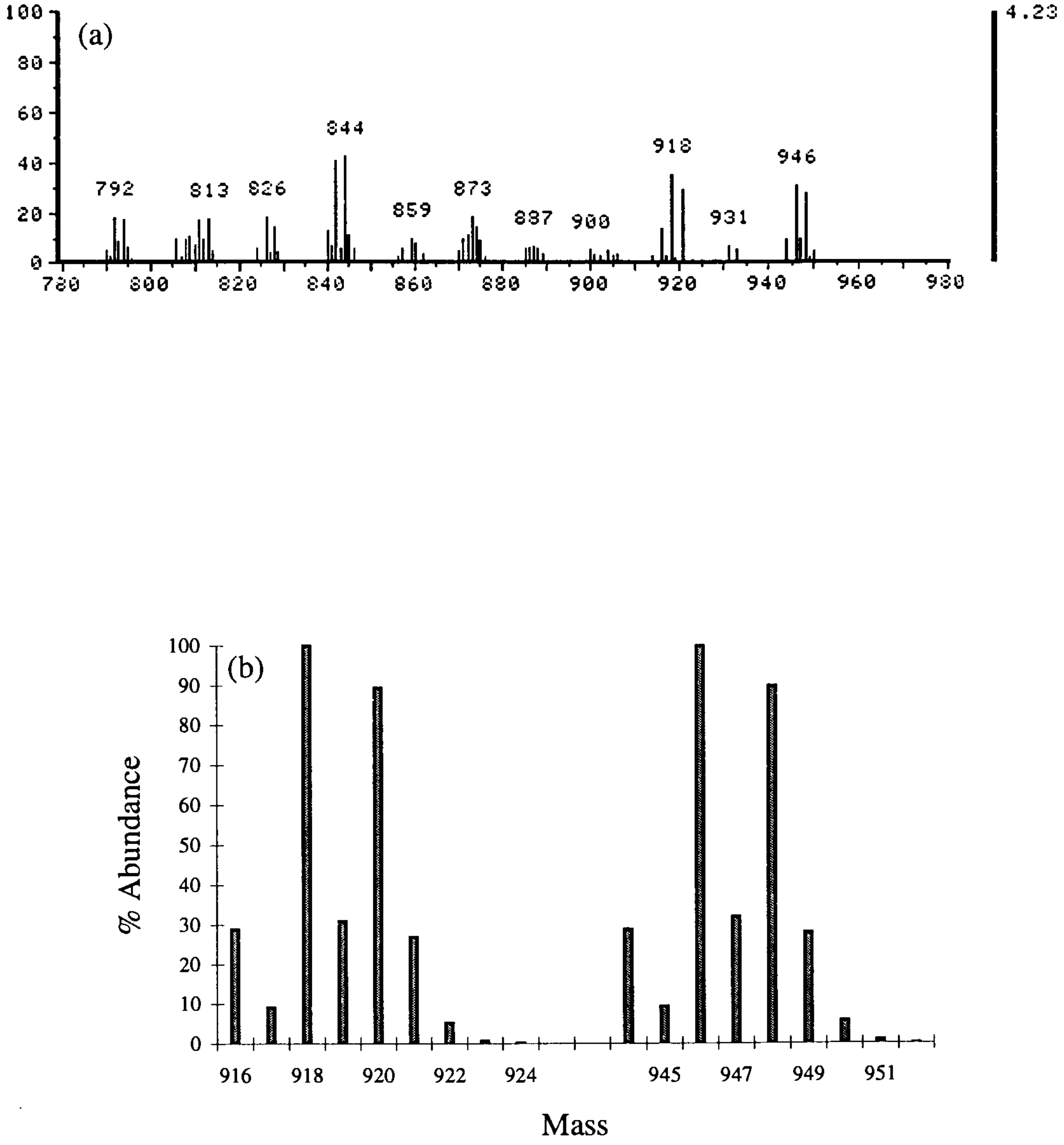


Figure 3.22 Mass spectrum of (a) [Cp*Re(CO)$_2${PO(OMe)$_2$}Me]$_2$ (**3.11**), and (b) Simulation of mass spectrum for **3.11**, M$^+$; (*m/z* = 946) and for M$^+$-CO; (*m/z* = 918).

So far, all attempts to obtain an X-Ray diffraction study of this complex have failed because of the poor quality of the crystals obtained, which in every case were long thin needles.

3.2.7 Photochemical Reaction of Cp*Re(CO)(PPh$_3$)(N$_2$) (3.5) in Benzene, Hexane, Cyclohexane, or Benzene-d_6.

Irradiation of the triphenylphosphine dinitrogen complex (**3.5**) in benzene, hexane, cyclohexane, or benzene-d_6 in a Pyrex vessel for 10 min gave the cyclometalated complex *cis*-Cp*Re(CO){η^2-P(C$_6$H$_4$)(C$_6$H$_5$)$_2$}H (*cis*-**3.12**) resulting from the intramolecular C-H activation of one of the phenyl groups in the triphenylphosphine ligand. The IR spectrum of ***cis*-3.12** showed a carbonyl stretch $\nu_{(CO)}$ at 1913 cm^{-1} in benzene.

The ^{1}H NMR spectrum of the crude solution obtained after photolysis in benzene, exhibited two singlet resonances at δ 1.69 and 1.78, which were assigned to the Cp* ligands. In the metal hydride region the ^{1}H NMR spectrum showed two sets of doublets at δ -7.55 and -7.98 with coupling constants of 12.0 Hz and 73.0 Hz, respectively (Figure 3.23). The hydride at δ -7.55 was assigned to ***agostic*-3.12** (Figure 3.24) on the basis of the size of the coupling constant (see Section 3.2.1).

Photolysis of **3.5** in hexane, cyclohexane or benzene-d_6 showed the same result as did in the photolysis in benzene. As an example, after the photolysis of **3.5** in cyclohexane the ^{1}H NMR spectrum of the solution showed a hydride signal at δ -8.53 with a coupling constant of 11.0 Hz and a set of multiplets in the range δ 6.5-7.5

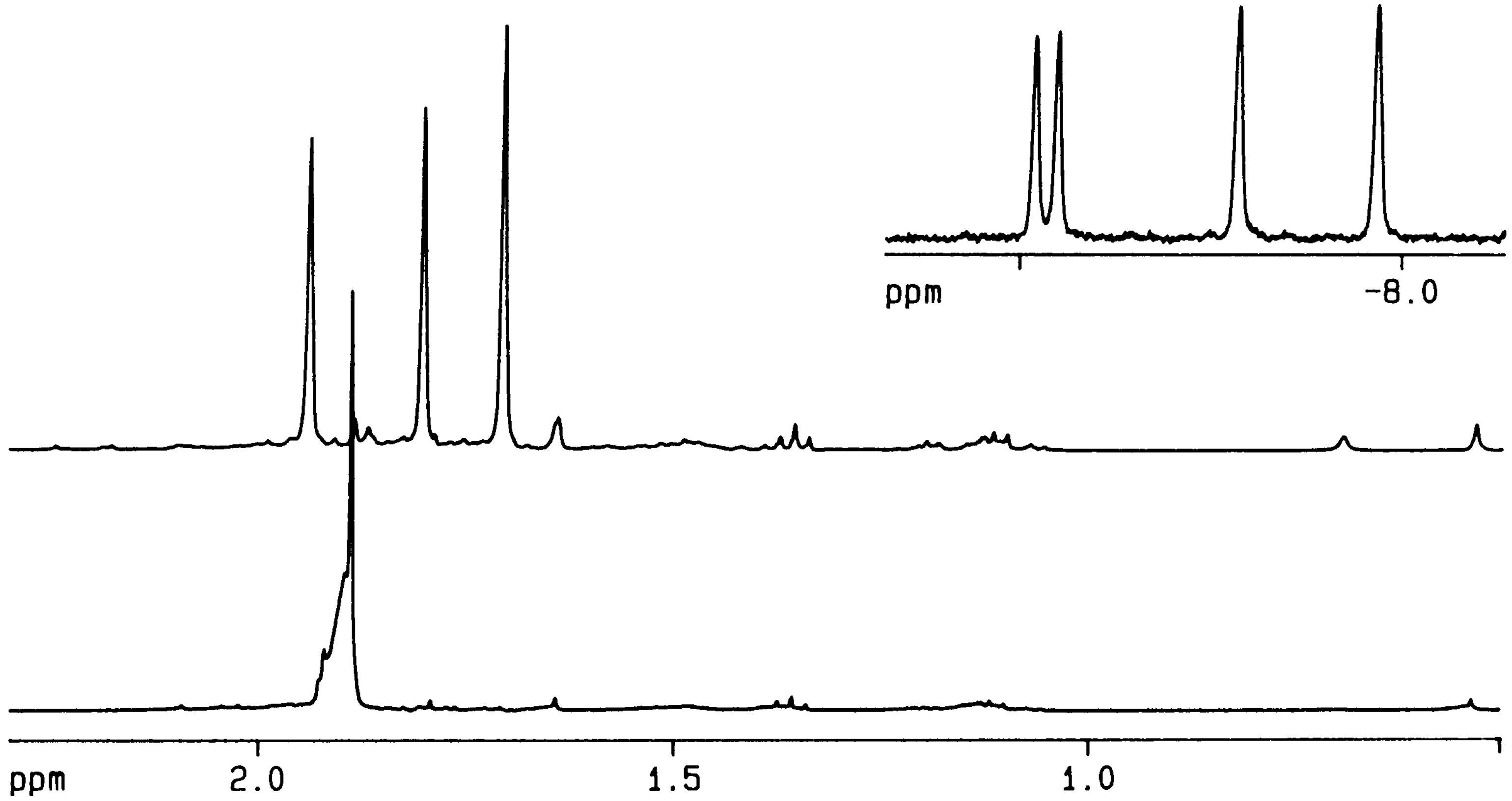


Figure 3.23 ^{1}H NMR spectrum of $Cp^*Re(CO)(PPh_3)(N_2)$ in benzene, (a) before , (b) after 10 min photolysis. Cp* and hydride region is expanded for clarity

corresponding to the aromatic protons. The Cp* resonance is, of course, obscured by cyclohexane solvent suppression.

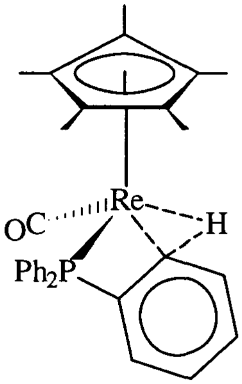


Figure 3.24 Proposed Structure for ***agostic*-3.12**

The small coupling constant was attributed to ***agostic*-3.12.** This isomer converted to the orthometalated complex ***cis*-3.12** over a period of 1 h at room temperature under nitrogen.

The cyclometalated complex **3.12** reacted with $CDCl_3$ or $CHCl_3$ (*ca* 2 h) at room temperature to give an orange-yellow solution from which was obtained a solid product which was assigned by ^1H NMR, $^{13}C\{^1H\}$ NMR and mass spectroscopy to be the corresponding chloro orthometalated complex (***cis*-3.13**) (Figure 3.25). A ^1H NMR spectrum of ***cis*-3.13** in $CDCl_3$ exhibited a singlet at δ 1.53 (integrating to 15H) and a set of multiplets in the range δ 6.90-7.30 (integrating to 14H) which were assigned to Cp* and η^2-$P(C_6H_4)Ph_2$ moieties, respectively. The $^{13}C\{^1H\}$ NMR spectrum for **3.13** showed the presence of the Cp* and η^2-$P(C_6H_4)Ph_2$ ligands. The carbonyl carbon resonance was observed at δ 209.6 as a singlet. The unobservable coupling constant between the phosphine ligand with the carbonyl moiety suggests that the phosphine in this complex is *trans* to the carbonyl group.[62b-c]

The formulation of **3.13** was corroborated by low voltage electron impact (EI) mass spectroscopy at 12 eV, which showed the molecular ion at *m/z* 646 based on ^{187}Re and ^{35}Cl, and a base peak at *m/z* 616 from loss of CO, both having the correct isotopic pattern.

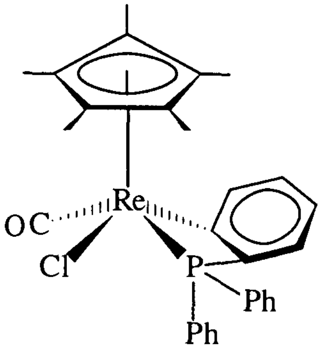


Figure 3.25 Structure of Cp*Re(CO){η^2-P(C_6H_4)Ph_2}(Cl) (**3.13**).

3.3 Discussion

3.3.1 Products of Photolysis of Phosphite Complexes Cp*Re(CO)(L)(N_2) (L = $P(OEt)_3$ (3.1), $P(OPh)_3$ (3.2), Pc (3.3), $P(OMe)_3$ (3.4), and PPh_3 (3.5)).

As a summary of the results presented in the previous section, the rhenium dinitrogen phosphite complexes Cp*Re(CO)(L)(N_2) (L = $P(OEt)_3$ (**3.1**), $P(OPh)_3$ (**3.2**), and PPh_3 (**3.5**)) studied, gave the intramolecular C-H activation as a final product with hydrocarbons. For **3.1** both inter- and intramolecular C-H activation was observed when the complex was irradiated in C_6H_6. However, the intramolecular product was the thermodynamically preferred one. For the complex Cp*Re(CO)(Pc)(N_2) (**3.3**) only the intermolecular C-H activation product was observed when the reaction was carried out in C_6H_6.

In the reaction of the complex Cp*Re(CO){$P(OMe)_3$}(N_2) (**3.4**) in hydrocarbons no evidence for any C-H activation product was observed. However, methyl migration from one of the methyl groups in the trimethylphosphite ligand to the rhenium center was observed.

Irradiation of Cp*Re(CO)(L)(N_2) (L = $P(OEt)_3$ (**3.1**), $P(OPh)_3$ (**3.2**), and PPh_3 (**3.5**) in hexane or cyclohexane produced a rapid loss of N_2 and presumably the formation of the coordinatively unsaturated intermediate "[Cp*Re(CO)L}". This intermediate was not observed and it did not react with these solvents to produce any intermolecular C-H activation products but did undergo internal cyclometalation. In the reaction of Cp*Re(CO)(Pc)(N_2) (**3.3**) in hexane or cyclohexane no C-H activation product was observed.

The irradiation of the $P(OEt)_3$ complex **3.1** generated the intramolecular C-H activation complexes *trans*- and *cis*-$Cp^*Re\{\eta^2\text{-}P(OCH_2CH_2)(OEt)_2\}H$ (**3.7**). The analogous reaction with $P(OPh)_3$ (**3.2**) and PPh_3 (**3.5**) complexes only showed cyclometalated products, *cis*-$Cp^*Re\{\eta^2\text{-}P(OC_6H_4)(OPh)_2\}H$ (**3.9**) and *cis*-$Cp^*Re\{\eta^2\text{-}P(C_6H_4)Ph_2\}H$ (**3.12**), respectively. Evidence to support the cyclometalated products in the reaction of **3.2** and **3.5** with hydrocarbons was found in the comparison of the aromatic region in the ^1H NMR spectra of the starting materials and the products obtained. Other evidence was the interpretation of the $^{13}C\{^1H\}$ NMR spectrum where the unmetalated complexes **3.2** and **3.5** showed only four carbon resonances (substituted, ortho, meta, and para) in the aromatic region, whereas in the cyclometalated ring, which has an ortho Re substitutent, there is usually no symmetry and all the six non-equivalent carbon resonances can be observed. The cis or trans configurations assigned for **3.7**, **3.9** and **3.12** were based on the coupling constants observed in the metal hydride region in the ^1H NMR spectra, and the $J_{C\text{-}P}$ coupling observed in the $^{13}C\{^1H\}$ NMR.

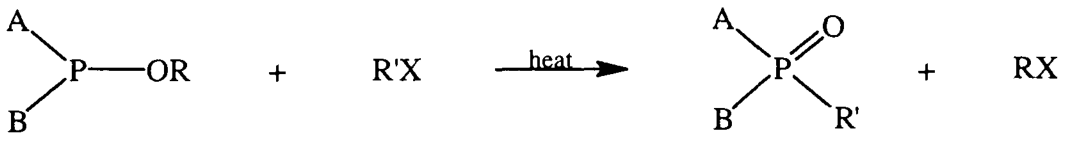
In the formation of the complexes $Cp^*Re\{\eta^2\text{-}P(OCH_2CH_2)(OEt)_2\}H$ (**3.7**), $Cp^*Re\{\eta^2\text{-}P(OC_6H_4)(OPh)_2\}H$ (**3.9**), and $Cp^*Re\{\eta^2\text{-}P(C_6H_4)Ph_2\}H$ (**3.12**) the ^1H NMR spectra of the reaction solutions soon after the irradiation showed in each case the presence of a new species which was interpreted as an *agostic* structure *i. e.* ***agostic*-3.7**, ***agostic*-3.9** or ***agostic*-3.12**. Evidence to support these structures was a new resonance in the metal hydride region that has a small coupling constant ($J_{P\text{-}H}$ = ~12 Hz) which is not typical for a classical metal hydride.[62a] Another piece of evidence to support this structure was the COSY NMR experiment performed on a mixture of ***cis*-, *trans*-3.7** and

***agostic*-3.7**. The *agostic* complexes **3.7**, **3.9** and **3.12** isomerized to the relatively more stable cyclometalated products in a short period of time (~2 h).

Irradiation of $Cp^*Re(CO)\{P(OEt)_3\}(N_2)$ (**3.1**) in benzene, however, produced the intermolecular benzene C-H activation complex $Cp^*Re(CO)\{P(OEt)_3\}(Ph)H$ (**3.8**) together with the intramolecular C-H activation product **3.7**. The intermolecular C-H product $Cp^*Re(CO)\{P(OEt)_3\}(Ph)H$ (**3.8**) converted to the cyclometalated species **3.7**. This result suggested that the intramolecular product was thermodynamically preferred. When **3.2** or **3.5** were irradiated in benzene, only the cyclometalated species ***cis*-3.9** and ***cis*-3.12** were observed; however, the irradiation of $Cp^*Re(CO)(Pc)(N_2)$ (**3.3**) in benzene produced only the intermolecular C-H activation product *cis*-$Cp^*Re(CO)(Pc)(Ph)H$ (**3.10**). We can conclude from the results that intermolecular C-H activation depends on the nature of the phosphite ligand.

When the trimethyl phosphine ligand (PMe_3) was substituted in the rhenium dinitrogen complex for a weaker σ-donor like $P(OMe)_3$ (**3.4**), no sign of any C-H activation product was detected. The experimental data were consistent with the formula $\{Cp^*Re(CO)\{PO(OMe)_2\}(CH_3)]_2$ (**3.11**) in which a methyl group has migrated to the rhenium center by an Arbuzov rearrangement. The formulation of this complex was corroborated by the EI (MS) spectrum which showed a parent peak for M^+ at *m/z* 946.

In a "classical" Arbuzov rearrangement an alkylated nucleophile, R'X, and a phosphorus (III) ester, ABP(OR), react, usually during prolonged heating and without solvent giving an organophosphorus (V) compound with alkyl transfer (Equation 3.2).[30a]



A, B = alkyl, aryl, or alkoxy; R or R' = alkyl

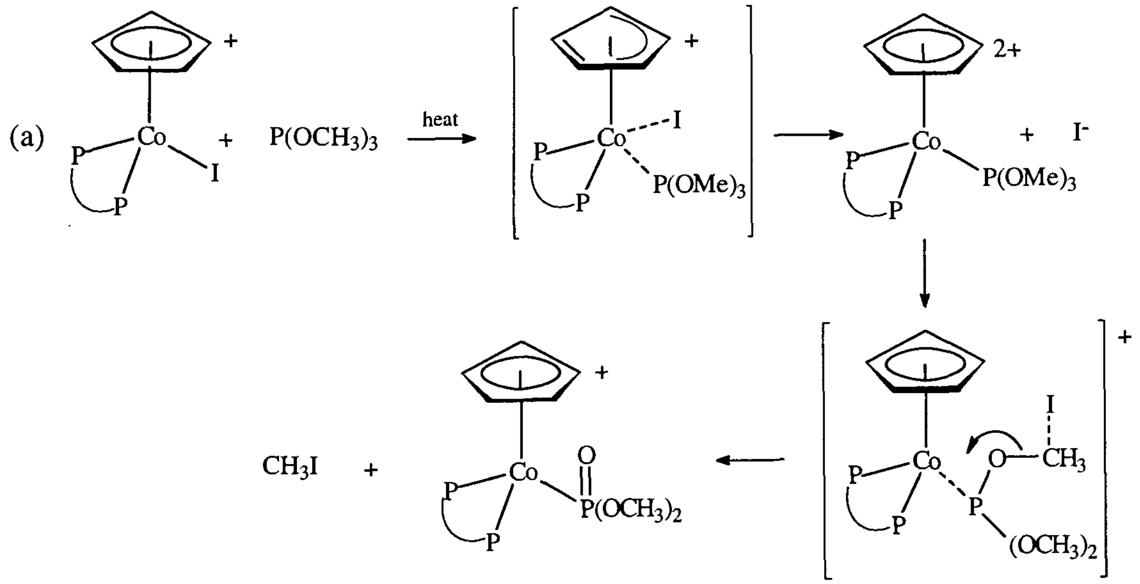
Eq 3.2

The reaction of $P(OR)_3$ with transition metal complex most often results in straighforward ligand substitution at the metal center. However, in some cases the final product constains a phosphonate rather than phosphite ligand (Equation 3.3).

$L_nMX + P(OR)_3 \longrightarrow L_nM\{P(O)(OR)_2 + RX$ Eq 3.3

L = ligand; R = alkyl

The reaction in Equation 3.3 may occur at room temperature or upon heating. The rearrangement of the phosphite molecule to a phosphonate is also witnessed in the absence of nucleophile and in the presence of radicals. Most of these rearrangements can be categorized into two different mechanisms, the "ionic" (**a**) and "radical (**b**) mechanisms. Examples of both mechanisms are described in Figure 3.26.[30a]



(b) $$\{CpCr(CO)_2[P(OMe)_3]\}_2 \rightleftharpoons 2\,CpCr(CO)_2[P(OMe)_3]^\bullet$$

$$CpCr(CO)_2[P(OMe)_3]^\bullet + P(OMe)_3 \longrightarrow CpCr(CO)_2(Me)[P(OMe)_3] + PO(OMe)_2^\bullet$$

$$CpCr(CO)_2[P(OMe)_3]^\bullet + PO(OMe)_2^\bullet \longrightarrow CpCr(CO)_2[P(OMe)_3][PO(OMe)_2]$$

Figure 3.26 Proposed mechanisms for the formation of phosphonate complexes. (a) ionic mechanism, (b) radical mechanism.[30a]

There are several examples of methyl migration involving a phosphite ligand which are difficult to categorize under the mechanisms shown above. As an example, the thermolysis of $Ru\{(P(OMe)_3\}_5$ in hexane in a sealed tube produces a solid which has been identified as $Ru\{P(OMe)_4\}\{PO(OMe)_2\}Me$ (Equation 3.3).[68a] Inhibition of this rearrangement by the presence of free $P(OMe)_3$ suggests that an equilibrium involving dissociation to $Ru\{(P(OMe)_3\}_4$ may exist in solution.[68a]

$$Ru\{P(OMe)_3\}_5 \xrightarrow[24\text{ h}]{\text{hexane}} Ru\{P(OMe)_3\}_4\{PO(OMe)_2\}(Me) \qquad \text{Eq 3.3}$$

Perutz and co-workers reported in their study of C-H activation in rhodium phosphine and phosphite complexes $CpRh(PR_3)(C_2H_4)$ (R = Me, OMe) in neat arenes under photochemical conditions, the formation of a rhodium phosphonate as the major product when the R group was OMe, and the activation of the arene solvent as the minor product (Figure 3.27).[68b]

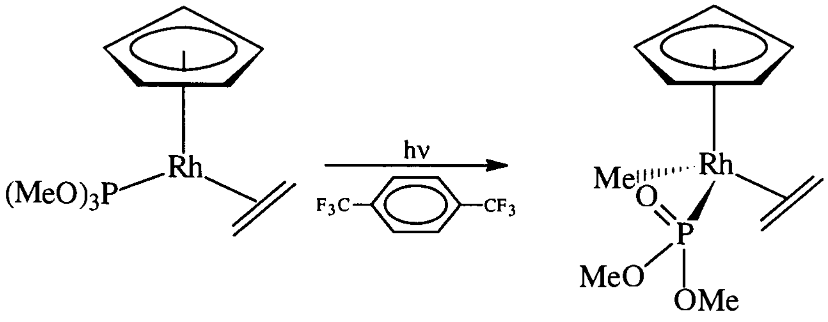


Figure 3.27 Formation of phosphonate in a rhodium complex.

Other metal-phosphite complexes have been converted to metal-phosphonate by thermolysis.[68c] The mechanism of this process is undoubtedly complex and could include inter- and intramolecular reactions as well as radicals.

It is possible that in the photochemical reaction of Cp*Re(CO){$P(OMe)_3$}(N_2) in benzene, some activation of the solvent may occur. However, it was not detectable under the experimental conditions. In contrast to the other phosphites no cyclometalated trimethylphosphite complex was observed either. This could be related with the relative instability of the four membered ring required in this case.[69] However, four membered ring formation has been observed in Pt complexes PtX_2L_2 (X = Cl, Br, or I; L = $PBu^tPr^n_2$, $Bu^t_2Pr^n$) when the β position of the propyl group was activated.[70]

The reaction of the rhenium hydride complexes (**3.7, 3.10**) with halogenated solvents appeared to produced rhenium dihalide complexes ($Cp^*Re(CO)(L)(X)_2$, (L= $P(OEt)_3$, Pc). The cyclometalated complex **3.9** did not react with halogenated solvents.

3.3.2 Comparison with Previous Rhenium C-H Activation.

It has been observed by Pasman *et al* that irradiation of $Cp^{*}Re(CO)_3$ in benzene led to the formation of the rhenium η^2-benzene complex, $Cp^{*}Re(CO)_2(\eta^2\text{-}C_6H_6)$.[71a] This result indicated that the tricarbonyl complex under photochemical conditions lost a CO molecule to give the reactive 16-electron species "$[Cp^{*}Re(CO)_2]$". No evidence for C-H bond activation was observed with this intermediate. A similar result was obtained when the dicarbonyl dinitrogen complex was irradiated in the same solvent.[71b]

Furthermore, photolysis of $Cp^{*}Re(CO)_3$[71c] or $Cp^{*}Re(CO)_2(N_2)$[71b] in cyclohexane, did not yield the C-H activation product; instead two dimers, $(Cp^{*})_2Re_2(CO)_5$ and $(Cp^{*})_2Re_2(CO)_3$ (Figure 3.28) were produced.[71b,c]

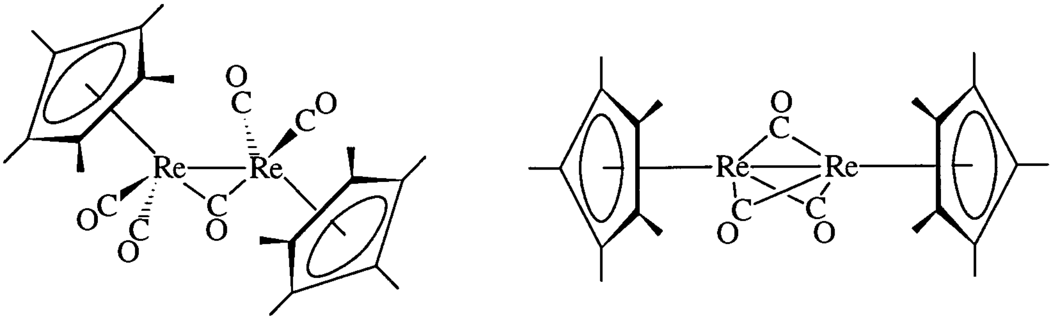
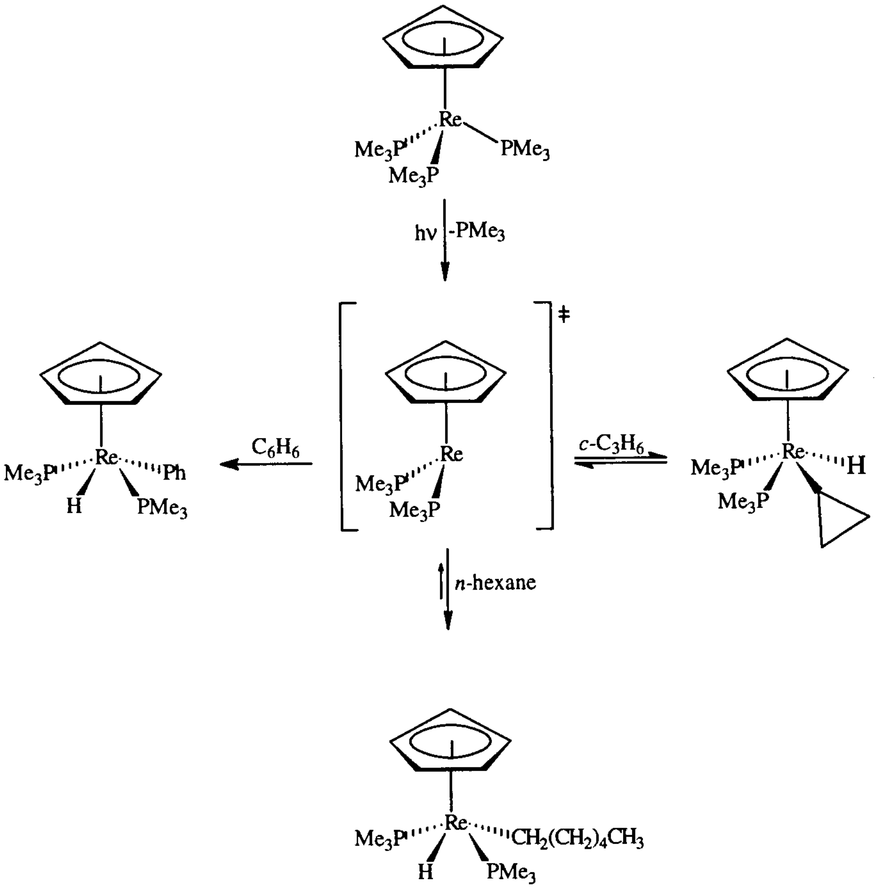


Figure 3.28 Products from the photolysis of $Cp^{*}Re(CO)_2(L)$ (L = N_2 or CO) in cyclohexane.

Bergman *et al.*[49a,49c,50] have studied C-H bond activation in Cp and Cp* rhenium phosphine systems. They reported that the rhenium complexes $CpRe(PMe_3)_3$, $Cp^{*}Re(L)(PMe_3)_2$, (L = CO or PMe_3) give isolable products from either cyclometalation or intermolecular C-H bond activation and a competition between the two processes was also observed. In the Cp rhenium system, $CpRe(PMe_3)_3$ under photochemical conditions produced an inter- or intramolecular C-H activation product (Scheme 3.2). Irradiation of $CpRe(PMe_3)_3$ in hexane gave the intermolecular activation product $CpRe(PMe_3)_2(C_6H_{13})H$, and after a prolonged period of time the product observed was the dihydride rhenium complex *trans*-$CpRe(PMe_3)_2(H)_2$.[51]



Scheme 3.2 Intermolecular C-H activation products formed from $CpRe(PMe_3)_3$ with hydrocarbons.

In the Cp* rhenium system, $Cp^*Re(CO)(PMe_3)(L)$ (L = CO or PMe) under photochemical conditions lost one CO ligand and the intermediate activated C-H bonds in an inter- or intramolecular fashion (see Scheme 3.1, p. 50). The reactivity of Cp* complexes compared to Cp complexes differs in the C-H activation with cycloalkanes or *n*-alkanes. When the reaction was carried out in these solvents the product observed was the cyclometalated complex *cis*-Cp*Re(L){η^2-$PCH_2(Me)_2$}H (L = CO or PMe_3).

It was observed that the cyclometalated complexes in the Cp and Cp* systems react with benzene to produce *cis*- $CpRe(PMe_3)_2(Ph)H$ or *cis*-Cp*Re(L)(PMe_3)(Ph)H (L = CO or PMe_3) in equilibrium with the above cyclometalated product.[49a,51]

Sutton *et al*[57,58] have studied the C-H activation of hydrocarbons with rhenium dinitrogen complexes Cp*Re(CO)(L)(N_2) (L = PMe_3 or PCy_3). It was found that the irradiation time required for the loss of N_2 in the dinitrogen complexes was shorter (ca. 5-10 min) compared with CO or PMe_3 ligands in Bergman's system. The result obtained in the photolysis of Cp*Re(CO)(PMe_3)(N_2) in benzene was otherwise in agreement with the results reported earlier by Bergman's group. Similarly, the photolysis of the trimethylphosphine complex in hexane or cyclohexane (at 275 K) provided only the cyclometalated complex *cis*-Cp*Re(CO){η^2-$PCH_2(Me)_2$}H as reported by Bergman, and when this complex was dissolved in C_6H_6 or C_6D_6, it converted to the intermolecular product *cis*-Cp*Re(CO)(PMe_3)(Ph)H.[57] Irradiation of Cp*Re(CO)(PCy_3)(N_2) in cyclohexane or benzene provided only the intramolecular C-H activation product *trans*-Cp*Re(CO){η^2-P(C_6H_{11})(Cy_2)}H and no evidence for the activation of benzene was observed.[58]

From our results, no evidence for hexane or cyclohexane C-H activation was observed with these rhenium dinitrogen phosphite complexes of the general formula

$Cp^*Re(CO)(L)(N_2)$ (L = $P(OEt)_3$ (**3.1**), $P(OPh)_3$ (**3.2**), Pc (**3.4**), and PPh_3 (**3.5**)) under these experimental conditions. Conversion of the intra- to intermolecular C-H activation product was not detected in the complex **3.7** where both products were observed. This result suggests that the cyclometalated product where a five membered ring was formed is more stable than the three membered ring formed in the reaction of $Cp^*Re(CO)(PMe_3)(N_2)$ in hexane.

In the photochemical reaction of $Cp^*Re(CO)(L)(N_2)$ (L = $P(OEt)_3$ (**3.1**), $P(OPh)_3$ (**3.2**), and PPh_3 (**3.5**)) in hydrocarbons, an intramolecular *agostic* interaction was observed. In all the previously studied rhenium dinitrogen complexes, no evidence for this kind of intermediate was detected. Cis and trans isomers were observed in the complexes **3.7** and **3.8** but only the cis isomer was observed for the complexes **3.9**, **3.10** and **3.12**. The formation of the cis isomer is in agreement with the previous report of C-H activation in rhenium complexes.[51,57] However, no evidence for the occurrence of both isomers was reported previously.

3.3.3 Mechanism of C-H Activation in Rhenium System

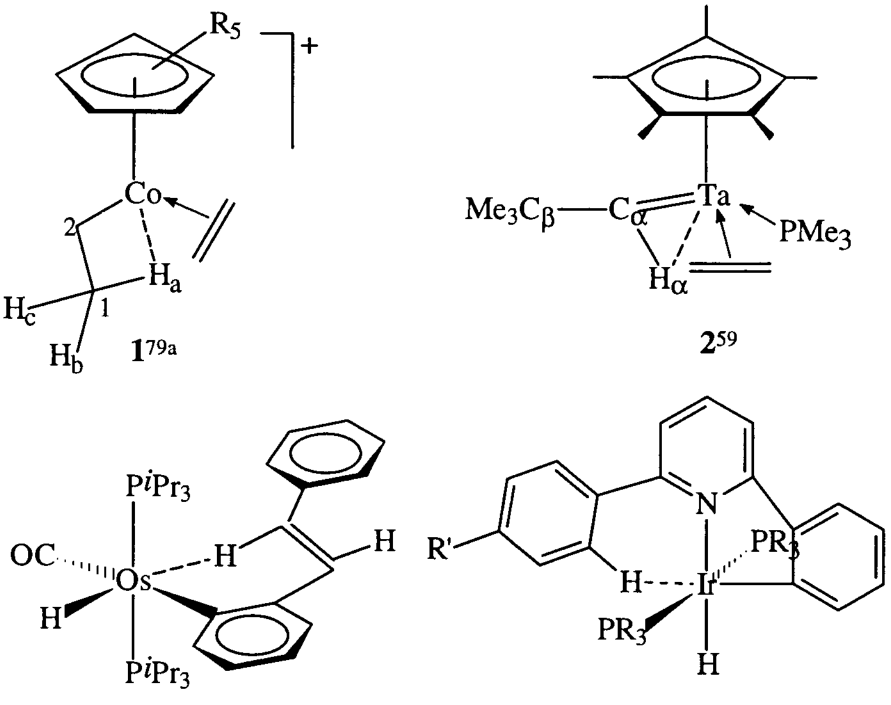
The mechanism of C-H activation and the formation of a 16-electron intermediate and its exact nature have been studied in detail for iridium and rhodium systems. Recently, Perutz *et al.*[72] reported experimental evidence for the 16-electron intermediate "$[CpIr(PMe_3)]$", and its Rh counterpart at low temperature in argon matrices. The same reactive intermediates have been postulated in the activation of alkane, arene and alkene C-H bonds, but have never been observed directly.[49b,73]

Studies of C-H activation in iridium and rhodium complexes with alkanes in a matrix system have been reported by several groups.[74] Bergman and co-workers have reported that the 16-electron intermediate "[Cp*Rh(CO)]" was stable in a rare gas, Rg (Rg = Kr or Xe) solution at low temperatures (163-193 K) by forming the solvated species Cp*Rh(CO)(Rg). When the reaction was carried out in the presence of alkanes (e. g. neopentane or cyclohexane),[75] the complex Cp*Rh(CO)(Rg) then quickly achieves an equilibrium with a weakly bound metal-alkane species, which is presumably a "σ-interaction" (*agostic* interaction) in which the metal atom interacts with, but has not yet activated, an alkane C-H bond. Recently, Harris *et al.* reported evidence for a similar "σ-interaction" in $Tp^*Rh(CO)_2$ at room temperature in an alkane solution.[76]

Theoretical calculations of C-H bond activation for CpML, (M = Ir, Rh; L = PH_3, PH_2R'; R' = CH_2, CH_2CH_2) showed that an *agostic* interaction appears to be an intermediate, and it must be preceded by a vacant coordination site, *i.e.* a coordinatively and electronically unsaturated complex.[77a] The formation of a similar intermediate in intra- or intermolecular C-H activation has been suggested in theoretical work by several other groups.[77b-d]

Studies of C-H activation by rhenium complexes have been known since 1981, but until now no work has been done to establish the precise mechanism operating for those rhenium complexes. Bergman *et al.*[51] suggested that in Cp and Cp* rhenium complexes the photoextrusion of CO or PMe_3 gave a 16-electron intermediate which reacted to generate the C-H activation product. An alternative mechanism to open the necessary coordination site for C-H bond activation, could be an η^5 to η^3 isomerization of the cyclopentadienyl ring. We presume that the likely mechanism that applies to our system is the formation of a 16-electron intermediate "[Cp*Re(CO)(L)]" rather than ring slippage, due to the ability of the dinitrogen complexes to readily extrude N_2 under photochemical or thermal conditions.[57,58]

In principle, there can be intermolecular activation of an external C-H bond or, since most intermediates also contain C-H bonds (e.g., of Cp* or another ligand), intramolecular activation. Oxidative-addition of the C-H bond (alkyl or aryl) is presumed to occur via an initial *agostic*-interaction. This interaction has been observed in several organometallic systems,[78] some examples of which are summarised in Figure 3.29.



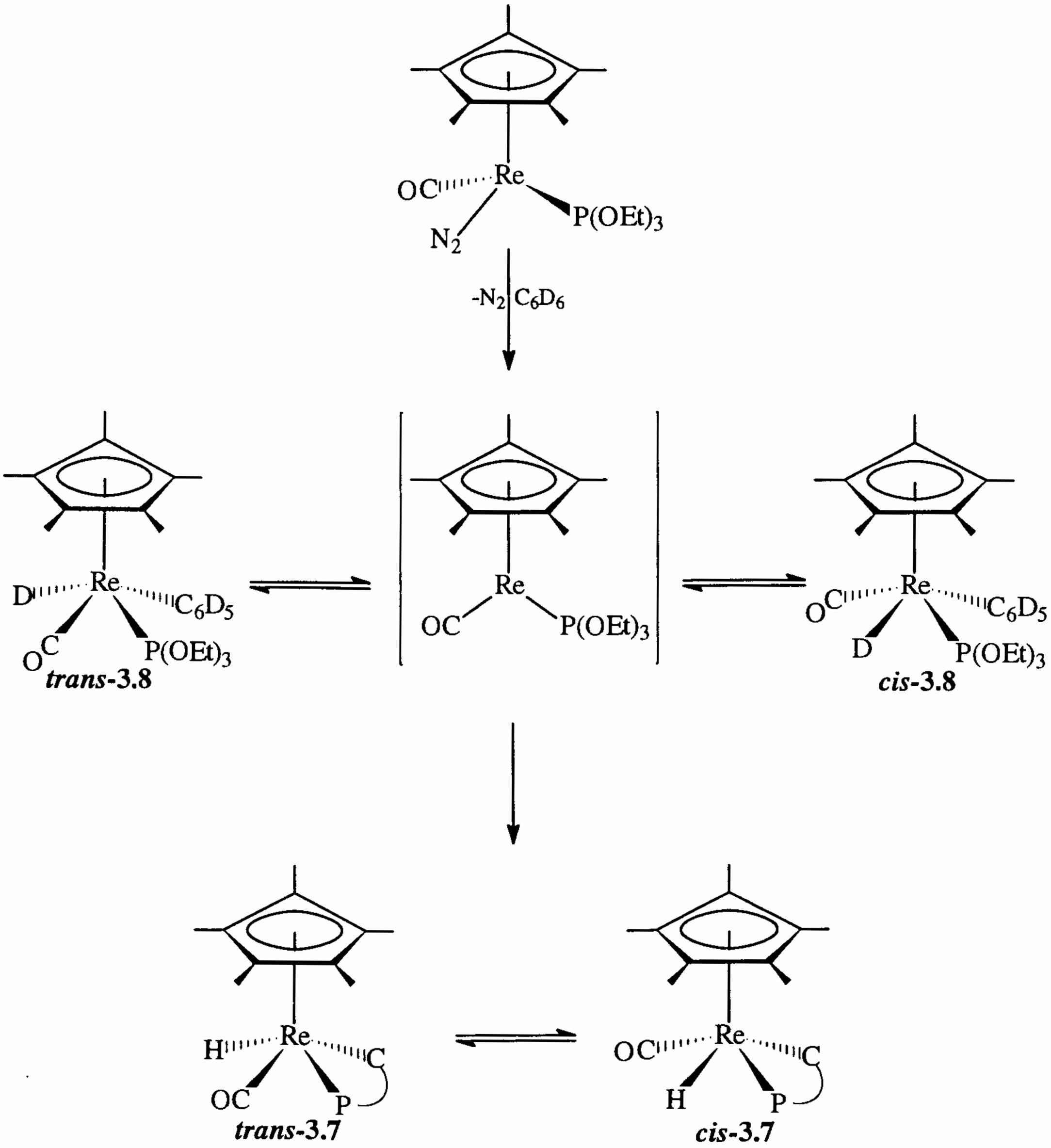
1[79a] 2[59] 3[79b] 4[79c]

Figure 3.29 Examples of *agostic* interactions in transition metal complexes.

Complex **1** (Figure 3.29) showed for the first time that the agostic η^2-alkyl could be the stable ground state, rather than the olefin hydride or the η^1-alkyl.[79a]

During the irradiation of **3.1** in benzene the intermolecular product $Cp^*Re(CO)\{P(OEt)_3\}(Ph)H$ (**3.8**) was observed to decay while the intramolecular activation product $Cp^*Re(CO)\{\eta^2\text{-}P(OCH_2CH_2)(OEt)_2\}H$ (**3.7**) increased. The final products of this reaction were ***trans-*** and ***cis*-3.7**. To account for this observation we propose that the intermolecular product (**3.8**) must be in reversible equilibrium with benzene and the 16-electron intermediate and the latter undergoes cyclometalation to produce the intramolecular product (Scheme 3.3). This means that the intramolecular product is the thermodynamically preferred one. This result is opposite to the previous work with the trimethylphosphine complex, where the cyclometalated $Cp^*Re(L)\{\eta^2\text{-}PCH_2(Me)_2\}H$ (L = CO or PMe_3) converted to the intermolecular product $Cp^*Re(L)(PMe_3)(Ph)H$.[50,57]

A competition between intra- and an intermolecular C-H activation has been observed by Jones *et al* in the photochemical reaction of the complex $Cp^*Rh\{P(n\text{-}Pr)Me_2\}(H)_2$ in propane (Figure 3.30).[80] They proposed that the cyclometalated product was thermodynamically favoured but kinetically disfavoured. Furthermore, they suggested that if the cyclometalation product was thermodynamically unstable, it might be possible to generate the intermolecular product in the presence of alkanes.



Scheme 3.3 Proposed mechanism to the conversion of the complex **3.8** to the complex **3.7**

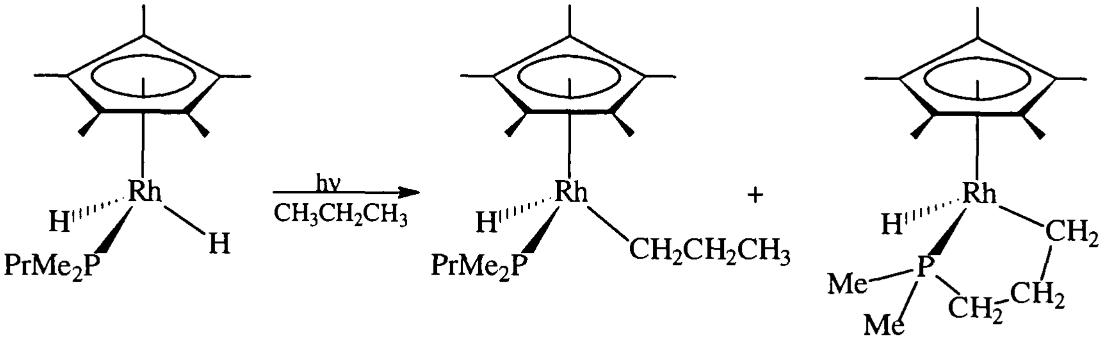
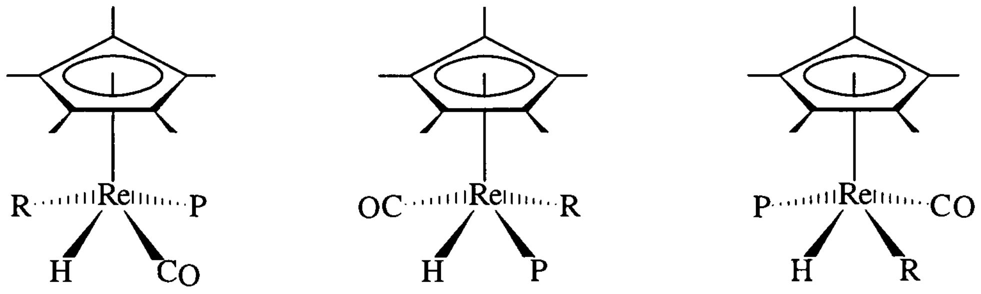


Figure 3.30 Competition of inter- versus intramolecular C-H activation in the photolysis of $Cp^*Rh\{P(n\text{-}Pr)Me_2\}(H)_2$ in propane.

A similar result was observed by Bergman *et al.*in the photochemical reaction of the complex $Cp^*Ir(PPh_3)(H)_2$ in benzene where inter- and intramolecular C-H products were observed.[48a,48c] In order to make the cyclometalation product less favoured, they replaced the PPh_3 ligand with PMe_3, and then the only product obtained was the intermolecular C-H activation product $Cp^*Ir(PMe_3)(Ph)H$. This result suggests that weak σ-donor ligands and crowded ligands (*i.e.*; those with a large cone angle (PMe_3 = 118° and PPh_3 = 145°))[81] might favour the intramolecular activation rather than the intermolecular activation.[82]

3.3.4 Stereochemistry in "Piano Stool" Complexes.

Theoretically, three isomers are possible for four-legged piano-stool configuration (Figure 3.31). For the isomer **I,** where the hydride ligand and the phosphorus group are trans, a typical $^2J_{P\text{-}H}$ value of ~27 Hz are observed. In isomers **II** and **III** the hydride ligand and phosphorus group are mutually *cis*. In this case the typical $^2J_{P\text{-}H}$ values are somewhat larger than 60 Hz.[62a] In isomers **I** and **III** the CO and P are mutually *cis*. In the ^{13}C NMR spectrum a typical $^{2}J_{C\text{-}P}$ values are larger than 27 Hz but less than 50 Hz.[62b-c] Isomer **II** is the only one in which the CO and P are mutually trans. Typical $^{2}J_{C\text{-}P}$ values are in the range 0 - 15 Hz.[62b-c] A similar trend has been observed in molybdenum hydride phosphine complexes where the large coupling corresponded to the phosphorus cis to the hydride and a small coupling corresponded to the phosphorus trans to the hydride group.[62a] In the ^{13}C{^{1}H} NMR spectra of CpMo(CO)(PR$_3$)(L) complexes there have been observed in cis and trans isomers typical $J_{P\text{-}C}$ coupling of 28.0 and 5.0 Hz, respectively.[62b-c]



I **trans** **II** **cis** **III** **cis**

Figure 3.31 The isomers which arise from C-H bond activation of rhenium complexes.

The stereochemistry of **3.7** (trans and cis) was inferred on the basis of $J_{P\text{-}H}$ value in the ^{1}H NMR, and chemical shift in the ^{31}P NMR. For this complex, the cis configuration corresponded to the isomer **II**. Isomer **III** can not be formed due to the geometry of the carbon in the cyclometalated complex. The complex **3.8** showed cis and trans stereochemistry and from the data obtained for this complex it was not possible to distinguish isomer **II** from **III** (in cis configuration). Upon the irradiation of Cp*Re(CO)(L)(N$_2$) (L = P(OPh)$_3$ (**3.2**), Pc (**3.4**), and PPh$_3$ (**3.5**)) in hydrocarbons, the only product observed was the cis isomer. The stereochemistry of Cp*Re{η^2-P(OC_6H_4)($OPh)_2$}H (**3.9**) and Cp*Re{η^2-P(C_6H_4)Ph_2}H (**3.12**) were deduced from the coupling constant $J_{P\text{-}H}$ = ~60 Hz and the value of $J_{P\text{-}C}$ for **3.9** and **3.12** and suggest that the cis isomer of these complexes is the structure **II**.

The intermolecular activation complex Cp*Re(CO)(Pc)(Ph)H (**3.10**) showed only the cis stereochemistry after the irradiation time. The stereochemistry was assigned on the basis of $J_{P\text{-}H}$ coupling observed in the ^{1}H NMR. It was not possible to distinguish isomers **II** from **III** from the data available for this complex. A cis stereochemistry has been observed in other rhenium systems as the only product.[83] However, there was no comment reported relating to the possible trans- to cis-isomerization in the rhenium complex. This might suggest that the trans form was not formed.[83]

The only example where the trans isomer was the isolable product and there was no evidence of the cis isomer was in Cp*Re(CO){η^2-P(C_6H_{11})Cy_2}H where it was proposed that the cis isomer was not formed for steric reasons.[58] Different ratios were observed (*trans-*:*cis-*) for complex **3.7** in benzene-d_6 (27:73) compared to toluene-d_8 (34:66). This difference can be attributed to the use of different solvents. This effect has been observed in several complexes, where the solvent modified the ratio of both isomers in solution.[84]

3.4 Conclusion

In this chapter we have shown that the phosphite dinitrogen complexes (**3.1-3.6**) are capable of promoting the C-H activation of hydrocarbons. The dinitrogen complexes required a shorter irradiation time (~10 min) to produce a quantitative reaction as a result of the facile photoextrusion of N_2 compared with the CO or PMe_3 in $Cp^*Re(CO)_2(PMe_3)$ or $Cp^*Re(CO)(PMe_3)_2$ complexes.[50,51]

Irradiation of **3.1** in hexane forms exclusively the intramolecular C-H activation products $Cp^*Re(CO)\{\eta^2\text{-}P(OCH_2CH_2)(OEt)_2\}H$ (**3.7**) in *cis* and *trans* form. However, photolysis of a benzene solution of **3.1** gives a competition of inter and intramolecular C-H activation. These results demonstrate that the complex $Cp^*Re(CO)\{P(OEt)_3\}(Ph)H$ (**3.8**) must be in an equilibrium with benzene and the 16-electron intermediate.

The C-H activation of $Cp^*Re(CO)\{P(OPh)_3\}(N_2)$ (**3.2**) and $Cp^*Re(CO)PPh_3(N_2)$ (**3.5**) produced only the cyclometalated product ***cis*-3.9** and ***cis*-3.12**. These results demonstrated that the rhenium phosphite system favoured the intramolecular activation rather than the intermolecular. We suggest that steric interaction was responsible for the selectivity observed in the rhenium phosphite complexes.

This is the first example where an *agostic* interaction has been observed in the formation of the C-H activation product at room temperature. Previously, this interaction has been proposed as an intermediate in the interconversion of two diastereoisomers in alkene complexes.[17]

Irradiation of $Cp^*Re(CO)\{P(OMe)_3\}(N_2)$ (**3.4**) in hydrocarbons did not produce any C-H activation product. However, a migration of one of the methyl groups to the rhenium center was observed similar to an Arbuzov rearrangement. We suggest that the formation of the phosphonate rhenium complex **3.11** is thermodynamically preferred compared with inter- or intramolecular C-H activation.

3.5 Experimental Section

3.5.1. General Methods

Manipulations, solvent purification, and routine spectroscopic measurements were carried out as described in Chapter 2.

Photochemical reactions were carried out at atmospheric pressure and at a temperature of 273-277 K with a water-jacketed 200 Watt Hanovia medium pressure mercury arc lamp as the UV source. The photochemical reactions were conducted in a Pyrex tube which was placed adjacent to the lamp. Nitrogen was passed through the reaction tube during the photolysis. Hexane, benzene and cyclohexane which were used as the solvent for the C-H activation reactions, were distilled over Na using standard methods and transferred directly into the Pyrex reaction tube under nitrogen (Linde).

The deuterated solvents (benzene-d_6, toluene-d_8, acetone-d_6, or chloroform-d_1) used for NMR spectroscopy were degassed prior to use to remove any residual oxygen. The ^{1}H and ^{13}C{^{1}H} NMR chemical shifts are reported in ppm downfield (positive) of tetramethylsilane. The ^{1}H NMR spectra in non-deuterated solvents was carried out using a standard suppression program from the Bruker pulse program library. The ^{31}P NMR chemical shifts are referenced to an external 85% H_3PO_4 sample.

3.5.2. Syntheses

Photochemical reaction of $Cp^*Re(CO)\{P(OEt)_3\}(N_2)$ (3.1) in hexane. A solution of the triethylphosphite dinitrogen complex **3.1** (20 mg, 0.036 mmol) in hexane (8 mL) was irradiated in a Pyrex tube for 10 min in a water bath at 278 K. The IR spectrum of the solution showed the total disappearance of the dinitrogen complex. The solvent was removed under vacuum at 273 K, and the residue was dissolved toluene-d_8 without purification. The ^{1}H NMR spectrum of this solution showed the intramolecular C-H activation complexes ***trans*-3.7** and ***cis*-3.7** to be present in a ratio of 26:7.0 relative to the integration area in the hydride region. The spectrum also exhibited a doublet in the metal hydride region (δ -9.67 , $J_{P\text{-}H}$ = 12.0 Hz) assigned to an *agostic-interaction* complex (***agostic*-3.7**) as a major product. ***agostic*-3.7** IR (hexane): 1860 cm^{-1} $\nu_{(CO)}$. ^{1}H NMR (toluene-d_8) at 273K: δ -9.82 (d, 1H, Re-H, $J_{P\text{-}H}$ = 12.0 Hz), 1.08 (t, $J_{H\text{-}H}$ = 7.0 Hz, $P(OCH_2C\underline{H}_3)_2$), 1.25 (t, $J_{H\text{-}H}$ = 7.0 Hz, $P(OCH_2C\underline{H}_3)_2$), 1.49 (m, $POCH_2C\underline{H}_2$), 1.87 (s, $J_{P\text{-}H}$ = 0.6 Hz, C_5Me_5) 2.85 (m, 1H, $P(OCH_2C\underline{H}_2)$, 3.32 (m, $POC\underline{H}_2CH_2$), 4.05 (m, 1H, $POC\underline{H}_2CH_2$), 3.70-4.30 (m, $P(OC\underline{H}_2CH_3)_2$). ^{31}P NMR (benzene-$d_6$) at 293 K: δ 163.93(s). ***trans*-3.7** IR (hexane): 1898 cm^{-1} $\nu_{(CO)}$. ^{1}H NMR (toluene-d_8) at 293 K: δ -10.11 (d, 1H, Re-H, $J_{P\text{-}H}$ = 28.0 Hz), 1.86 (s, C_5Me_5), 1.23 (t, 3H, $J_{H\text{-}H}$ = 7.0 Hz, $P(OCH_2C\underline{H}_3)_2$), 1.27 (t, 3H, $J_{H\text{-}H}$ = 7.0 Hz, $P(OCH_2C\underline{H}_3)_2$). ^{31}P NMR (benzene-$d_6$): δ 46.62 (d, $J_{P\text{-}H}$ = 27.0 Hz). ***cis*-3.7** IR (hexane): 1898 cm^{-1} $\nu_{(CO)}$. ^{1}H NMR (toluene-d_8) at 293 K: δ -10.20 (d, 1H, Re-H, $J_{P\text{-}H}$ = 60.0 Hz), 1.85 (d, $J_{P\text{-}H}$ = 0.8 Hz, C_5Me_5), 1.08 (t, 3H, $J_{H\text{-}H}$ = 7.0 Hz, $P(OCH_2C\underline{H}_3)_2$), 1.13 (t, 3H, $J_{H\text{-}H}$ = 7.0 Hz, $P(OCH_2C\underline{H}_3)_2$), 2.39 (m, 1H, $J_{H\text{-}H}$ = 5.6 Hz, $J_{H\text{-}H}$ = 2.0 Hz, $POCH_2CH_2$), 3.40 (m, 2H, $J_{H\text{-}H}$ = 6.5 Hz, $POCH_2CH_2$).

^{31}P NMR (benzene-d_6): δ 158.89 (d, $J_{P\text{-}H}$ = 58.8 Hz). The assignment for methylene protons for the cyclometalated products (***trans*-3.7** and ***cis*-3.7**) in the ^1H NMR were in the range of 3.75-4.40 ppm. A variable temperature ^1H NMR for the ***agostic*-3.7** was performed and the results were explained in the Results Section 3.2.2. Purification of the metal hydride complexes by either solvent extraction or column chromatography failed to produce pure products.

Photochemical reaction of $Cp^*Re(CO)\{P(OEt)_3\}(N_2)$ (3.1) in benzene-*d*$_6$. A solution of the triethylphosphite dinitrogen complex **3.1** (10 mg, 0.018 mmol) in benzene-d_6 (3 mL) was irradiated in a Pyrex tube for 12 min. The IR spectrum of the solution showed the total disappearance of the dinitrogen complex. Immediately after irradiation a ^1H NMR spectrum was taken without purification. The ^1H NMR spectrum of this solution showed the intra- and intermolecular C-H activation complexes ***cis*-, *trans*-3.7**, and ***cis*-, *trans*-3.8**, and ***agostic*-3.7**. IR (benzene-d_6): 1885 cm^{-1} (broad) $\nu_{(CO)}$. ^1H NMR (benzene-d_6): (***cis*-3.7**) δ -10.28 (d, Re-H, $J_{P\text{-}H}$ = 60.0 Hz), 1.11 (t, $P(OCH_2C\underline{H}_3)_2$, $J_{H\text{-}H}$ = 7.0 Hz), 1.18 (t, $P(OCH_2C\underline{H}_3)_2$, $J_{H\text{-}H}$ = 7.0 Hz), 1.88 (s, C_5Me_5). (***trans*-3.7**) δ -9.98 (d, 1H, Re-H, $J_{P\text{-}H}$ = 28.0 Hz), 1.25 (t, $P(OCH_2C\underline{H}_3)_2$, $J_{H\text{-}H}$ = 7.0 Hz), 1.32 (t, $P(OCH_2C\underline{H}_3)_2$, $J_{H\text{-}H}$ = 7.0 Hz), 1.89 (s, C_5Me_5). (***cis*-3.8**) δ 1.02 (t, $P(OCH_2C\underline{H}_3)_3$, $J_{H\text{-}H}$ = 7.0 Hz), 1.10 (t, $P(OCH_2C\underline{H}_3)_3$, $J_{H\text{-}H}$ = 7.0 Hz), 1.83 (s, C_5Me_5) 3.74 (m, $P(OC\underline{H}_2CH_3)_3$), 3.95 (m, $P(OC\underline{H}_2CH_3)_3$). (***trans*-3.8**) δ 1.86 (s, C_5Me_5). The ^1H NMR for the methyl in ***trans*-3.8** and methylene in complex **3.7** and ***trans*-3.8** appeared in the range of 1.15-1.35 and 3.70-4.40 ppm respectively. The sample was monitored by ^1H and ^{31}P NMR in benzene-d_6 at room temperature, and the results are summarised in the Results Section in Tables 3.4

and 3.5. Purification of the metal hydride complexes by either solvent extraction or column chromatography failed to produce pure products.

Photochemical reaction of $Cp^*Re(CO)\{P(OPh)_3\}(N_2)$ (3.2) in hexane, benzene and cyclohexane. A solution of triphenylphosphite dinitrogen complex **3.2** (50 mg, 0.07 mmol) in 10 mL of freshly distilled benzene was degassed twice from liquid nitrogen and then irradiated for 9 min at 277 K. During the photolysis a slow flux of N_2 was maintained. The IR spectrum after the photolysis reaction indicated the disappearance of the dinitrogen complex. The solvent was removed and the residual solid was redissolved in *ca* 2 mL of benzene and transferred to an air-free neutral alumina column and eluted with a mixture of benzene:hexane (2:1). Evaporation of the solvent under vacuum gave ***cis*-3.9** as a pale yellow solid which was recrystallized from benzene-hexane at 258 K in 80% yield (38 mg, 0.058 mmol). IR (hexane): 1946 cm^{-1} $\nu_{(CO)}$. ^1H NMR (acetone-d_6) δ -10.09 (d, 1H, ReH, $J_{P\text{-}H}$= 63 Hz.), 2.03 (s, 15H, C_5Me_5), 6.79-7.46 (m, 14H, η^2-$P(OC_6\underline{H}_4)(OC_6\underline{H}_5)_2$). $^{13}C\{^1H\}$NMR (benzene-d_6): δ 10.94 (s, $C_5\underline{Me}_5$), 97.55 (s, $\underline{C}_5Me_5$), 110.14(d, η^2-$P(O\underline{C}_6H_4)(O\underline{C}_6H_5)_2$, $J_{C\text{-}P}$ = 15.2 Hz), 121.42 (d, η^2-$P(O\underline{C}_6H_4)(O\underline{C}_6H_5)_2$, $J_{C\text{-}P}$ = 4.6 Hz), 121.70 (d, η^2-$P(O\underline{C}_6H_4)(O\underline{C}_6H_5)_2$, $J_{C\text{-}P}$ = 4.6 Hz), 123.32 (s, η^2-$P(O\underline{C}_6H_4)(O\underline{C}_6H_5)_2$), 124.00 (s, η^2-$P(O\underline{C}_6H_4)(O\underline{C}_6H_5)_2$), 125.22 (s, η^2-$P(O\underline{C}_6H_4)(O\underline{C}_6H_5)_2$), 126.86 (s, η^2-$P(O\underline{C}_6H_4)(O\underline{C}_6H_5)_2$), 129.78 (d, η^2-$P(O\underline{C}_6H_4)(O\underline{C}_6H_5)_2$, $J_{C\text{-}P}$ = 9.2 Hz), 132.52 (d, η^2-$P(O\underline{C}_6H_4)(O\underline{C}_6H_5)_2$, $J_{C\text{-}P}$ = 16.0 Hz), 144.29 (d, η^2-$P(O\underline{C}_6H_4)(O\underline{C}_6H_5)_2$, $J_{C\text{-}P}$ = 5.3 Hz), 152.01 (d, η^2-$P(O\underline{C}_6H_4)(O\underline{C}_6H_5)_2$, $J_{C\text{-}P}$ = 3.8 Hz), 153.39 (d, η^2-$P(O\underline{C}_6H_4)(O\underline{C}_6H_5)_2$, $J_{C\text{-}P}$ = 16.0 Hz), 162.99 (d,

η^2-P(O$\underline{C}_6H_4$)(O$\underline{C}_6H_5$)$_2$, $J_{C\text{-}P}$ = 25.9 Hz), 202.38 (d, $\underline{C}$O, $J_{C\text{-}P}$=15 Hz). ^{31}P{^{1}H} (acetone-*d*$_6$): δ 83.49 (s). M.S. (EI): *m/z* 660 (M$^+$), 630 (M$^+$- CO-2H), 537 (M$^+$-CO-2H- OC$_6$H$_4$). Anal. Calc^d. for $C_{29}H_{30}O_4PRe$: C, 52.80; H, 4.58. Found: C, 52.69; H, 4.60.

Photochemical reaction of Cp*Re(CO){P(OPh)$_3$}(N$_2$) in benzene-*d*$_6$. A solution of triphenylphosphite dinitrogen complex **3.2** (10 mg, 0 .015 mmol) in benzene-d$_6$ (2 mL) was irradiated in Pyrex tube for 5 min. Immediately after the irradiation and without purification a ^{1}H NMR spectrum was taken. The ^{1}H NMR spectrum showed the intramolecular C-H activation complex ***cis*-3.9** to be present as a minor product from this reaction. However, the spectrum also exhibited a broad doublet in the metal hydride (δ -7.95, $J_{P\text{-}H}$= 11.0 Hz.) assigned to ***agostic*-3.9**. IR (benzene-*d*$_6$): 1933 cm^{-1} $\nu_{(CO)}$. ^{1}H NMR (benzene-*d*$_6$) (ratio ***cis*-3.9:*agostic*-3.9**) (36:64) δ -9.78 (d, 1H, ReH, $J_{P\text{-}H}$ = 62.9 Hz.), -7.95 (d, 1H, ReH, $J_{P\text{-}H}$ = 11.0 Hz.), 1.84 (s. 30H, C$_5$Me$_5$), 2.03 (s, 15H, C$_5$Me$_5$), 6.79-7.46 (m, 29H, η^2-P(OC$_6\underline{H}_4$)(OC$_6\underline{H}_5$)$_2$). The ^{1}H NMR spectrum of the same sample acquired after 3 h showed the total disappearance of ***agostic*-3.9** and the concomitant growth of the ***cis*-3.9** complex. Conversion from ***agostic*-3.9** to ***cis*-3.9** was estimated to be ca. 95% complete by ^{1}H NMR spectroscopy.

Photochemical reaction of Cp*Re(CO)(Pc)(N$_2$) (3.3) in hexane. A solution of the Pc dinitrogen complex **3.3** (12 mg, 0.022 mmol) in hexane (5 mL) was irradiated in a Pyrex tube for 10 min. An IR spectrum of the resulting green solution showed the total disappearance of the dinitrogen complex and no evidence of any product. Immediately after the irradiation, the solvent was removed under vacuum at room temperature and the residue was taken up in benzene-*d*$_6$ without purification. The ^{1}H NMR spectrum of this solution exhibited only some of the free Pc ligand and organic materials that were not identified.

Photochemical reaction of Cp*Re(CO)(Pc)(N_2) (3.3) in benzene. A solution of the Pc dinitrogen complex **3.3** (20 mg, 0.038 mmol) in benzene (6 mL) was irradiated in a Pyrex tube for 10 min. During the photolysis a slow flux of N_2 was maintained. The IR spectrum of the slightly yellow solution indicated the total disappearance of the dinitrogen complex. After the irradiation the sample was taken up in benzene without purification. A ^{1}H NMR spectrum of this solution exhibited one resonance in the metal hydride region. IR (benzene): 1913 cm^{-1} $\nu_{(CO)}$. ^{1}H NMR (benzene): δ -9.20 (d, 1H, Re-H, $J_{P\text{-}H}$ = 68.8 Hz), -0.50 (s, 3H, P(OCH_2)$_3$C$\underline{H_3}$), 1.72 (s, 15H, C_5Me_5), 3.34 (d, 6H, P(OC$\underline{H_2}$)$_3$CCH_3, $J_{P\text{-}H}$ = 6.0 Hz). The limited spectroscopic evidence was assigned to the intermolecular benzene C-H activation product *cis*-Cp*Re(CO)(Pc)(C_6H_5)H (***cis*-3.10**). A ^{1}H NMR spectrum of the same sample acquired after 1 h at room temperature showed a decrease in intensity in the metal hydride region. Purification of the new complex by either solvent extraction or column chromatography failed.

Photochemical reaction of Cp*Re(CO){P(OMe)$_3$}(N_2) (3.4) in hexane, cyclohexane and benzene. A solution of the trimethylphosphite dinitrogen complex **3.4** (50 mg, 0.10 mmol) in hexane (10 mL) was irradiated in a Pyrex tube for 15 min. An IR spectrum of the resulting brown-yellow solution showed the total disappearance of the dinitrogen complex. After removal of the volatile materials under vacuum at room temperature, the remaining residue was redissolved in *ca.* 2 mL of hexane and carefully transferred to an air-free neutral alumina column and eluted with hexane-ether (4:1).

Removal of the solvent under vacuum gave a yellow solid which was recrystallized from hexane at 265 K to provide **3.11** as a pale yellow solid in 49% yield (23 mg, 0.024 mmol). IR (hexane): 1900, 1879 cm^{-1} $\nu_{(CO)}$. ^1H NMR (acetone-d_6): δ 0.74 (s, 3H, Re-CH_3), 1.68 (s, 15H, C_5Me_5), 3.42-3.49 (d-d, 6H, $PO(OMe)_2$, $J_{P\text{-}H}$ = 8.0 Hz). $^{13}C\{^1H\}$NMR (acetone-d_6): δ -0.98 (d, $J_{C\text{-}P}$ = 11.7 Hz, Re-$\underline{C}H_3$), 10.15 (s, C_5Me_5), 51.35 (d, $PO(O\underline{C}H_3)_2$, $J_{C\text{-}P}$ = 11.4 Hz) 52.66 (d, $PO(O\underline{C}H_3)_2$, $J_{C\text{-}P}$ = 11.4 Hz), 100.42 (s, $\underline{C}_5Me_5$), 221.35 (d, $\underline{C}O$, $J_{C\text{-}P}$ = 28.9 Hz). $^{31}P\{^1H\}$ (acetone-d_6): δ 80.70 (s). M.S. (EI): *m/z* 946 (M^+), 918 (M^+- CO), 844 (M^+-CO-$C_4H_{10}O$). Anal. Calc^d. for $C_{28}H_{48}O_8P_2Re_2$: C, 35.52; H, 5.07. Found: C, 35.55; H, 4.98.

Photochemical reaction of Cp*Re(CO)(PPh_3)(N_2) (3.5) in benzene, benzene-*d_6*, hexane, and cyclohexane. A solution of triphenylphosphine dinitrogen **3.5** (50 mg, 0.07 mmol) in 10 mL of freshly distilled benzene was degassed twice from liquid nitrogen and then irradiated for 10 min at 277 K in a Pyrex tube. During the photolysis a slow flux of N_2 was maintained. The IR spectrum after the photolysis reaction indicated the disappearance of the dinitrogen complex. Immediately after the irradiation and without purification a ^1H NMR spectrum was taken. The ^1H NMR spectrum showed the intramolecular C-H activation complex ***cis-* 3.12**. The spectrum also exhibited a broad doublet in the metal hydride region assigned to ***agostic-* 3.12.** IR (benzene): 1913 cm^{-1} $\nu_{(CO)}$. ^1H NMR (benzene) ***agostic*-3.12** δ -7.55 (d, ReH, $J_{P\text{-}H}$= 12 Hz), 1.69 (s, C_5Me_5); ***cis*-3.12** δ -7.89 (d, ReH, $J_{P\text{-}H}$= 73 Hz), 1.78 (s, C_5Me_5).

Reaction of *cis*-Cp*Re(CO){η^2-P(C_6H_4)Ph_2}(H) (*cis*-3.12) with $CHCl_3$ or $CDCl_3$. The intramolecular C-H activation product ***cis*-3.12** was dissolved in $CHCl_3$ or

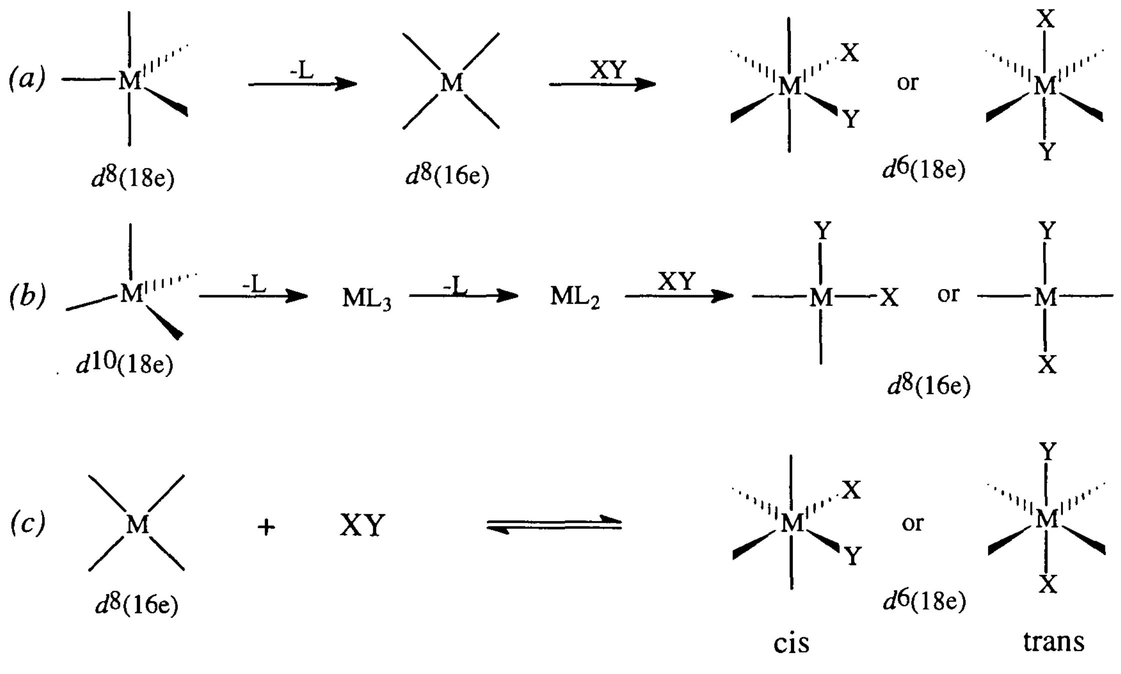
$CDCl_3$ (2 mL) at room temperature under nitrogen and the solution was allowed to stir for 3 h. A ^1H NMR spectrum ($CDCl_3$) of the solution showed the complete disappearance of ***cis*-3.12** and the presence of the orthometalated-chloro complex *cis*-Cp*Re(CO){η^2-$P(C_6H_4)Ph_2$}(Cl) (***cis*-3.13**). Removal of the solvent under vacuum and subsequent extraction with diethyl ether (3 x 20 mL) gave ***cis*-3.13** as a yellow-orange solid. IR (benzene): 1908 cm^{-1} $\nu_{(CO)}$. ^1H NMR ($CDCl_3$): δ 1.53 (s, 15H, C_5Me_5), 6.92 (m, 2H, η^2-$P(C_6H_4)Ph_2$), 7.14 (m, 1H, η^2-$P(C_6H_4)Ph_2$, 7.25 (m, 1H, η^2-$P(C_6H_4)Ph_2$), 7.31 (m, 3H, η^2-$P(C_6H_4)Ph_2$), 7.46 (m, 3H, η^2-$P(C_6H_4)Ph_2$), 7.55 (m, 2H, η^2-$P(C_6H_4)Ph_2$), 7.76 (m, 2H, η^2-$PC_6H_4)(Ph_2)$. $^{13}C\{^1H\}$NMR ($CDCl_3$): δ 9.62 (s, $C_5\underline{Me_5}$), 101.02 (s, $\underline{C_5}Me_5$), 123.50-137.51 (η^2-$P(\underline{C}_6H_4)(\underline{C}_6H_5)_2$), 209.64 (s, $\underline{C}O$). M.S. (EI): *m/z* 646 (M^+), 618 (M^+- CO). Anal. Calc^d. for $C_{29}H_{29}ClOPRe$: C, 53.91; H, 4.49. Found: C, 53.73; H, 4.59.

CHAPTER 4

Oxidative-Addition of the C-Cl bond to Rhenium Dinitrogen Complexes.

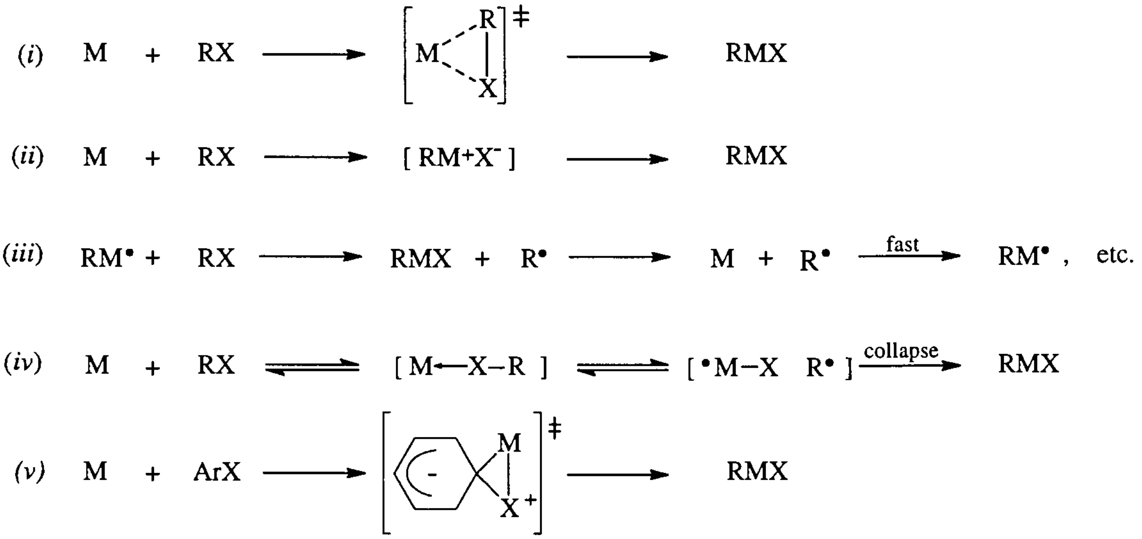
4.1. Introduction

The oxidative-addition reaction represents one of the most basic transformations in organometallic chemistry.[85] Oxidative-addition is a reaction in which the metal center is oxidized by addition of a substrate (XY) to form an M(X)(Y) complex. The electron count in the metal center increases by two units and a vacant site is usually required. The reaction can go via a 16-electron complex (Scheme 4.1 *(c)*) or a 2-electron site can be opened in an 18-electron complex by loss of a ligand (Scheme 4.1 *(a* or *b)*). As shown in Scheme 4.1, either a cis or a trans isomer complex can be obtained .[86]



Scheme 4.1 General scheme for oxidative-addition reaction

It is well known that the oxidative-addition of alkyl or aryl halides may proceed by different mechanisms (Scheme 4.2), such as; *(i)* concerted frontside displacement (3-center), *(ii)* concerted nucleophilic displacement (2-center, S_N2), *(iii)* radical chain (propagation sequence), *(iv)* radical non-chain (electron transfer), and *(v)* aromatic nucleophilic substitution (S_NAr).[87] The mechanism operating in a particular case depends upon the properties of the metal, the substrate (XY), as well as the ancillary ligands and experimental conditions.[85c]



Scheme 4.2 Different mechanisms proposed for oxidative-addition.

Extensive studies of mechanisms for the oxidative-addition reaction of *alkyl* halides have been carried out for d^{10} Ni(0), Pt(0) and Pd(0), and d^8 Ir(I), and Pt(II) complexes,[85,86] but less attention has been paid to the oxidative-addition reactions of *aryl* halides because of the low reactivity observed in the case of the *aryl* carbon chlorine bond.[86-90]

In the previous chapter, we reported that "[Cp*Re(CO)(L)]" (L = $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$, PPh_3, and Pc) (**3.1-3.5**) generated *in situ* by the photochemical reaction of Cp*Re(CO)(L)(N_2) in benzene did not yield the isolable phenyl hydride complex.

According to the literature, unstable alkyl or aryl hydride complexes can generally be stabilized in the halide form by thermal exchange of the hydride ligand by using a halogenated solvent (such as: CCl_4, $CHBr_3$) to generate the more stable alkyl or aryl halide complex.[48a,48c]

However, we found that the treatment of the photolysis product with a halogenated solvent did not afford the corresponding phenyl halide complex. Instead, the only species detectable was the rhenium dihalide complex Cp*Re(CO)(L)X_2 (X = Cl, Br).

Because of this, it was of interest to attempt to prepare the expected phenyl halide complexes [Cp*Re(CO)(L)PhX] by an alternative method in order to assess their stabilities. It was possible that these species were, in fact, the primary products of reaction of an unstable phenyl hydride complex Cp*Re(CO)(L)PhH with a halogenated solvent which then further reacts to give the dihalide complexes. Therefore, in an attempt to prepare Cp*Re(CO)(L)PhCl, we investigated the photochemical reaction of the rhenium dinitrogen complexes Cp*Re(CO)(L)(N_2) (L = $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$, PMe_2Ph, and Pc) (**3.1-3.6**) (Figure 4.1) in chlorobenzene and the reactivity of the product formed in chlorinated solvents.

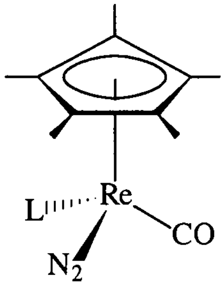


Figure 4.1 Structure of dinitrogen rhenium complexes L = $P(OEt)_3$ (**3.1**), $P(OPh)_3$ (**3.2**), Pc (**3.3**), $P(OMe)_3$ (**3.4**), and PMe_2Ph (**3.6**).

4.2. Results

4.2.1. Syntheses and Characterization of Rhenium Phenyl Chloride Complexes.

The complexes with a general formula Cp*Re(CO)(L)PhCl, (L= $P(OEt)_3$ (**4.1**), $P(Me_2Ph)$ (**4.2**), Pc (**4.3**), and $P(OMe)_3$ (**4.4**), and Cp*Re(CO)$\{\eta^2\text{-}P(OC_6H_4)(OPh)_2\}$H (**3.9**) were prepared by irradiation of the corresponding rhenium dinitrogen complex (**3.1-3.6**) in chlorobenzene. These complexes were purified by chromatographic techniques and were obtained as yellow-orange microcrystalline solids in greater than 60% yield by recrystallization from hexane-benzene. They are air-stable in the solid state and in solution.

The complexes **4.1-4.4** were obtained only as the single isomers in which the phenyl is *trans* to chloride (Figure 4.2). These new complexes have been identified by IR, ^{1}H NMR, ^{13}C{^{1}H} NMR and mass spectroscopy, and spectroscopic data are listed in Table 4.1.

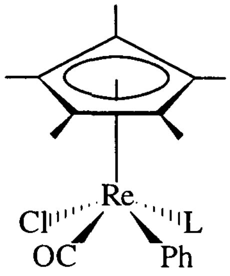


Figure 4.2 Structure of Cp*Re(CO)(L)PhCl, (L = $P(OEt)_3$ (**4.1**), PMe_2Ph (**4.2**), Pc (**4.3**), and $P(OMe)_3$ (**4.4**).

Contrasting with the above, irradiation of the triphenylphosphite complex Cp*Re(CO){$P(OPh)_3$}(N_2) (**3.2**) under similar conditions gave the orthometalated C-H activation product Cp*Re(CO){η^2-$P(OC_6H_4)(OPh)_2$}H (***cis*-3.9**), which was characterized by ^{1}H NMR and MS. This compound is identical to the one described in Chapter 3 and its stereochemistry was based on assignments similar to those in Section 3.3.2.

The IR spectra of **4.1-4.4** exhibited a single absorption in the range 1910-1860 cm^{-1} attributed to the carbonyl group. The ^{1}H NMR spectrum of **4.1** exhibited the expected resonances for Cp*, phosphite, and the phenyl ligand. The Cp* resonance was a singlet at δ 1.61 (relative integral 15H), the ethylphosphite ligand gave a methyl resonance at δ 1.26 (9H) and a methylene resonance at δ 4.12 (6H). The aromatic region for **4.1** clearly showed the presence of three distinguishable proton environments corresponding to the *ortho-*, *meta-* and *para-* position protons of the phenyl ligand: a multiplet at δ 6.94, (relative integral area 1H) assigned to the *p-* proton, a multiplet at δ 7.09, (relative integral 2H) assigned to the *m-* protons, and a high field multiplet at

Table 4.1. Spectroscopic data for complexes Cp*Re(CO)(L)PhCl (**4.1-4.4**), and Cp*Re(CO){η^2-P(OC_6H_4)($OPh)_2$}H (*cis*-**3.9**).

Complex	(L)	**IR** {$\nu_{(CO)}$, **cm^{-1}**}^{a}	^{13}C{^{1}H}, $\delta_{(CO)}$^{b}	**MS** (*m/z*) **M$^+$**	 **Base**
cis-3.9	P(OPh)$_3$	1927	202 (15)	660	630
4.1	P(OEt)$_3$	1884	207 (20)	628	600
4.2	P(Me_2Ph)	1867	224 (24)		523
4.3	Pc	1898	194	610	528
4.4	P(OMe)$_3$	1889	221 (34)	586	558

a. In CH_2Cl_2; b. In $CDCl_3$ and coupling constant ($^2J_{P\text{-}C}$ Hz) in parenthesis

δ 7.92 (relative integral 2H) assigned to the *o*- protons (Figure 4.3). These assignments are similar to those established previously for CpRe(CO)(NO)Ph and related substituted phenyl complexes by using NOE and decoupling experiments.[91] Corresponding ^{1}H NMR spectra were observed for the complexes **4.2-4.4,** but for **4.2** the phenyl resonances from the phenyl ligand and the PMe_2Ph ligand were overlapped and two resonances were observed for the methyl groups in the phosphine ligand at δ 2.02 and δ 2.12 with a $J_{P\text{-}H}$ = 9.8 Hz.

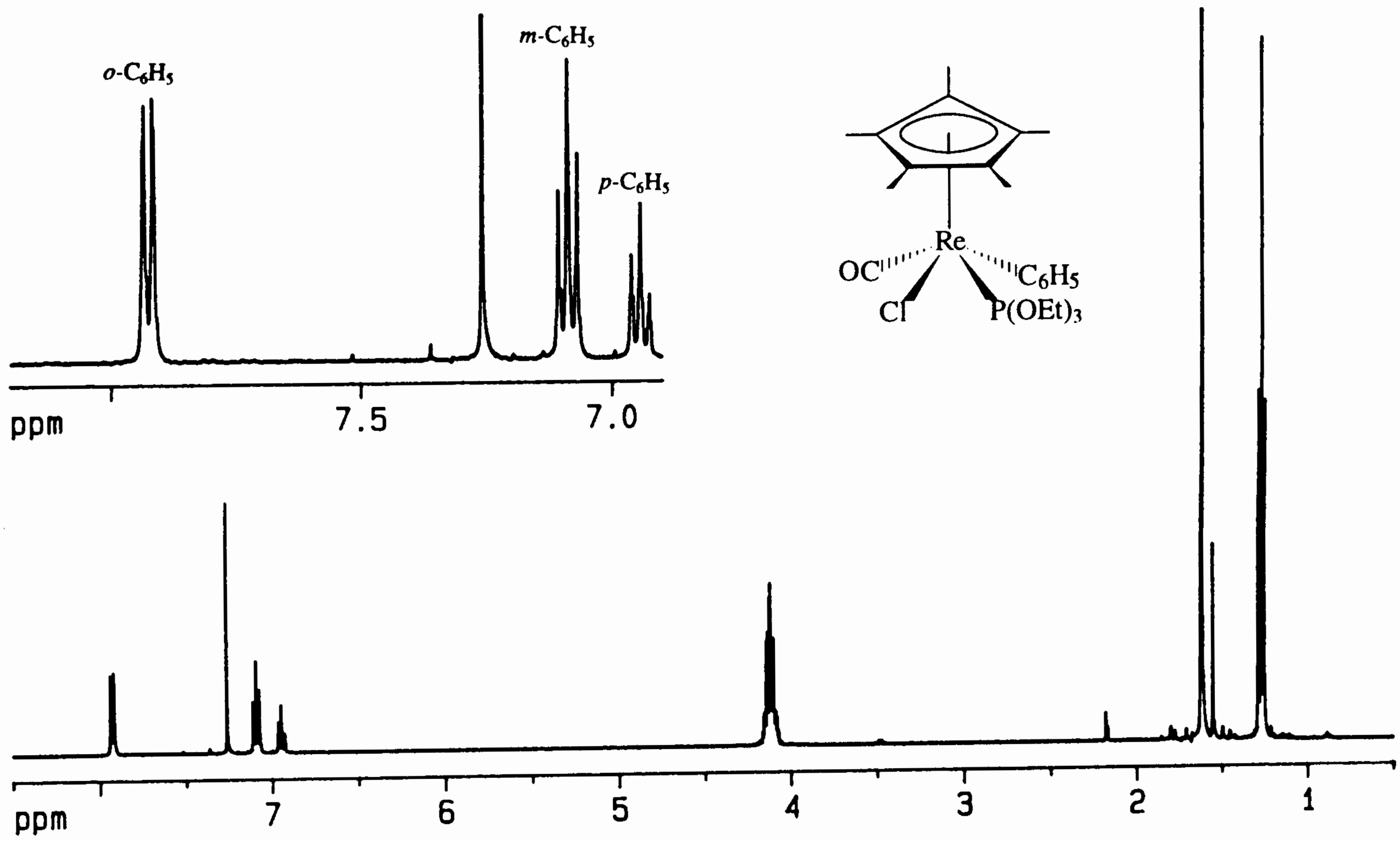


Figure 4.3 ^{1}H NMR spectrum of Cp*Re(CO)[(P(OEt)$_3$]PhCl (**4.1**) in CDCl$_3$.

The $^{13}C\{^1H\}$ NMR spectra were also recorded for complexes **4.1-4.3** respectively. The aromatic carbons showed their expected resonances in the region δ 120-145, the resonances for the methyl and ring carbons of the η^5-C_5Me_5 ligand were observed at *ca.* δ 10.05 and 102.00 respectively and the carbonyl carbon resonances were observed in the region δ 225-190. To lend further evidence to the phosphorus coordination in these complexes, the $^{13}C\{^1H\}$ NMR also showed that the carbonyl resonance was split into a doublet with a $^2J_{C\text{-}P}$ coupling of 15-34 Hz. The Pc complex **4.3** exhibited the carbonyl resonance only as a singlet which indicated that the $^2J_{C\text{-}P}$ was too small to be observed. The magnitude of this coupling constant suggests that the phosphorus group in these four legged "piano stool" complexes is *trans* to the carbonyl moiety.[92] An appreciable downfield shift for the carbonyl carbon resonance was observed in the $^{13}C\{^1H\}$ NMR spectra in Cp*Re(CO)(L)PhCl as L is changed in the sequence L = Pc, $P(OMe)_3$, $P(OEt)_3$ and PMe_2Ph. A similar observation has been reported in $R_3PNi(CO)_3$ (R = alkyl or alkoxy) complexes.[93] The overall magnitude of the shift was ~30 ppm (Table 4.1).

The EIMS spectrum of **4.1** gave a weak parent M^+ peak at *m/z* 628, the base peak at *m/z* 600 corresponded to the loss of CO, and then loss of C_6H_6 gave a fragment of *m/z* 522. The complexes **4.3** and **4.4** showed corresponding fragmentation patterns. The EIMS spectrum of **4.2** did not give a parent M^+ peak, but a base peak at *m/z* 523 corresponding to the loss of C_6H_5 was observed.

The IR spectrum for ***cis*-3.9** showed a single $\nu_{(CO)}$ absorption at 1927 cm^{-1} in CH_2Cl_2. In the ^1H NMR spectrum, obtained in $CDCl_3$, a singlet at δ 1.99 with a relative integral of 15H was assigned to the Cp* ligand, and a set of multiplets in the range

δ 6.80 - 7.41 in the aromatic region with total relative integral 14H were assigned to the ortho-metalated phenylphosphite moiety. The spectrum also exhibited a doublet in the metal hydride region at δ -10.12, with a relative integral 1H, and $J_{P\text{-}H}$ = 61.0. The complex ***cis-* 3.9** showed a parent M^+ peak at *m/z* 660 and a base peak at *m/z* 630 corresponded to the loss of CO and 2H from M^+ (Figure 4.4).

4.2.2 Reactivity of Cp*Re(CO){P(OEt)$_3$}PhCl (4.1) Cp*Re(CO)(PMe$_2$Ph)PhCl (4.2), and Cp*Re(CO){η^2-P(OC$_6$H$_4$)(OC$_6$H$_5$)$_2$}H (*cis*-3.9) with Chlorinated Solvents.

When Cp*Re(CO){P(OEt)$_3$}PhCl (**4.1**) was dissolved and stirred in either $CHCl_3$ or CCl_4 at room temperature for 6 h , no change of $\nu_{(CO)}$ was observed in the IR spectrum. By heating the same solution under refluxing condition for 5 h, still no change was observed in the IR spectrum. A similar situation was also encountered for the complex Cp*Re(CO)(PMe$_2$Ph)PhCl (**4.2**).

When Cp*Re(CO){η^2-P(OC$_6$H$_4$)(OC$_6$H$_5$)$_2$}H (***cis*-3.9**) was dissolved in $CHCl_3$ and stirred under nitrogen overnight at room temperature, the ^{1}H NMR and IR spectra in $CDCl_3$ and $CHCl_3$ respectively, showed no evidence of deterioration or exchange of the hydride ligand with chlorine. A solution of Cp*Re(CO){η^2-P(OC$_6$H$_4$)(OC$_6$H$_5$)$_2$}H in chlorobenzene was warmed to 313 K for 2 h under nitrogen, and the reaction was followed by IR spectroscopy. After this time, the IR showed no change in the carbonyl region. The same solution was heated under refluxing conditions for 3 h, and the IR spectrum again showed no evidence of change.

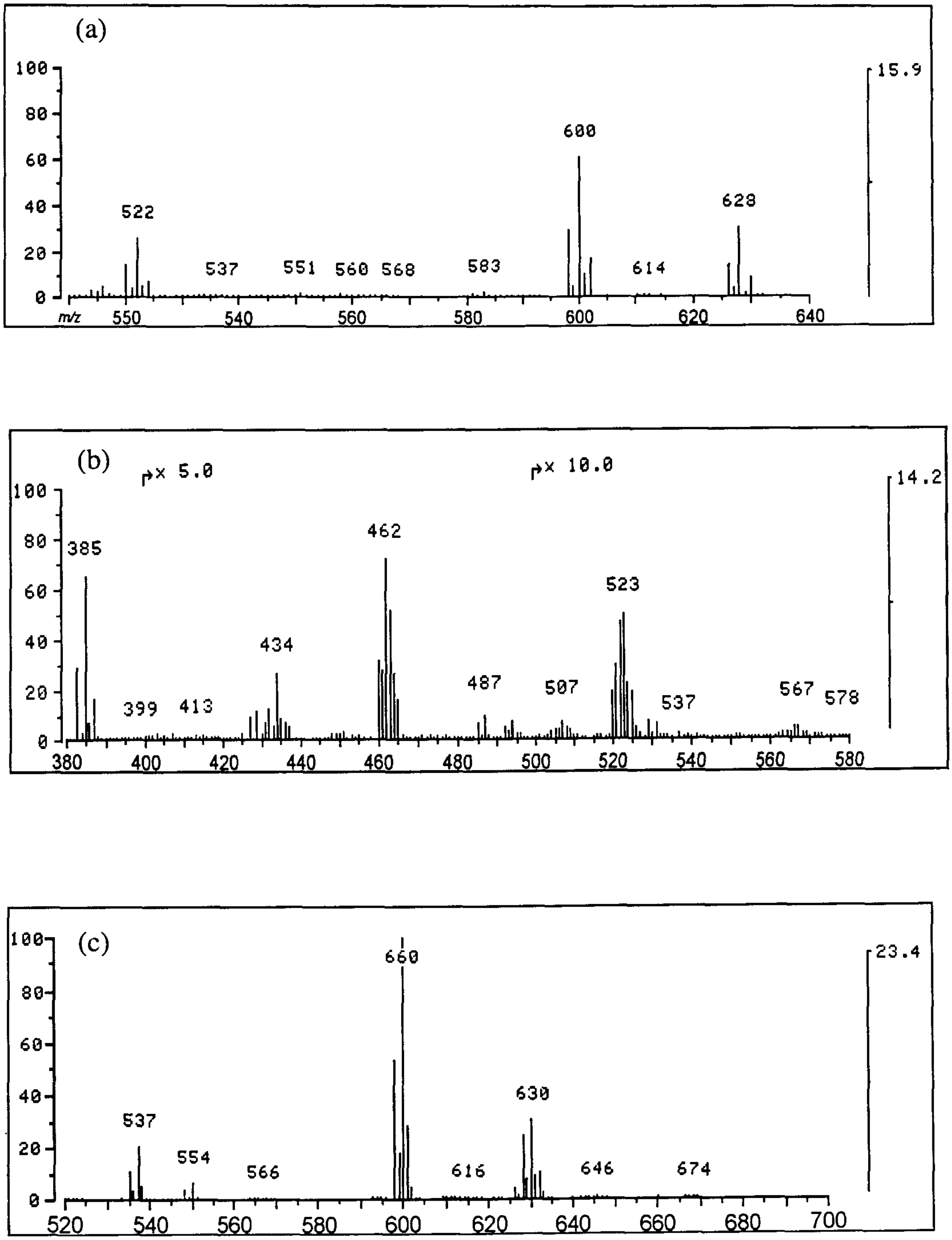


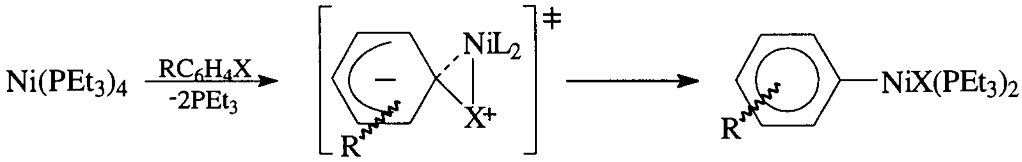
Figure 4.4 Mass spectra of the complexes **4.1**, **4.2** and ***cis*-3.9**.

(**a**) Cp*Re(CO){P(OEt)$_3$}PhCl (**4.1**); (**b**) Cp*Re(CO)(PMe$_2$Ph)PhCl (**4.2**); (**c**) Cp*Re(CO){η^2-P(OC$_6$H$_4$)(OPh)$_2$}H (*cis*-**3.9**).

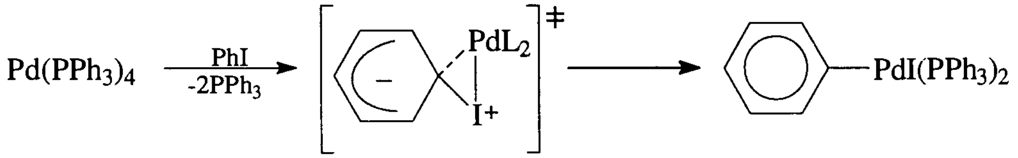
4.3. Discussion

4.3.1. Oxidative-Addition of the C-Cl Bond of Chlorobenzene.

According to the literature, the most common mechanism proposed for oxidative-addition of *aryl* halides proceeds via an "aromatic nucleophilic displacement" (Scheme 4.2 *(v)*). This mechanism has been proposed in oxidative-addition studies in Ni(0)[88], and Pd(0)[89] complexes.



Eq 4.1



Eq 4.2

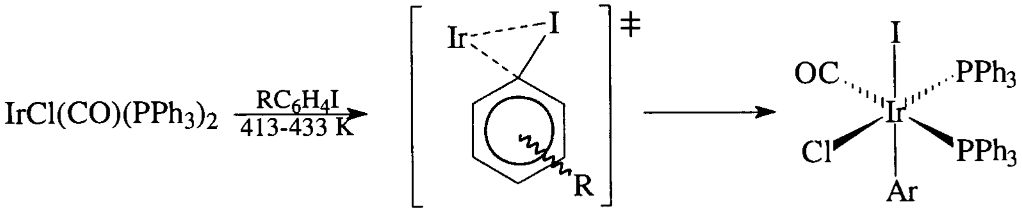
Pflüger's group[94] have studied the mechanism of the reaction of $Pd(PPh_3)_4$ with *aryl* iodides, and they proposed that an electron transfer mechanism (Scheme 4.2 *(iv)*) is the preferred route for the formation of the oxidative-addition product $PdPhI(PPh_3)_2$ (Equation 4.3) rather than S_NAr, which was proposed early by Fitton's group.[89a]

$$\mathrm{Pd(PPh_3)_4} \xrightarrow[\mathrm{-PPh_3}]{\mathrm{PhI^a}} \left[\mathrm{R^\bullet\ PdI(PPh_3)_2^\bullet}\right]^\ddagger \longrightarrow \mathrm{PhPdI(PPh_3)_2} \qquad \text{Eq 4.3}$$

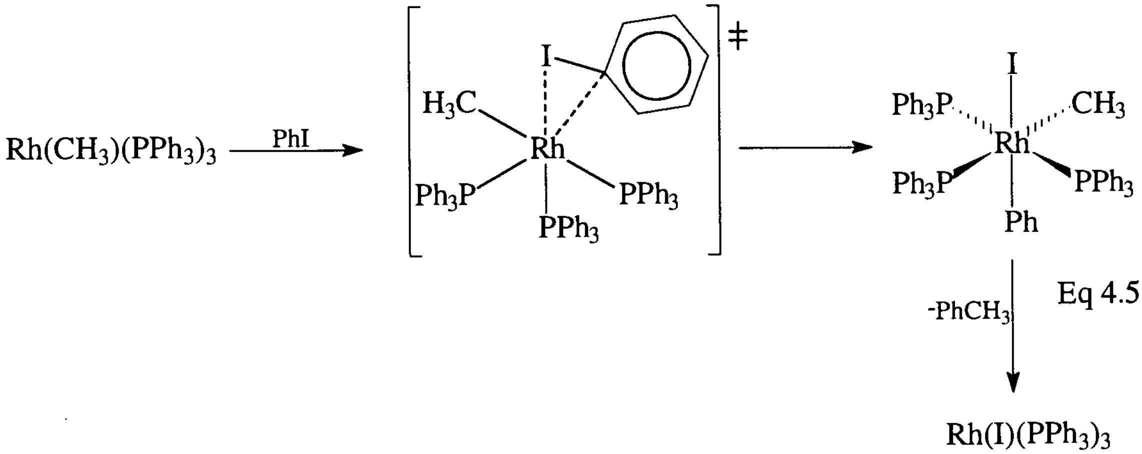
a. In C_7H_8 or THF

They observed that the change of the solvent (polarity) in the experimental conditions did not affect the enthalpy of activation and lead to similar activation entropies in both solvents ($\Delta G^{\#}$ = 13 J mol^{-1}K^{-1} (THF), $\Delta G^{\#}$ = 7 J mol^{-1}K^{-1} (toluene)). These results suggested that the transition state of addition of *aryl* halide to the unsaturated intermediate "[$Pd(PPh_3)_2$]" had no significant ionic character.[94]

A second mechanism has been proposed for *aryl* halides, one that was originally suggested by Ugo and co-workers for *alkyl* halides.[95] They proposed a concerted frontside displacement (Scheme 4.2 *(i)*) as an intermediate in the formation of *alkyl* halide complexes. The same mechanism has been observed for iridium(I)[90a], rhodium(I)[96] and platinum(II)[97] for *aryl* halides (Eqs. 4.4 - 4.5).



Eq 4.4



Eq 4.5

In contrast, a radical non-chain mechanism (Scheme 4.2 *(iv)*) has been proposed for oxidative-addition of aryl halide to $IrCl(CO)(PMe_3)_2$. It has been suggested that the difference in the phosphine ligand is probably the key in the alternative pathway proposed for this complex.[90b]

The discrimination of the two mechanisms (Scheme 4.2 *(i)* and *(iv)*) on the basis of correlation between rate constant of oxidative-addition and the driving force for single-electron transfer is difficult. However, the two mechanisms can be distinguished on the basis of their activation entropies. The concerted mechanism (Scheme 4.2 *(i)*) involves a specific organization of the organic and metallic moieties in the activated complex which should be reflected in relatively large activation entropies.[98] By comparison, an outer-sphere electron-transfer (Scheme 4.2 *(iv)*) should involve a relatively small entropy of activation.[94] It is important to point out that in all the examples shown in oxidative-addition with *aryl* halide, the only isomer observed was the *trans* form.

Only a few examples of oxidative-addition have been reported for "piano stool" rhenium complexes with *alkyl* or *aryl* halides (See Equations 4.6- 4.7).[99]

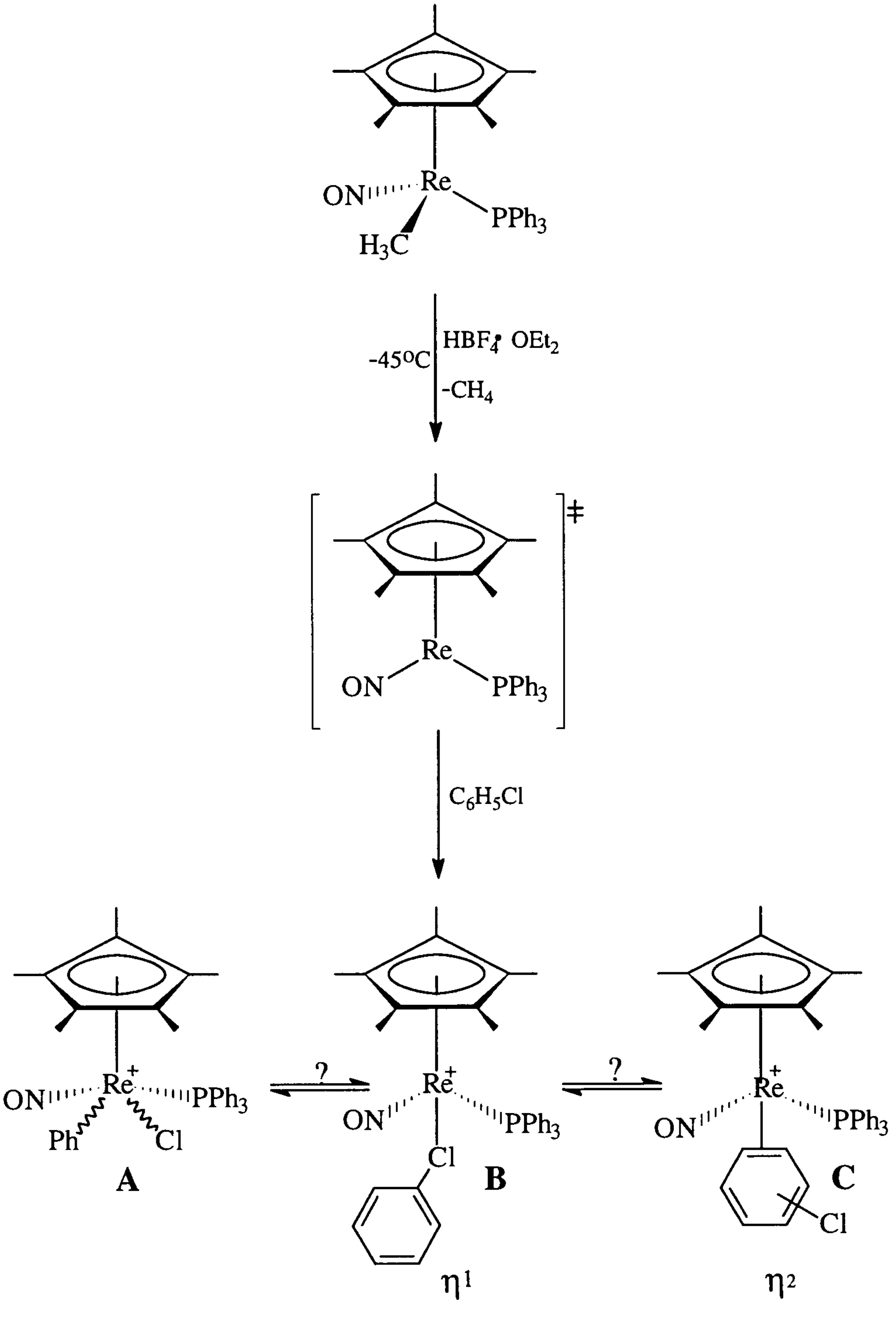
$$[(\eta^6\text{-}C_6H_6)Re(PMe_3)_2]_2 \xrightarrow[\text{THF, rt}]{\text{MeI}} (\eta^6\text{-}C_6H_6)Re(PMe_3)_2I \qquad \text{Eq 4.6}$$

$$\begin{tikzcd}
(C_5H_5)Re(NO)(PPh_3)(CH_3) \arrow[r, "HBF_4\bullet Et_2O", "MeX"'] & {[(C_5H_5)Re(NO)(PPh_3)(XCH_3)]^+} \arrow[d, "r\,t"] \\
 & {[(C_5H_5)Re(NO)PPh_3(X)(CH_3)]^+}
\end{tikzcd} \qquad \text{Eq 4.7}$$

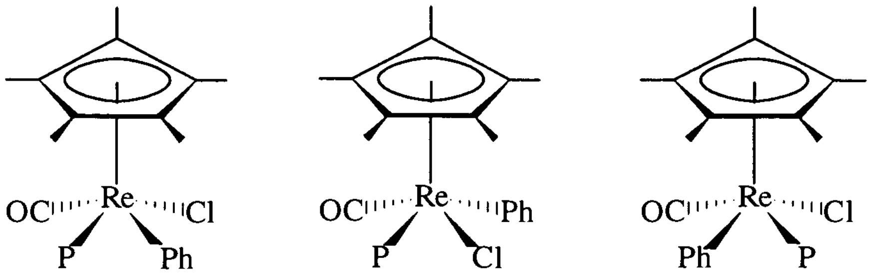
In particular, from Gladysz's group there have been studies of the reactivity of $CpRe(NO)(PPh_3)(CH_3)$ with chlorobenzene at low temperature. The intermediate "$[CpRe(NO)(PPh_3)]^+$" reacts with chlorobenzene and they observed three different species at 225 K (Scheme 4.3). The complex **A** is an oxidative-addition of chlorobenzene, complex **B** is a η^1- species where the chloride group is coordinated to the metal center and complex **C** is a η^2- species where the phenyl group is coordinated to the metal center. No isolable products were obtained at room temperature.[100]

When the complexes Cp*Re(CO)(L)(N_2) (L= $P(OMe)_3$, $P(OEt)_3$, Pc, PMe_2Ph, and $P(OPh)_3$) are irradiated in chlorobenzene, an intermediate [Cp*Re(CO)(L)] is proposed to be generated by loss of N_2, as in the case of photolysis in hydrocarbons.[57,58] This intermediate has also been proposed by Bergman *et al.* in their studies of C-H activation with hydrocarbons in other "piano stool" rhenium complexes (for futher discussion see Chapter 3).[51] This reactive 16-electron intermediate is then considered to undergo oxidative-addition of the C-Cl bond of the chlorobenzene to give the observed phenyl chloro complex.

In this work, no specific experiments have been undertaken to determine the preferred mechanism of the oxidative-addition. However, it may be significant that only a single isomer was observed in each case. Theoretically two other isomers are possible for the four-legged piano-stool configuration (Figure 4.5). The stereochemistry of isomer **III** was deduced on the basis of the observed $^2J_{C\text{-}P}$ value for $\delta_{(CO)}$ in the $^{13}C\{^1H\}$ NMR. Isomer **III** is the only one in which the CO and P are mutually *trans*. Typical $^2J_{C\text{-}P}$ values for this situation are in the range 0 - 15 Hz. In isomer **I** and **II** the CO and P are mutually *cis*. In this case typical $^2J_{C\text{-}P}$ value are somewhat larger than 30 Hz.[92] A similar trend has been observed in CpMo(CO)(PR_3)(L) complexes where *cis* and *trans* isomers have been characterized.[92]



Scheme 4.3 Proposed products from the reaction of Cp*Re(NO)(PPh_3)Me with chlorobenzene at 225 K by Gladysz's group.[100]



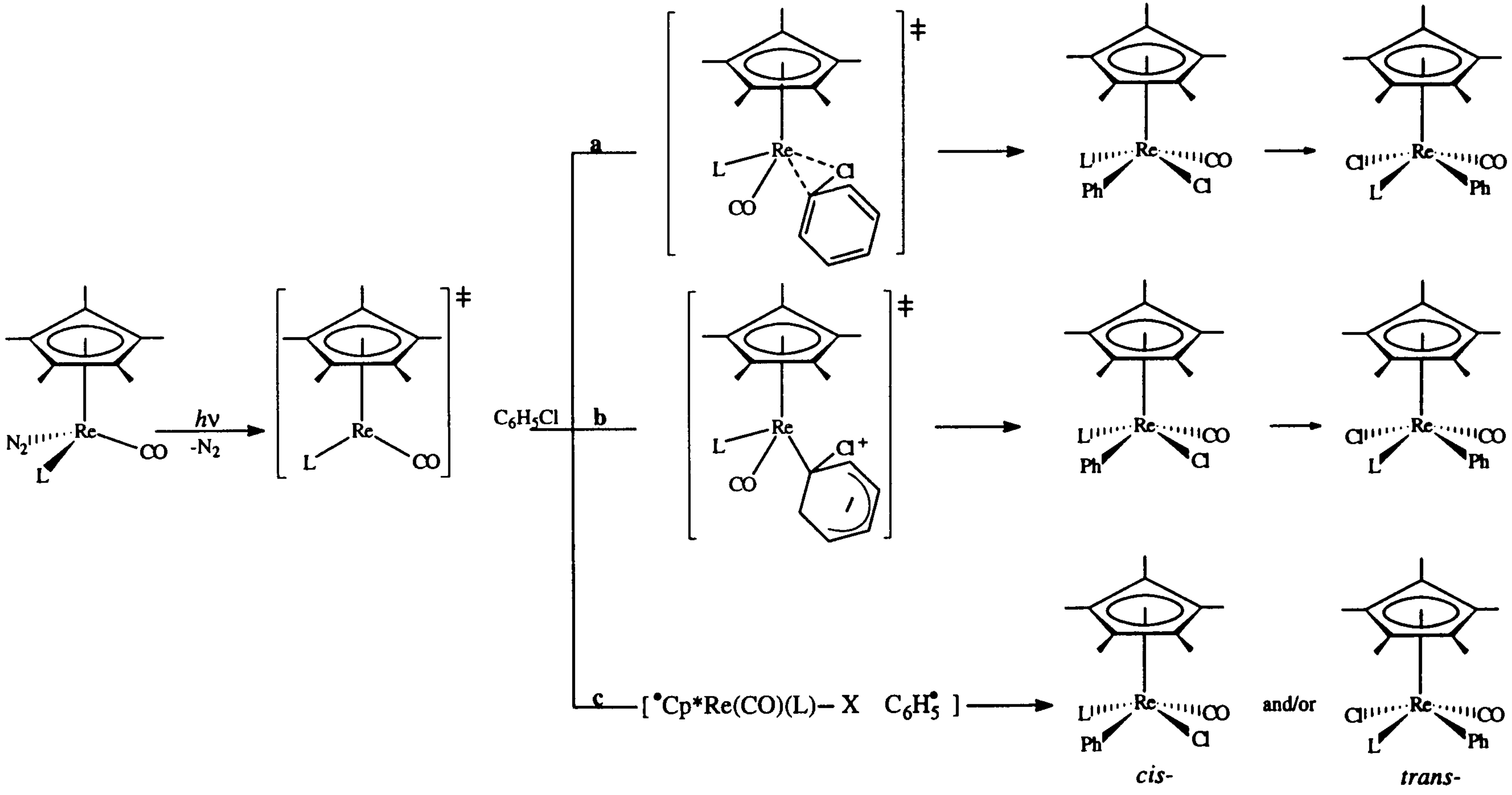
I cis **II** cis **III** trans

Figure 4.5 Proposed isomers for the oxidative-addition reaction (P = phosphite ligand).

In general, three possible mechanisms can be proposed for the oxidative-addition of an *aryl* halide, and these are summarized in the Scheme 4.4. In (**a**) a three-center 2e interaction of the C-Cl bond with Re is proposed for the transition state, and in (**b**) a S_NAr mechanism. These pathways will produce only a *cis* isomer, which then may isomerize to the more stable *trans* form and, (**c**), an electron transfer mechanism, where the configuration of the final product can be either the *cis* or *trans* isomer or both.

However, we observed only the trans isomer after the phoytolysis in chlorobenzene. From this observation, it is possible that this reaction might not go by three-center 2 electron transition state, but we can not exclude the possibility that the *cis* isomer under photochemical or thermal conditions isomerized to a more stable *trans* isomer.

In summary, several possible routes exist for these oxidative-addition reactions with *aryl* halides. The choice of a particular pathway will depend on the nucleophilicity of the metal center, the ability of the metal complex to undergo one-electron processes and the nature of the ligands.



Scheme 4.4 Proposed mechanisms for the formation of complexes **4.1-4.4**.

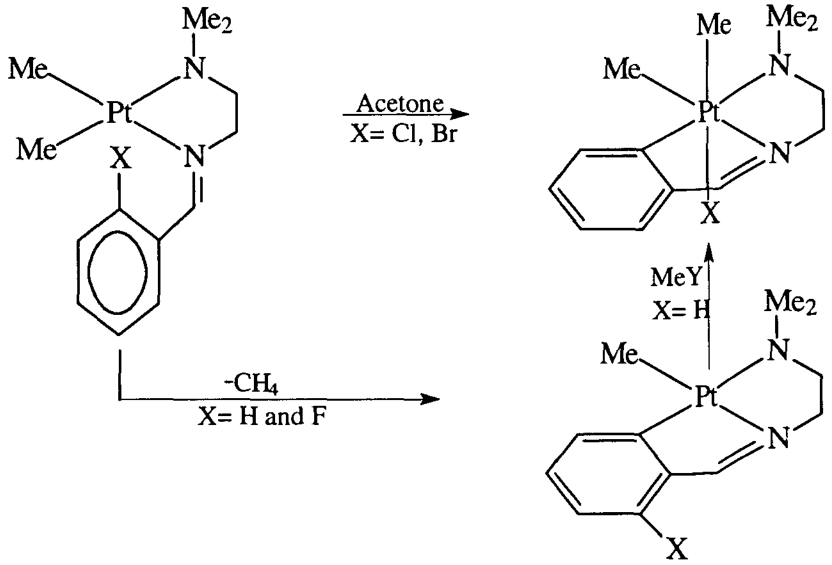
4.3.2 Synthesis and Characterization of New Rhenium Phenyl Chloride Complexes

From the IR spectra it was observed that the carbonyl band shifted depending on the phosphorus ligand (see Table 4.1). This effect was produced by the electronic properties of the phosphorus group (σ-donor or π-acceptor abilities). The greater the σ-donor (or the poorer the π-acceptor) ability of the phosphorus ligand, the higher the degree of charge delocalization into the carbonyl antibonding orbitals and the lower the $\nu_{(CO)}$. For example, the IR values for $\nu_{(CO)}$ followed the order Pc > $P(OMe)_3$ > $P(OEt)_3$ >PMe_2Ph which correlates with the increasing σ donor ability of the phosphorus ligand. This effect was corroborated in the chemical shift of the carbon in the carbonyl group where the better σ-donor (PMe_2Ph > $P(OEt)_3$ > Pc) showed a more upfield resonance.[93]

4.3.3 C-H Bond Activation vs C-Cl Bond Activation.

The photochemical reaction of $Cp^*Re(CO)\{P(OPh)_3\}(N_2)$ (**3.2**), in chlorobenzene gave only $Cp^*Re(CO)\{\eta^2\text{-}P(OC_6H_4)(OC_6H_5)_2\}H$ (**3.9**), the product of intramolecular C-H activation, and no evidence of oxidative-addition of the C-Cl bond of chlorobenzene was observed. The ^1H NMR and the MS spectroscopic data for this product were compared with the product obtained in Chapter 3 (Section 3.2.3) and are in agreement with the formation of ***cis*-3.9** in both cases. Therefore, in this reaction orthometalated C-H bond activation of the triphenylphosphite ligand competed effectively with intermolecular C-Cl bond activation of chlorobenzene

Puddephatt *et al.* in 1989 reported the first example of oxidative-addition of aryl halides in Pt(II) complexes. The reaction of $[PtMe_2NH_2CH_2N{=}CHAr]$ (Ar = $2\text{-}BrC_6H_4$, 2-ClC_6H_4, C_6F_6, 2-FC_6H_4, and C_6H_5) in acetone goes by intramolecular oxidative-addition of the aryl-halogen bond or *ortho*-metallation with loss of methane (Equation 4.8). The competition of intramolecular C-X bond addition vs orthometallated product depended on the nature of Ar in the [$PtMe_2NH_2CH_2N$=CHAr] complex.[101]



Eq 4.8

Y= Cl, Br, and I

The formation of Cp*Re(CO){η^2-P(OC_6H_4)(OC_6H_5)$_2$}H (**3.9**) in chlorobenzene, suggests that the aromatic C-H bond is more reactive than the C-Cl bond when triphenylphosphite is coordinated to the rhenium center. Furthermore, it is important to point out that the complex Cp*Re(CO){P(OPh)$_3$}(N_2) (**3.2**) did not produce the phenyl hydride complex under photochemical conditions in benzene (Chapter 3, section 3.3.2). This result may suggest that the orthometallated complex is more stable than an intermolecular addition complex or that the triphenylphosphite ligand produces a steric interaction which then favours the formation of the intermolecular product.

4.3.4 Reactivity of $Cp^*Re(CO)\{P(OEt)_3\}PhCl$ (4.1), $Cp^*Re(CO)(PMe_2Ph)PhCl$ (4.2), and $Cp^*Re(CO)\{\eta^2\text{-}P(OC_6H_4)(OC_6H_5)_2\}H$ (3.9) with Halogenated Solvents.

The reactivity of $Cp^*Re(CO)\{P(OEt)_3\}PhCl$ (**4.1**) and $Cp^*Re(CO)(PMe_2Ph)PhCl$ (**4.2**) with halogenated solvents did not provide the expected dihalide complex $Cp^*Re(CO)(L)X_2$. These results suggest that the complex [$Cp^*Re(CO)(L)PhCl$] was not an "intermediate" in the production of the dihalide rhenium complex in the reaction of $Cp^*Re(CO)(L)PhH$ with halogenated solvents (Section 3.2.3). We propose that the dihalide rhenium complex was formed from the 16-electron intermediate [$Cp^*Re(CO)L$] produced from the reductive elimination of benzene.

The reaction of $Cp^*Re(CO)\{\eta^2\text{-}P(OC_6H_4)(OC_6H_5)_2\}H$ (*cis*-**3.9**) in $CHCl_3$ or PhCl did not replace the hydride with a chloride ligand. This result suggests that the orthometalated hydride complex (*cis*-**3.9**) was stable even at high temperatures. Similar results have been observed in "piano stool" rhenium allyl hydride and propene hydride complexes, where treating the hydride in halogenated solvent did not produce the respective rhenium allyl chloride complex.[102]

4.4 Conclusion

In this chapter we have shown that the phosphite dinitrogen complexes $Cp^*Re(CO)(L)(N_2)$ where L = $P(OMe)_3$, $P(OEt)_3$, Pc and PMe_2Ph are capable of reacting with Ph-Cl under photochemical conditions to produce stable rhenium phenyl chloride complexes. As far as we know this is the first demonstration of oxidative-addition of an aryl chloride in a rhenium system. The only isomer isolated under these condition was the thermodynamically more stable *trans* isomer. However, the complex $Cp^*Re(CO)\{P(OPh)_3\}(N_2)$ (**3.2**) under similar conditions gave the product of intramolecular C-H activation rather than intermolecular C-Cl bond activation. The final product ***cis*-3.9** was stable to chlorinated solvents at room temperature and under refluxing condition, and no substitution of chloride for the hydride ligand took place.

The reactivity studies of ***trans*-4.1-4.4** in halogenated solvent demonstrated that the phenyl chloride rhenium complexes were thermally stable at room temperature and under reflux conditions.

4.5. Experimental Section

4.5.1. General Methods

Manipulations, solvent purification, and routine spectroscopic measurements were carried out as described in Chapter 2.

Photochemical reactions were carried out as described in Chapter 3. Chlorobenzene was distilled over $CaSO_4$ and transferred directly into the reaction Pyrex tube under nitrogen (Linde).

The complexes which were investigated in this chapter were prepared and purified following the procedures detailed in Chapter 3.

The ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm downfield (positive) of tetramethylsilane. The masses are reported for ^{35}Cl and ^{187}Re.

4.5.2. Syntheses

Photochemical reaction of $Cp^*Re(CO)\{P(OEt)_3\}(N_2)$. A solution of the triethylphosphite dinitrogen complex **3.1** (30 mg, 0.055 mmol) in chlorobenzene (10 mL) was irradiated in a Pyrex tube for 12 min. An IR spectrum of the resulting orange-red solution showed the total disappearance of the dinitrogen complex. The solvent was removed under vacuum at room temperature and the residue was redissolved in *ca* 2 mL of benzene and transferred to an air-free neutral alumina column prepared in hexane and eluted with benzene-hexane (3:1). Removal of the solvent under vacuum gave a yellow-orange solid which was recrystallized from a mixture benzene-hexane at 269 K to provide ***trans-* 4.1** as a yellow solid in 70% yield (25 mg, 0.039 mmol). IR (CH_2Cl_2): 1884 cm^{-1} $\nu_{(CO)}$. ^1H NMR ($CDCl_3$): δ 1.26 (t, 9H, $P(OCH_2C\underline{H}_3)_3$, $J_{H\text{-}H}$ = 7.0 Hz), 1.61 (s, 15H, C_5Me_5), 4.12 (qq, 6H, $P(OC\underline{H}_2CH_3)_3$, $J_{P\text{-}H}$ = 25.0 Hz, $J_{H\text{-}H}$ = 4.8 Hz), 6.94 (m, 1H, *p*-C_6H_5, $J_{H\text{-}H}$ = 7.7 Hz), 7.09 (m, 2H, *m*-C_6H_5, $J_{H\text{-}H}$ = 7.4 Hz), 7.92 (m, 2H, *o*-C_6H_5, $J_{H\text{-}H}$ = 8.2 Hz,$J_{H\text{-}H}$ = 1.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.95 (s, $C_5\underline{Me}_5$), 16.14 (d, $P(OCH_2\underline{C}H_3)_3$, $J_{C\text{-}P}$ = 5.7 Hz), 64.56 (d, $P(O\underline{C}H_2CH_3)_3$, $J_{C\text{-}P}$ = 8.3 Hz), 101.57 (s, $\underline{C}_5Me_5$), 123.41(s, *p*-C_6H_5), 126.94 (s, *m*-C_6H_5), 141.70 (s, *o*-C_6H_5), 207.10 (d, CO, $J_{C\text{-}P}$ = 20.0 Hz). M.S. (EI): *m/z* 628 (M^+), 600 (M^+ -CO), 522 (M^+ - CO-C_6H_6). Anal. Calc^d. for $C_{24}H_{35}O_4ClPRe$: C, 45.03; H, 5.51. Found: C, 45.08; H, 5.56.

Photochemical reaction of $Cp^*Re(CO)(PMe_2Ph)(N_2)$. A solution of the dimethylphenylphosphine dinitrogen complex **3.2** (50 mg, 0.096 mmol) in chlorobenzene (10 mL) was irradiated in a Pyrex tube for 13 min. An IR spectrum of the resulting yellow solution showed the total disappearance of the dinitrogen complex. After removal of the volatile materials under vacuum at room temperature, the remaining oily residue was redissolved in *ca.* 2 mL of benzene and filtered through a short neutral alumina column. Removal of the solvent under vacuum gave a pale yellow-red solid which was recrystallized from benzene-hexane at 269 K to provide ***trans-* 4.2** in 80% yield (46 mg, 0.077 mmol). IR (CH_2Cl_2): 1867 cm^{-1} $\nu_{(CO)}$. ^1H NMR ($CDCl_3$): δ 1.47 (s, 15H, C_5Me_5), 2.02 (d, 3H, $PMe_2C_6H_5$, J_{H-P} = 9.8 Hz), 2.12 (d, 3H, $PMe_2C_6H_5$, J_{H-P} = 9.8 Hz), 6.97 (m, 1H, *p*-C_6H_5, J_{H-H} = 7.0 Hz), 7.10 (m, 2H, *m*-C_6H_5, J_{H-H} 7.1 Hz), 7.8 (m, 3H, $P(Me_2C_6\underline{H}_5)$)), 7.82 (m, 2H, $P(Me_2C_6\underline{H}_5)$), 7.96 (m, 2H, *o*-$C_6H_5$, J_{H-H} = 6.8 Hz, J_{H-H} = 1.2 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.13 (s,$C_5\underline{Me}_5$), 13.62 (d, $P\underline{Me}_2C_6H_5$, J_{C-P} = 36.8 Hz), 18.01 (d, $P\underline{Me_2}C_6H_5$, J_{C-P} = 36.8 Hz), 100.93 (s, $\underline{C}_5Me_5$), 123.40 (s, $\underline{C}_6H_5$ or $PMe_2\underline{C}_6H_5$), 127.10 (s, $\underline{C}_6H_5$ or $PMe_2\underline{C}_6H_5$), 128.30. (d, $\underline{C}_6H_5$ or $PMe_2\underline{C}_6H_5$, J_{C-P} = 9.2 Hz), 129.90 (broad doublet, $\underline{C}_6H_5$ or $PMe_2\underline{C}_6H_5$, J_{C-P} = 2.3 Hz), 132.00 (d, $\underline{C}_6H_5$ or $PMe_2\underline{C}_6H_5$, J_{C-P} = 7.6 Hz), 136.76 (d, $\underline{C}_6H_5$ or $PMe_2\underline{C}_6H_5$, J_{C-P} = 46.5 Hz), 140.14 (d, $\underline{C}_6H_5$ or $PMe_2\underline{C}_6H_5$, J_{C-P} = 10.7 Hz), 142.18 (s, $\underline{C}_6H_5$ or $PMe_2\underline{C}_6H_5$), 224.93 (d, CO, J_{C-P} = 24.0 Hz). M.S. (EI): *m/z* 523 (M^+ - C_6H_5). Anal. Calcd:$C_{25}H_{31}ClOPRe$ C, 50.08; H, 5.22. Found: C, 50.19; H, 5.14.

Photochemical reaction of Cp*Re(CO)(Pc)(N_2). A solution of the Pc dinitrogen complex **3.3** (15 mg, 0.030 mmol) in chlorobenzene (6 mL) was irradiated in a Pyrex tube for 12 min. An IR spectrum of the resulting yellow-red solution showed the total disappearance of the dinitrogen complex. The solvent was removed under vacumn and the residue was washed with two portions (2 mL) of hexane and redissolved in benzene and filtered through a short neutral alumina column. The fraction containing the product was evaporated and the residue was recrystallized from benzene-hexane at 269 K to afford ***trans*-4.3** in 61 % yield (12 mg, 0.018 mmol). IR (CH_2Cl_2): 1898 cm^{-1} $\nu_{(CO)}$. ^1H NMR ($CDCl_3$): δ 0.81 (s, 3H, $P(OCH_2)_3CC\underline{H}_3$), 1.69 (s, 15H, C_5Me_5), 4.33 (d, 6H, $P(OC\underline{H}_2)_3CCH_3$, $J_{H\text{-}P}$ = 5.4 Hz), 6.93 (m, 1H, *p*-C_6H_5, $J_{H\text{-}H}$ = 7.1 Hz), 7.06 (m, 2H, *m*-C_6H_5, $J_{H\text{-}H}$ = 7.7 Hz), 7.81 (m, 2H, *o*-C_6H_5, $J_{H\text{-}H}$ = 7.6 Hz, $J_{H\text{-}H}$ = 1.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.09 (s, $C_5\underline{Me}_5$), 15.54 (s, $P(OCH_2)_3C\underline{C}H_3$), 32.94 (d, $P(O\underline{C}H_2)_3CCH_3$, $J_{C\text{-}P}$ = 33.5 Hz), 76.84 (d, $P(OCH_2)_3\underline{C}CH_3$, $J_{C\text{-}P}$ = 8.0 Hz), 102.16 (s, C_6H_5), 123.52 (s, C_6H_5), 127.32 (d, C_6H_5), 141.87 (s, C_6H_5), 194.29 (s, CO). M.S. (EI, 12 eV): *m/z* 610 (M^+) 582 (M^+ - CO). Anal. Calc^d. for $C_{22}H_{29}O_4ClPRe$: C, 43.31; H, 4.79. Found: C, 43.85; H, 4.88.

Photochemical reaction of Cp*Re(CO){P(OMe)$_3$}(N$_2$). A solution of the trimethylphosphite dinitrogen complex **3.4** (30 mg, 0.060 mmol) in chlorobenzene (5 mL) was irradiated in a Pyrex tube for 6 min. An IR spectrum of the resulting yellow-orange solution showed the total disappearance of the dinitrogen complex. After the irradiation, the solvent was removed under vacuum at room temperature and the residue was extracted with benzene. The product was chromatographed on a neutral alumina column made up in hexane and eluted with benzene-hexane (5:1). Recrystallization from benzene-hexane at 269 K gave only ***trans*- 4.4** in 60% yield (21 mg, 0.036 mmol). IR (CH_2Cl_2): 1889 cm^{-1} $\nu_{(CO)}$. ^1H NMR ($CDCl_3$): δ 1.62 (s, 15H, C_5Me_5), 3.76 (d, 9H, $P(OMe)_3$, $J_{H\text{-}P}$ = 8.9 Hz), 6.95 (m, 1H, *p*-C_6H_5, $J_{H\text{-}H}$ = 7.5 Hz), 7.09 (m, 2H, *m*-C_6H_5, $J_{H\text{-}H}$ = 7.5 Hz), 7.92 (m, 2H, *o*-C_6H_5, $J_{H\text{-}H}$ = 7.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.94 (s, $C_5\underline{Me}_5$), 55.79 (d, $P(O\underline{C}H_3)_3$, $J_{C\text{-}P}$ = 7.8 Hz), 101.91 (s, C_6H_5), 123.59 (s, *p*-C_6H_5), 127.08 (s, *m*-C_6H_5), 141.48 (s, *o*-C_6H_5), 221.30 (d, CO, $J_{C\text{-}P}$ = 34.0 Hz). M.S. (EI, 12 eV): *m/z* 586 (M^+) 558 (M^+ - CO), 480 (M^+ - CO - C_6H_6).

Photochemical reaction of Cp*Re(CO){P(OPh)$_3$}(N_2). A solution of the triphenylphosphite dinitrogen complex **3.5** (20 mg, 0.029 mmol) in chlorobenzene (6 mL) was irradiated in a Pyrex tube for 6 min. An IR spectrum of the resulting pale yellow solution showed the total disappearance of the dinitrogen complex. Immediately after the irradiation, the volatile materials were removed under vacuum at room temperature and the resulting oily residue was taken up in $CDCl_3$ without purification. A ^{1}H NMR spectrum of this solution showed the intermolecular C-H activation complex ***cis*- 3.7** to be present as an only product from this reaction. The solvent was then removed under vacuum at room temperature and the remaining oily residue was redissolved in *ca.* 2 mL of benzene and filtered through a short neutral alumina column. Recrystallization from benzene-hexane at 269 K provided exclusively ***cis*-3.7** in 80% yield (15 mg, 0.023 mmol). This product was shown to be identical with that synthesized and characterized in Section 3.3. from the following data. (CH_2Cl_2): 1927 cm^{-1} $\nu_{(CO)}$. ^{1}H NMR ($CDCl_3$): δ -10.12 (d, 1H, ReH, $J_{H\text{-}P}$ = 61.0 Hz), 1.99 (s, 15H, C_5Me_5), 6.80 (m, 3H, OC_6H_5 or η^2-OC_6H_4), 6.97 (m, 3H, OC_6H_5 or η^2-OC_6H_4) 7.12 (m, 2H, OC_6H_5 or η^2-OC_6H_4), 7.19 (m, 1H, OC_6H_5 or η^2-OC_6H_4), 7.34 (m, 1H, OC_6H_5 or η^2-OC_6H_4), 7.41 (m, 4H, OC_6H_5 or η^2-OC_6H_4)). M.S. (EI, 12 eV): *m/z* 660 (M^+) 630 (M^+ - CO - 2H), 537 (M^+ - CO - 2H - C_6H_5O).

CHAPTER 5

Photochemical Study of Cp*Re(CO)$_2$MeR (R = *p*-Tolyl, Ph, and Me)

5.1. Introduction

The insertion of an unsaturated molecule into a transition metal-alkyl or metal-hydride bond is one of the most fundamental steps in organometallic reactions and it is often a primary process in reactions catalysed by homogeneous solutions of transition-metal complexes.[103] The insertion of CO,[104] an alkyne,[105] or an alkene[106] molecule into a metal-alkyl bond is of particular interest because it generates a new C-C bond. If a complex bearing two alkyl groups reacts in this way, two new C-C bonds can be formed. Insertion followed by reductive elimination in the new acyl-alkyl, vinyl-alkyl, or dialkyl complex can generate a ketone, olefin, or alkane, respectively.

The carbon-carbon bond-forming reactions of cobalt complexes have been extensively studied under thermal and photochemical conditions in an attempt to elucidate their mechanism.[107,108a] In addition to cobalt, mechanistic studies of other transition metal alkyl complexes (such as Ti, Ni, Fe, and Re) have also been studied under photochemical conditions. This has arisen primarily through the recognition that the metal-carbon bond in a metal alkyl complex is inherently strong and that decomposition does not readily occur by its simple homolytic cleavage.[108,109]

Bergman *et al.* have studied the reaction of *cis* and *trans*-CpRe(CO)$_2$Me$_2$ under photochemical and thermal conditions.[110] They found that irradiation of CpRe(CO)$_2$Me$_2$

under CO (20 atm) yielded 2,3-butanedione, $CpRe(CO)_3$, and a trace of acetone but no evidence of ethane or methane was observed (Equation 5.1).

$$CpRe(CO)_2Me_2 \xrightarrow[20\text{ atm CO}]{h\nu} CpRe(CO)_3 + CH_3COCOCH_3 \qquad \text{Eq 5.1}$$

Upon photolysis of $CpRe(CO)_2Me_2$ in CCl_4, acetyl chloride (CH_3COCl), CH_3Cl, and $CpRe(CO)_3$, and a trace of acetone were obtained. When the reaction was carried out with a better radical trap ($CBrCl_3$) the only products observed were CH_3Br and $CpRe(CO)_2MeBr$ (Equation 5.2).[111]

$$CpRe(CO)_2Me_2 \xrightarrow[20\text{ atm CO}]{h\nu\ \ CBrCl_3} CpRe(CO)_2MeBr + CH_3Br \qquad \text{Eq 5.2}$$

In a similar Cp* system, Hill *et al.* have investigated the photochemistry of *cis*-$Cp^*Re(CO)_2Me_2$ in methylcyclohexene alone, and found that room temperature photolysis led to the production of *trans*-$Cp^*Re(CO)_2Me_2$ and $Cp^*Re(CO)_3$.[112] At lower temperature, however, the cis-trans isomerization was the only detectable reaction. The focus of this preliminary study was solely cis - trans isomerization. No further mechanistic study was done in this rhenium system such as to examine the formation of $Cp^*Re(CO)_3$ in this reaction.

The studies on *trans*-$Cp^*Re(CO)_2MeR$ (R = *p*-Tolyl (**5.1**), Ph (**5.2**), and Me (**5.3**)) reported in this chapter were conducted to determine the primary photoprocess responsible for the formation of $Cp^*Re(CO)_3$ and the identification of other products that are generated under photochemical conditions.

5.2 Results

5.2.1 Characterisation of the Products.

The photolysis ($\lambda \geq 275$ nm) of degassed cyclohexane solutions of *trans*-$Cp^*Re(CO)_2Me$(*p*-Tolyl) (**5.1**) in a Pyrex vessel at room temperature under CO (1 atm) for 20 min, led to the loss of IR $\nu_{(CO)}$ bands due to the starting complex at 2002 and 1927 cm^{-1}, and the production of $Cp^*Re(CO)_3$ which showed $\nu_{(CO)}$ at 2012 and 1921 cm^{-1} in the IR spectrum. The ^1H NMR spectrum of the sample after irradiation showed in the aromatic region the presence of starting material and a new set of resonances at δ 7.73 (d, J_{H-H} = 8.0 Hz), 7.17 (t, J_{H-H} =8.0 Hz), and 7.00 (d, J_{H-H} = 8.0 Hz) which were assigned to free toluene (Figure 5.1). The organometallic and organic components from the photolysis of **5.1** in cyclohexane, were separated via vacuum transfer and analyzed independently. The organic material was analyzed by gas chromatography (GC), and mass spectroscopy (GC/MS) and the organometallic product by IR and ^1H NMR.

The GC spectrum showed a peak with a retention time (RT) at 2.11 min and the GC/MS spectrum of the organic fraction showed peaks at *m/z* 92 (M^+, 37) and 91 (M^+-H, 100). A toluene sample in cyclohexane showed a similar RT and fragmentation pattern to that observed for the organic component in the GC, and GC/MS. This suggests that one of the products generated in the photochemical reaction of **5.1** in cyclohexane was toluene. No evidence of the possible 1,4-dimethyl benzene (*p*-xylene) was observed.

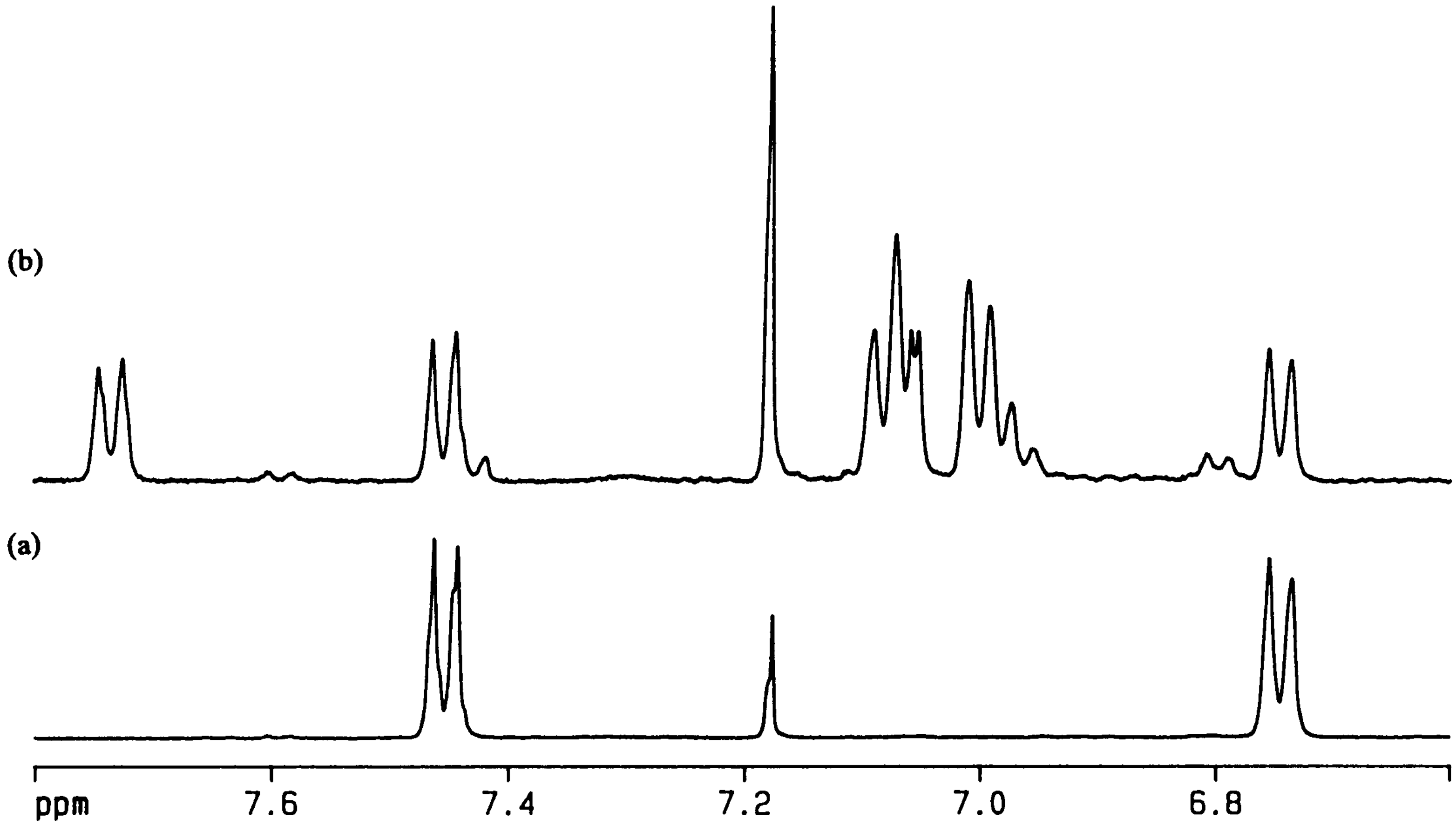


Figure 5.1 ^{1}H NMR spectra of Cp*Re(CO)$_2$Me(*p*-Tolyl) (**5.1**) in cyclohexane (a) before, (b) after, irradiation.

The organometallic component was dissolved in benzene-d_6 and the ^{1}H NMR was obtained. A resonance at δ 1.72 was assigned to Cp*Re(CO)$_3$, and resonances corresponding to the starting material were also observed. The IR spectrum in hexane showed $\nu_{(CO)}$ bands corresponding to the starting material and the tricarbonyl complex. The identification of the tricarbonyl complex was based upon the data reported previously in the literature.[113]

The experiment was repeated under the same conditions, but this time the gas phase product(s) generated upon the irradiation were analyzed by GC/MS. The GC/MS showed a peak with a RT of 2.71 min with *m/z* 16 (M^+, 100), 15 (M^+-H, 80), 14 (M^+-2H, 25) as the sole product(s). Methane and CO samples were analyzed independently (the latter to check the purity of the gas used), and to provide data on the retention time (RT) and the fragmentation of the parent under our experimental conditions. The CH_4 showed a RT of 2.71 min with *m/z* 16 (M^+, 100), 15 (M^+-H, 76), 14 (M^+-2H, 28), and CO gave a RT of 2.48 min and *m/z* 28 (M^+, 100). The gas phase product was therefore identified as methane. No evidence of ethane or acetone was observed.

Photolysis for 20 min of a degassed pentane solution of *trans*-Cp*Re(CO)$_2$MePh (**5.2**) in a Pyrex vessel at room temperature under CO (1 atm), led to loss of IR $\nu_{(CO)}$ at 2002, 1927 cm^{-1} due to the starting material and the formation of Cp*Re(CO)$_3$. The IR spectrum showed the characteristic $\nu_{(CO)}$ frequencies for Cp*Re(CO)$_3$ at 2010 and 1920 cm^{-1}.

The organometallic and organic components from the photolysis of **5.2** in pentane, were separated via vacuum transfer and analyzed independently. The GC spectrum of the organic phase showed a peak with a RT of 1.32 min and the GC/MS showed peaks at *m/z* 78 (M^+, 100), and 77 (M^+-H, 30). A benzene sample in pentane was analyzed and the data showed similar RT and fragmentation as were observed for the organic fraction. The organometallic component remaining was dissolved in hexane and the IR spectrum showed the presence of complex **5.2** and Cp*Re(CO)$_3$.

Photolysis of **5.2** was carried out in cyclohexane at room temperature for 20 min, and the gas phase product was analysed by GC/MS, and the solution by NMR spectroscopy. Methane was the only product observed in the GC/MS of the head space gases. A ^{1}H NMR spectrum of the starting material in cyclohexane was taken before and after the photolysis. After photolysis, the resonances in the aromatic region suggested the presence of a phenyl group coordinated to the metal center and were assigned to **5.2**. A new resonance observed at δ 7.20 was assigned as free benzene. No evidence of toluene was observed in either the ^{1}H NMR or GC/MS.

Photolysis of *trans*-Cp*Re(CO)$_2$Me$_2$ (**5.3**) under CO (1 atm) in cyclohexane at room temperature for 20 min gave Cp*Re(CO)$_3$ and methane as the only products. Again, the identification of Cp*Re(CO)$_3$ was based on the $\nu_{(CO)}$ frequencies in the IR and ^{1}H NMR spectra, and methane was detected by GC/MS in the analysis of the head space gases. No evidence of the formation of ethane, acetone or 2,3-butanedione was obtained.

A degassed *n*-hexane solution of *trans*-Cp*Re(CO)$_2$MeR (R = Ph (**5.2**) or Me (**5.3**)) (1×10^{-3} M) and PPh$_3$ (0.1 M) in a Pyrex vessel was photolysed for 25 min at room temperature in the absence of CO. Gas chromatographic analysis of the product mixture indicated the production of methane in both cases and for **5.2** the GC/MS of the organic sample showed the production of benzene as one of the products generated. The IR spectrum of the organometallic material showed new $\nu_{(CO)}$ frequencies at 1913 and 1865 cm^{-1} identified as those of $Cp^*Re(CO)_2PPh_3$ by reference to the literature.[114]

5.2.2 Irradiation of *trans*-$Cp^*Re(CO)_2MeR$ (R = *p*-Tolyl (5.1), and Me (5.3)) in CCl_4.

When the photolysis of *trans*-$Cp^*Re(CO)_2Me$(*p*-Tolyl) (**5.1**) under CO at room temperature for 20 min was carried out in CCl_4, **5.1** disappeared and the only products observed were $Cp^*Re(CO)_2$(*p*-Tolyl)Cl and CH_3Cl. The ^1H NMR was taken before and after irradiation in CCl_4. The former showed resonances at δ 0.76 (integral 3H), δ 1.75 (integral 15H), and δ 2.39 (integral 3H) assigned to the methyl coordinated to the rhenium center, to the Cp* and to the methyl group in the tolyl ligand, respectively. The aromatic region exhibited two resonances at δ 6.87 (integral 2H) and at δ 7.52 (integral 2H) with $J_{H\text{-}H}$ = 7.5 Hz, respectively. The latter showed new resonances at δ 1.78 (s, 15H) and δ 2.37 (s, 3H) assigned to the Cp* and to the methyl group in the tolyl ligand of the product, respectively. In the aromatic region, the spectrum showed resonances at δ 6.93 (d, 2H, $J_{H\text{-}H}$ = 8.0 Hz), and 7.51 (d, 2H, $J_{H\text{-}H}$ = 8.0 Hz) corresponding to the tolyl moiety coordinated to the metal center. The IR spectrum showed two new bands at $\nu_{(CO)}$ 2039, and 1961 cm^{-1} (Figure 5.2). The crude product was purified on a short neutral alumina columm prepared in hexane and a yellow-orange band was eluted with a mixture of hexane-diethylether (5:1). The IR and the ^1H NMR spectra are in agreement with those observed for the crude product. The EIMS gave a weak parent peak at *m/z* 504. A fragment at *m/z* 476 and a base peak at *m/z* 446 are consistent with loss of CO and a second CO with 2H. The base peak was based on ^{187}Re and ^{35}Cl. All the spectroscopic data suggested that the complex was Cp*Re(CO)$_2$(*p*-Tolyl)Cl (Figure 5.3).

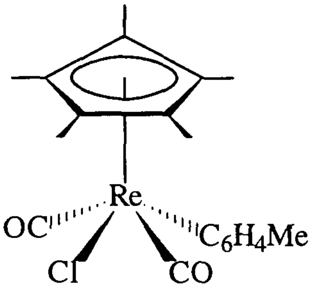


Figure 5.3 Structure of Cp*Re(CO)$_2$(*p*-Tolyl)Cl

The GC/MS of the head space gases showed a peak at RT 8.12 min with *m/z* 50 (M$^+$,100) and a peak at RT 12.65 min with *m/z* 117 (M$^+$-Cl, 100). These were identified as CH_3Cl and CCl_4 (these assignments were based on the comparison with the retention time and fragmentation pattern observed for a standard sample of CH_3Cl and CCl_4). From the spectrum, traces of CH_4 present in the sample (RT 2.73 min with *m/z* 16 (M$^+$, 100)) were observed (Figure 5.4a, and 5.4b), the formation of which will be discussed later in this chapter. This experiment was repeated in the absence of CO and the same products (CH_3Cl, CH_4 (traces) and Cp*Re(CO)$_2$(*p*-Tolyl)Cl were observed in the GC/MS and IR spectra. The sample was photolyzed an additional period of time (~30 min) and no evidence of decomposition or any new products was observed.

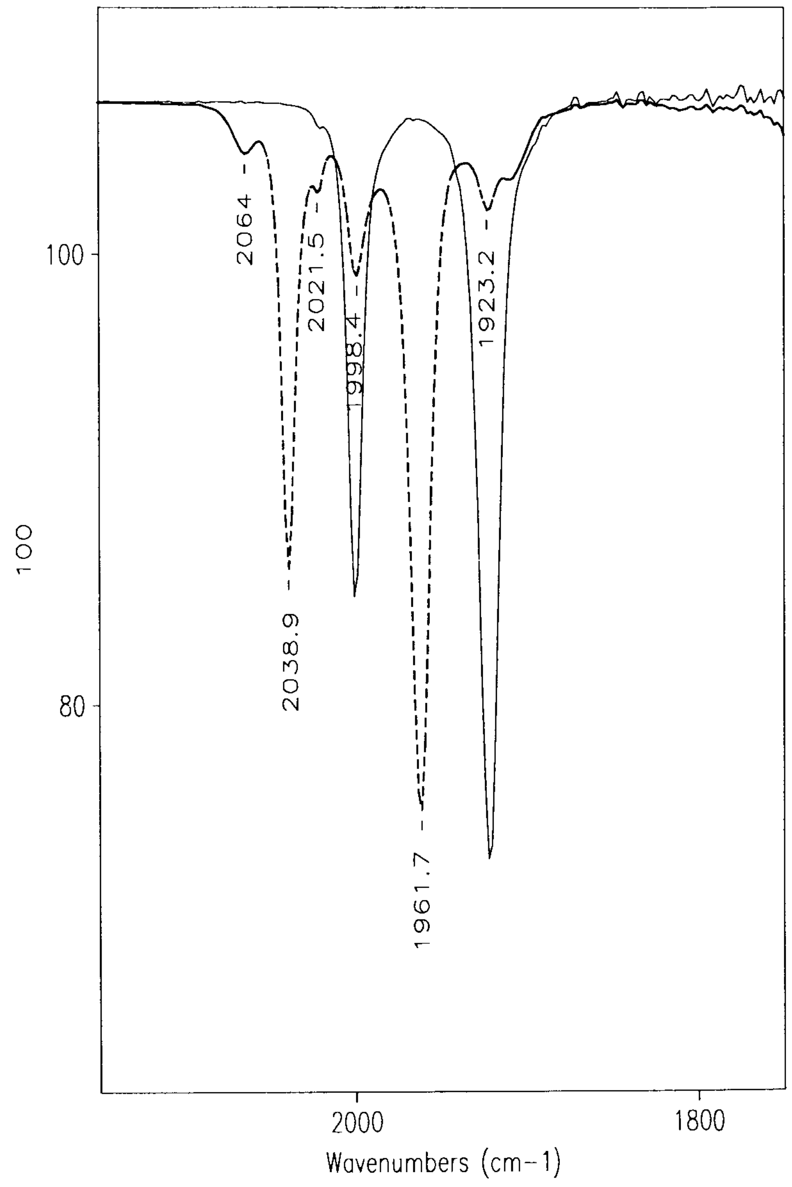
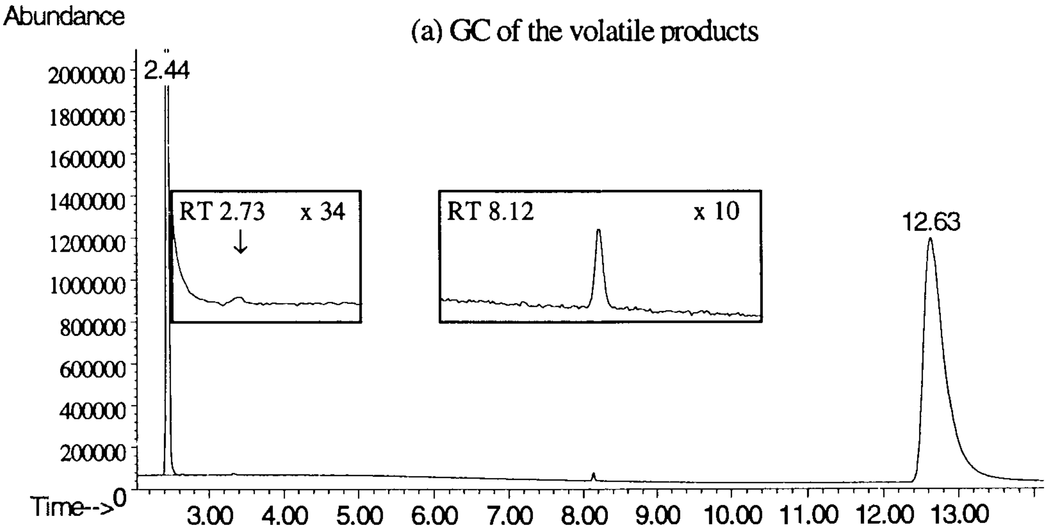


Figure 5.2 IR Spectra of **5.1** before and after photolysis in CCl_4.

— IR spectrum of **5.1** -- IR spectrum after 10 min photolysis.


(a) GC of the volatile products

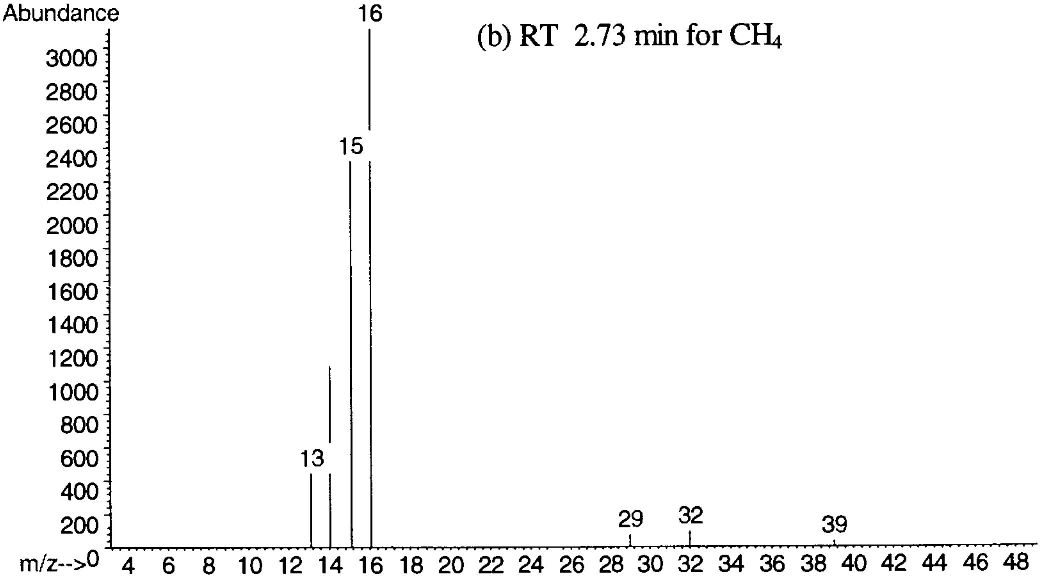
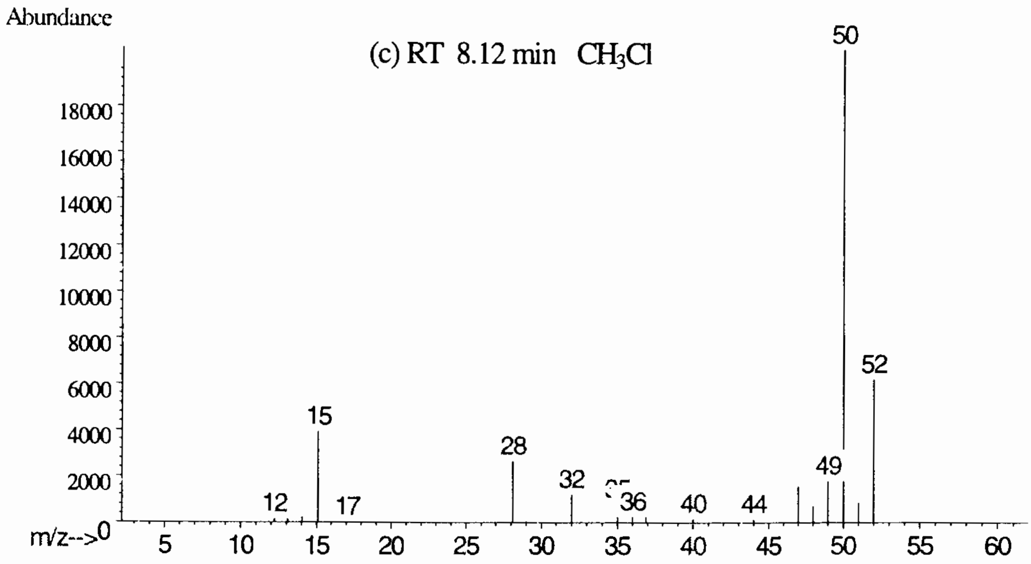

(b) RT 2.73 min for CH_4

Figure 5.4a GC/MS of the volatile products of the reaction of **5.1** in CCl_4.



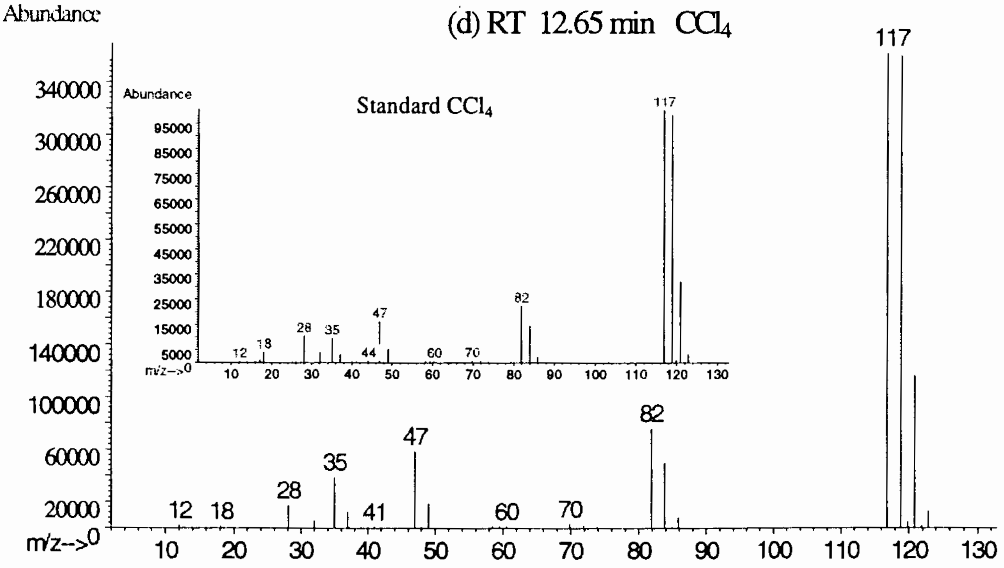


Figure 5.4b GC/MS of the volatile products of the reaction of **5.1** in CCl_4.

Photolysis of *trans*-Cp*Re(CO)$_2$Me$_2$ (**5.3**) in CCl$_4$ under CO at room temperature for 10 min, led to the loss of IR $\nu_{(CO)}$ absorption bands due to the starting material (1993, and 1915 cm^{-1}) and the formation of four new bands in the carbonyl region at 2064, 2031, 1997, and 1956 cm^{-1} (Figure 5.5). The $\nu_{(CO)}$ bands at 2064 and 1997 cm^{-1} were assigned to *trans*-Cp*Re(CO)$_2$Cl$_2$.[71b,115] The extra $\nu_{(CO)}$ bands were tentatively assigned to Cp*Re(CO)$_2$MeCl. The gas phase was analysed by GC/MS. The spectrum showed a peak (RT 7.66 min) with *m/z* 50 (M$^+$, 100) which was identified as CH$_3$Cl. This was the major product. The spectrum also showed evidence of the formation of CH$_4$ (RT 2.64 min, *m/z* 16 (M$^+$, 100)) and CH$_2$Cl$_2$ (RT 9.94 min, *m/z* 84 (M$^+$, 100)) as minor products (Figure 5.6). The identification of CH$_4$ and CH$_2$Cl$_2$ was based on a comparison with the retention times and the fragmentation of standard samples.

This reaction was repeated and the photolysis was followed by ^{1}H NMR spectroscopy in CCl$_4$. The ^{1}H NMR spectrum after 5 min photolysis showed resonances at δ 1.93 (s, 15H, Cp*) and at δ 0.82 (s, 3H, Me) which were tentatively assigned to the Cp*Re(CO)$_2$MeCl. The spectrum also showed a broad resonance at δ 5.15 which was identified as CH$_2$Cl$_2$; no evidence of Cp*Re(CO)$_3$ was observed. The ^{1}H NMR spectrum taken after 22 min photolysis showed the Cp* signal corresponding to *trans*-Cp*Re(CO)$_2$Cl$_2$ at δ 2.00 and a weak signal at δ 2.21 (Cp*) indicating traces of the cis isomer. The reaction was repeated to try to isolate the complex that showed IR bands at $\nu_{(CO)}$ 2031 and 1958 cm^{-1}. The reaction was monitored by IR every 5 min. The IR spectrum after 10 min photolysis showed the carbonyl bands associated to the unreacted starting material **5.3** and *trans*-Cp*Re(CO)$_2$Cl$_2$ and a small amount of the tentatively-assigned Cp*Re$(CO)_2$MeCl. The solvent was removed and the residue was dissolved in hexane and purificated by column chromatography on neutral alumina with a mixture of hexane-diethylether (5:1) as an eluent. The yellow-orange solid obtained was analyzed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum showed the resonances attributed to Cp*Re$(CO)_2$MeCl at δ 0.74 (integral 3H) and at δ 1.80 (integral 15H) corresponding to a methyl coordinated to the rhenium center and to the Cp* ligand, respectively. The spectrum also showed a resonance at δ 1.88 which was assigned to Cp*Re$(CO)_2Cl_2$ as the major product.

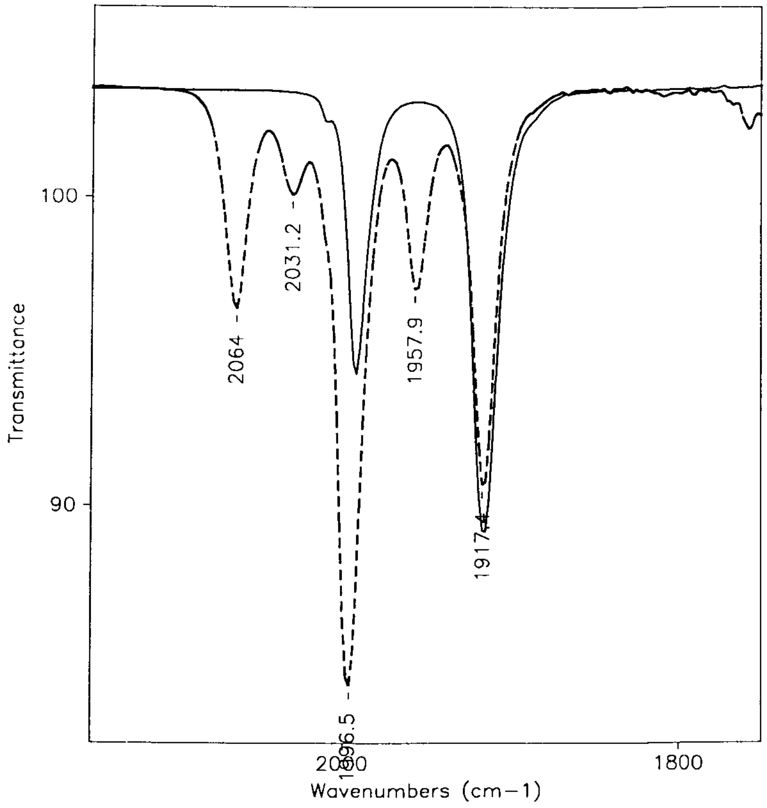


Figure 5.5 IR spectra of **5.3** before and after photolysis in CCl_4.

— IR spectrum of **5.3** -- IR spectrum after 10 min photolysis.

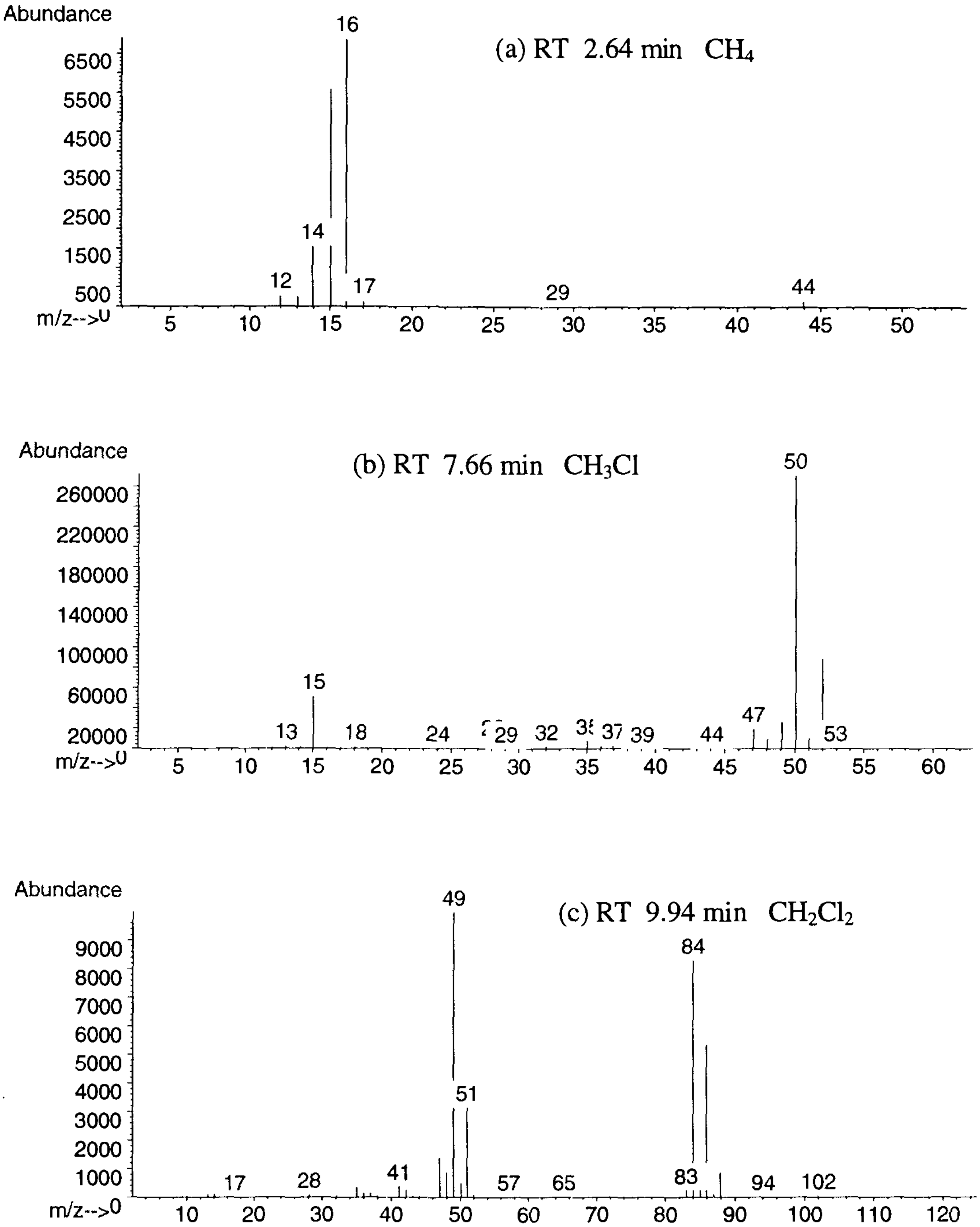


Figure 5.6 GC/MS of volatile products of the reaction of **5.3** in CCl_4.

5.2.3 Isotopic Labeling Studies

Isotopic labeling experiments were done in order to elucidate the hydrogen source in the production of toluene, benzene and methane in the photolysis of Cp*Re(CO)$_2$MeR R = Me, Ph, *p*-Tolyl) (see Section 5.2.1). The photolysis of *trans*-Cp*Re(CO)$_2$Me(Tolyl) (**5.1**) in degassed benzene-d_6 in a sealed NMR tube under CO (1 atm) was monitored by ^{1}H NMR. After ~20 min of irradiation, we observed the decrease in intensity of the resonances due to the starting material and an apparent increase of the resonances due to toluene-4-d_1 and Cp*Re(CO)$_3$. The resonance at δ 1.72 was assigned to Cp*Re(CO)$_3$ and the free toluene-4-d_1 was observed at δ 7.51 (d, 2H, $^2J_{H-H}$ = 8.0 Hz), 7.11 (d, 2H, $^2J_{H-H}$ = 8.0 Hz), and 2.21 (s, 3H).

After ~45 min photolysis, the ^{1}H NMR spectrum showed the complete disappearance of the starting material, a decrease in intensity of the resonance due to Cp*Re(CO)$_3$, and new resonances were observed in the Cp* region (Figure 5.7) assigned to new rhenium complexes. These rhenium complexes were identified as Cp*$_2$Re$_2$(CO)$_5$ at δ 1.64 (Cp*), and Cp*$_2$Re$_2$(CO)$_3$ at δ 1.86 (Cp*), by comparison of the ^{1}H NMR and IR spectra with those reported previously in the literature.[71a,71c] The resonance at δ 1.59 (Cp*) was tentatively assigned to Cp*Re(CO)$_2$(η^2-C$_6$D$_6$), by comparison of the ^{1}H NMR and IR spectrum of the known Cp*Re(CO)$_2$(η^2-C$_6$H$_6$).[71c]

GC/MS analysis of the organic fraction showed a peak with RT 3.19 min which gave peaks at *m/z* 93 (M$^+$, 64) and 92 (M$^+$-H, 100), from which it was identified as C$_6$H$_4$DCH$_3$. The GC/MS also indicated a small amount of C$_6$D$_5$CH$_3$ which gave *m/z* 97

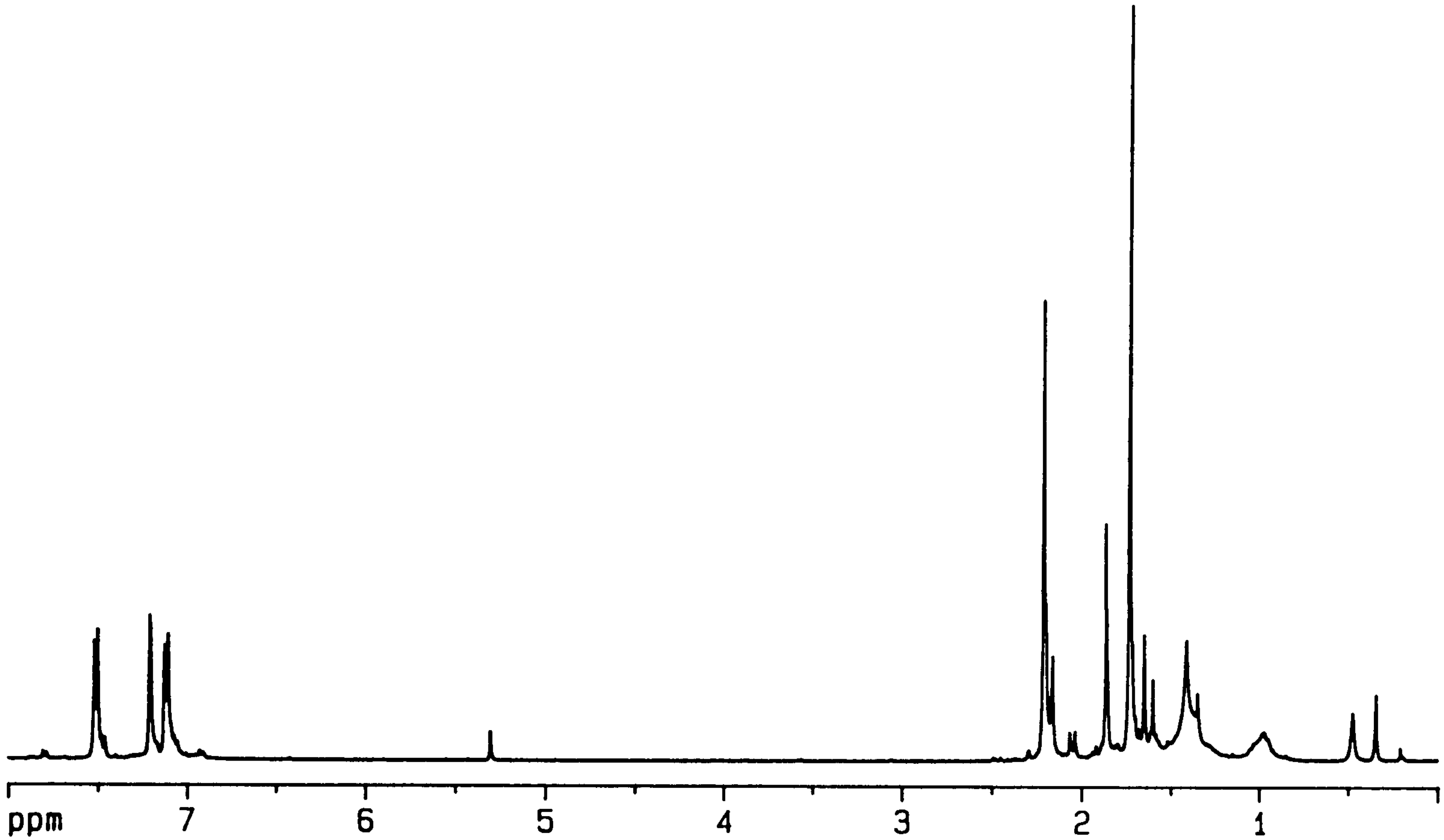


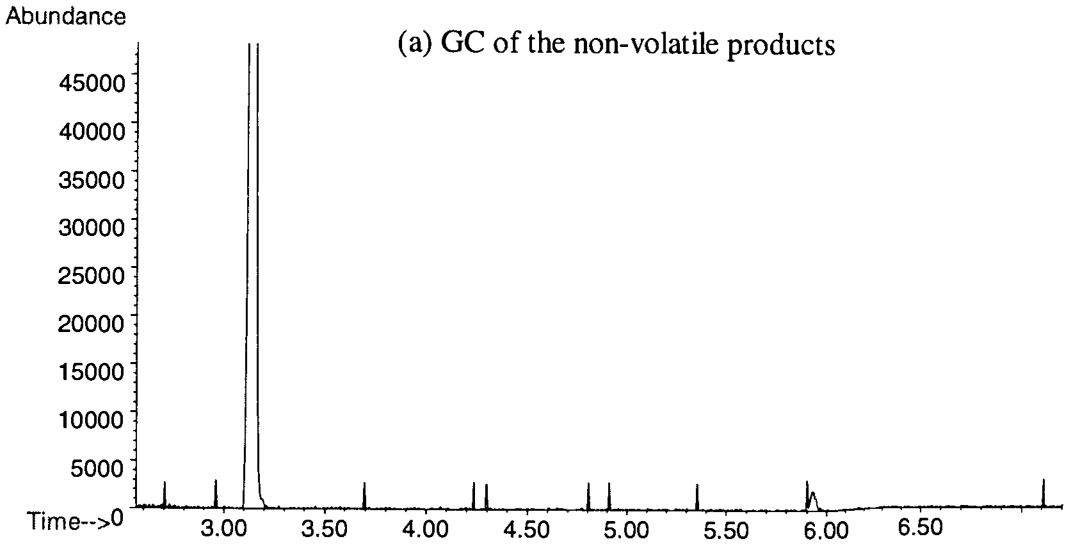
Figure 5.7 ^{1}H NMR spectrum of Cp*Re(CO)$_2$Me(*p*-Tolyl) (**5.1**) after 45 min irradiation in benzene-d_6.

(M^+, 23). A similar pattern in the mass spectrum was observed for a synthetic sample of toluene-4-d_1 (see later in the text). It also showed trace amounts of a material giving a peak with RT 5.95 with *m/z* 106 (M^+, 50) and 91 (M^+-CH_3, 100). This compound was identified as 1,4-dimethyl benzene (*p*-xylene) (Figure 5.8a, and 5.8b).

The same experiment was carried out for *trans*-$Cp^*Re(CO)_2MePh$ (**5.2**) under conditions similar to those above. The ^1H NMR in benzene-d_6 after 25 min photolysis showed the formation of $Cp^*Re(CO)_3$, $Cp^*_2Re_2(CO)_5$, $Cp^*_2Re_2(CO)_3$ and $Cp^*Re(CO)_2(\eta^2\text{-}C_6D_6)$ as observed in the reaction of **5.1** in benzene-d_6. The GC/MS of the organic fraction after photolysis showed a peak with RT 3.30 min with *m/z* 97 (M^+, 100) which was identified as $C_6D_5CH_3$ (Figure 5.9). The spectrum also showed a small peak with RT 6.54 min with *m/z* 107 (M^+, 100), this peak could be assigned as 1,4-dimethylbenzene-d_1, but the fragmentation pattern is not consistent with the non-deuterated 1,4-dimethylbenzene. We cannot propose any mechanism for the formation of this species.

When a benzene-d_6 solution of *trans*-$Cp^*Re(CO)_2Me_2$ (**5.3**) was photolysed in a sealed NMR tube under CO (1 atm) for 20 min, the ^1H NMR spectrum exhibited a resonance at δ 1.60 assigned to the presence of $Cp^*Re(CO)_3$, and new Cp* resonances assigned to the complexes $Cp^*Re(CO)_2(\eta^2\text{-}C_6D_6)$, $Cp^*_2Re_2(CO)_5$, and $Cp^*_2Re_2(CO)_3$. The same species were observed in the reaction of **5.1** in benzene-d_6.

These experiments were repeated under the same conditions in a Pyrex vessel and this time we analyzed the gas phase and the organic material by GC and GC/MS. Irradiation of a solution of *trans*-$Cp^*Re(CO)_2Me(p\text{-Tolyl})$ (**5.1**) in benzene-d_6 under CO


(a) GC of the non-volatile products

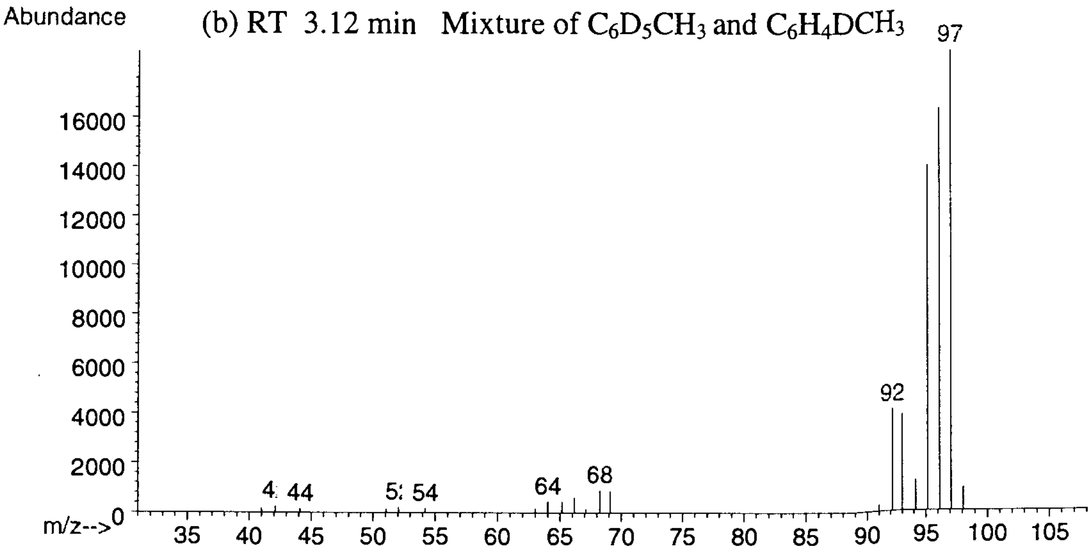
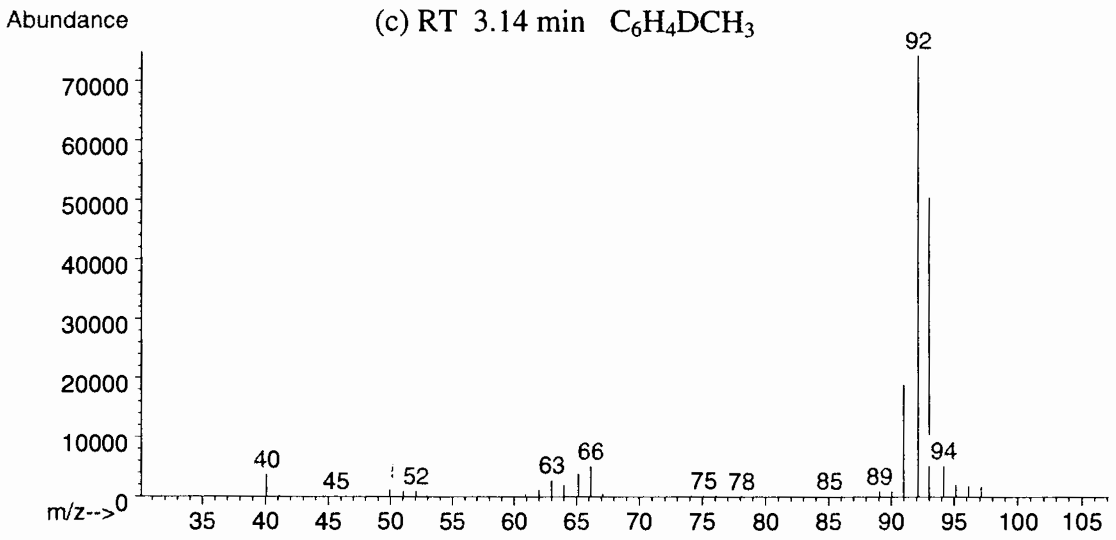
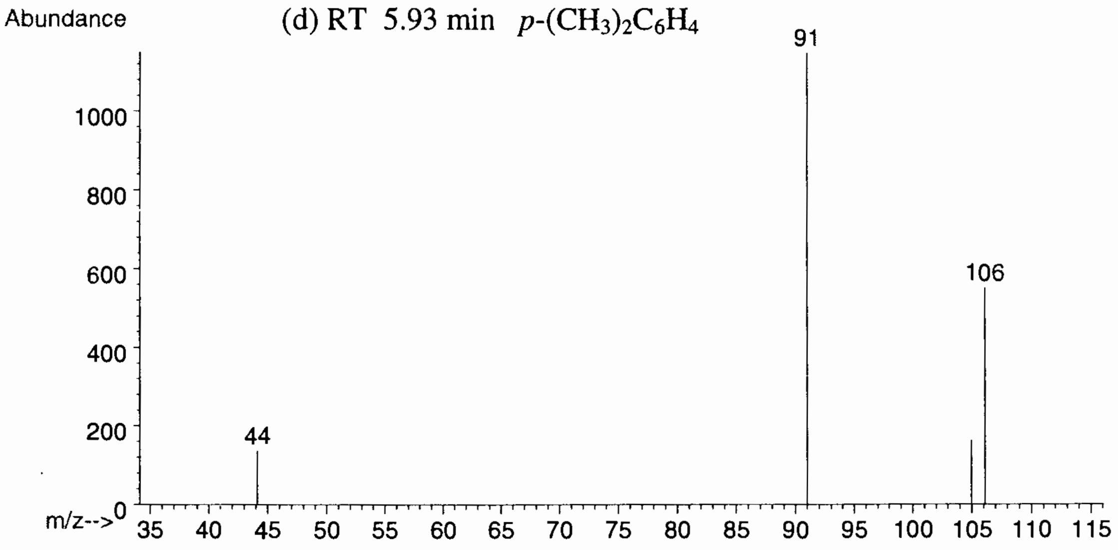

(b) RT 3.12 min Mixture of $C_6D_5CH_3$ and $C_6H_4DCH_3$

Figure 5.8a GC and GC/MS of the organic fraction after photolysis of **5.1** in benzene-d_6. (a) GC of the non-volatile products (b) MS of the peak at RT 3.12 min.



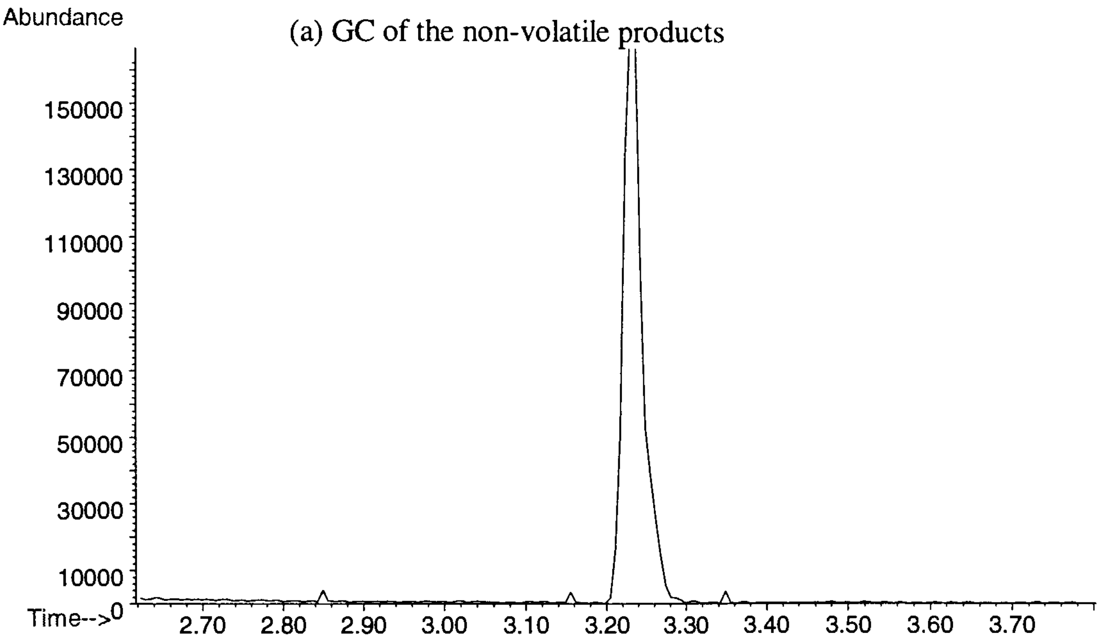
(c) RT 3.14 min $C_6H_4DCH_3$



(d) RT 5.93 min $p\text{-}(CH_3)_2C_6H_4$

Figure 5.8b GC/MS of the organic fraction after photolysis of **5.1** in benzene-d_6. (c) MS of the RT 3.14 min. (d) MS of the RT 5.93 min

(a) GC of the non-volatile products



(b) RT 3.23 min $C_6D_5CH_3$

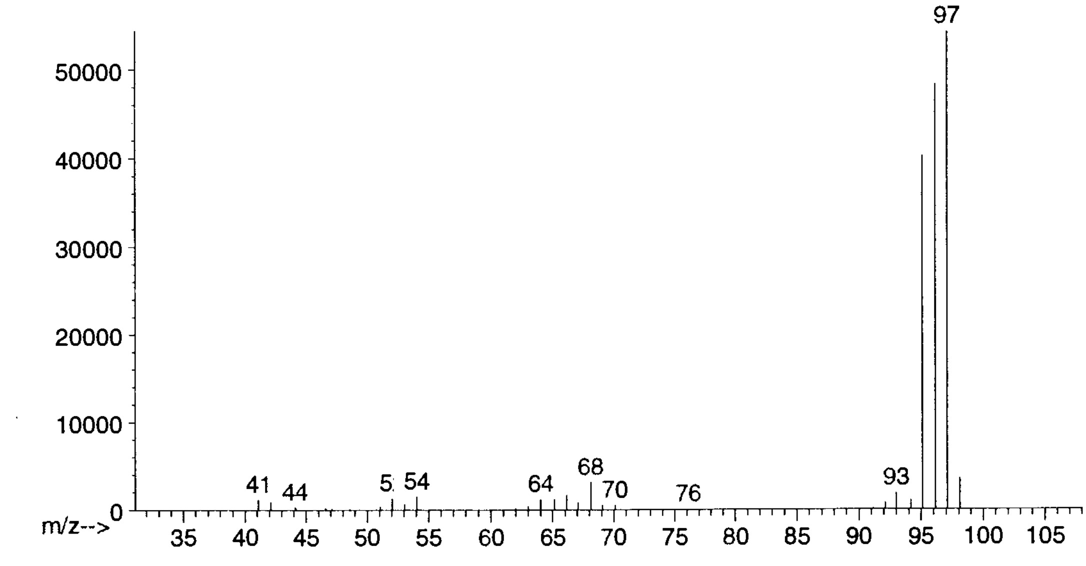
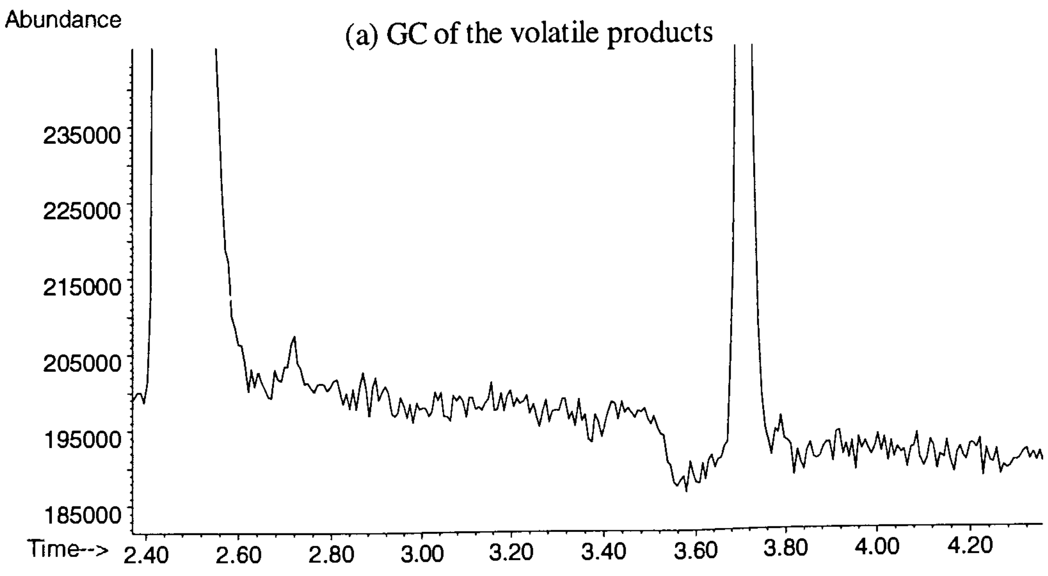


Figure 5.9 GC and GC/MS of the organic fraction after photolysis of **5.2** in benzene-d_6

(1 atm) for 20 min showed the formation of Cp*Re(CO)$_3$, $C_6H_4DCH_3$, CH_4 and CH_3D as photolysis products. The IR spectrum of the solution showed $\nu_{(CO)}$ bands corresponding to the tricarbonyl complex Cp*Re(CO)$_3$ at 2008 and 1912 cm^{-1}, and two new peaks in the carbonyl region at 1952 and 1877 cm^{-1}, which were assigned to the Cp*Re(CO)$_2$(η^2-C_6D_6) complex by comparison with the known spectrum of Cp*Re(CO)$_2$(η^2-C_6H_6).[71c]

The GC/MS of the gas phase showed a peak with RT 2.72 min with *m/z* 17 (M^+, 53), 16 (M^+-H, 100), and 15 (M^+-2H, 40). This spectrum was deduced to be that of a mixture of CH_4 and CH_3D (Figure 5.10). The highest mass (*m/z*) value of 17 corresponds to M^+ of CH_3D. However, the peak at *m/z* 16 is the most intense. In order to compare our mass spectrum with an authentic mass spectrum of a pure CH_3D, we synthesized and analysed the mass spectrum of CH_3D (Figure 5.11). A comparision of the spectra of CH_4, CH_3D, and our spectra suggested that the gas obtained contained a relative proportion of 68 % CH_4 and 32 % CH_3D. The GC and GC/MS of the organic fraction showed the presence of $C_6H_4DCH_3$ as the major product with traces of $C_6D_5CH_3$. Attempts to synthesize toluene-4-d_1 for comparison, by photolysis of [$CH_3C_6H_4N_2$][BF_4] in acetone-d_6 were unsuccessful. Reduction of [$CH_3C_6H_4N_2$][BF_4] with $NaBD_4$, resulted in a product, for which the GC/MS showed only the *m/z* 91 which corresponded to unsubstituted toluene.[116] The synthesis of toluene-4-d_1 was successfully carried out by treating MeC_6H_4MgBr with 99.9% D_2O (see Experimental Section). The compound showed a peak in the GC/MS with a RT of 3.45 min with *m/z* 93 (M^+, 65), 92 (M^+-H, 100) and 91 (M^+-2H or M^+-D, 25). The compound showed the same parent peak and fragments observed for toluene but with a parent of one mass greater which indicated the incorporation of one deuterium in the molecule (Figure 5.12).

The photolysis of *trans*-Cp*Re(CO)$_2$Me$_2$ (**5.3**) in benzene-d_6 under CO (1 atm) gave Cp*Re(CO)$_3$ and methane-d_1. The identification of the tricarbonyl complex was based on the IR and ^{1}H NMR spectra obtained after photolysis. The GC/MS of the gas phase also showed a peak with a RT of 2.05 min with *m/z* 18 (M^+, 66), 17 (M^+-H, 32) 16 (M^+-2H,100), 15 (M^+-3H, 39), and 14 (M^+-4H, 35) (Figure 5.13). This spectrum was deduced to be that of a mixture of CH_4, CH_3D and CH_2D_2. The highest peak (*m/z*) value of 18 corresponds to M^+ for CH_2D_2. However, the peak at *m/z* 16 is the most intense. Methane-d_2 was synthesized and the mass spectrum showed that M^+ at *m/z* 18 is the most intense peak and *m/z* 17 corresponds to the loss of H (Figure 5.14). It was observed that the loss of H is preferred over the loss of D. This result suggests that in the photochemical reaction of *trans*-Cp*Re(CO)$_2$Me$_2$ in benzene-d_6, CH_4, CH_3D, and CH_2D_2 were generated. The relative proportion of the different constituents in the gas mixture were calculated to be for CH_4 (73 %), CH_3D (8 %) and CH_2D_2 (32 %). The mechanism for the formation of CH_3D and CH_2D_2 will be discussed in Section 5.3.


(a) GC of the volatile products

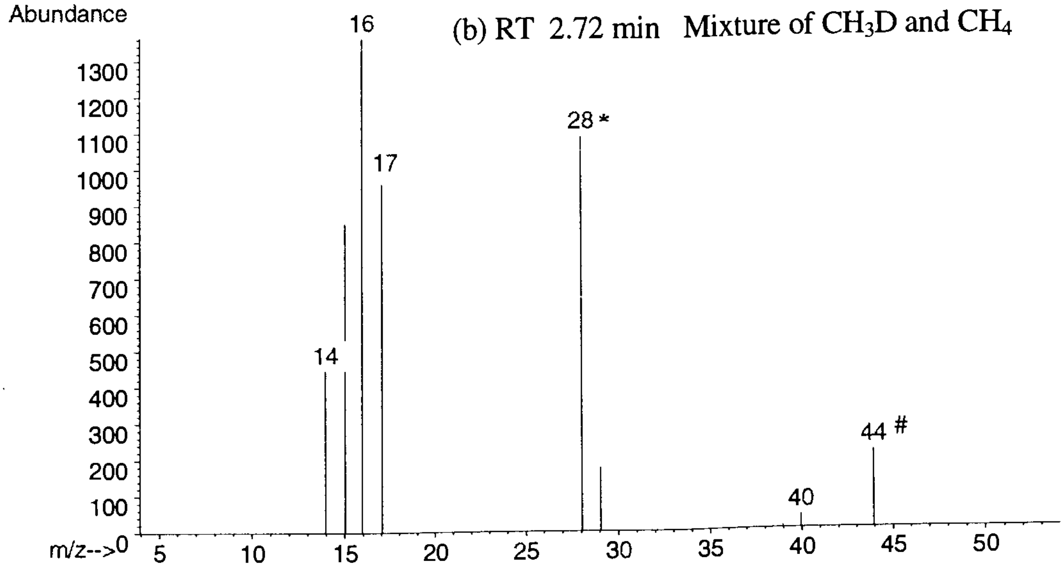

(b) RT 2.72 min Mixture of CH_3D and CH_4

Figure 5.10 GC and GC/MS of the volatile products of the reaction of **5.1** in benzene-*d*$_6$ under CO at room temperature. * N_2 impurity , # CO_2 impurity.

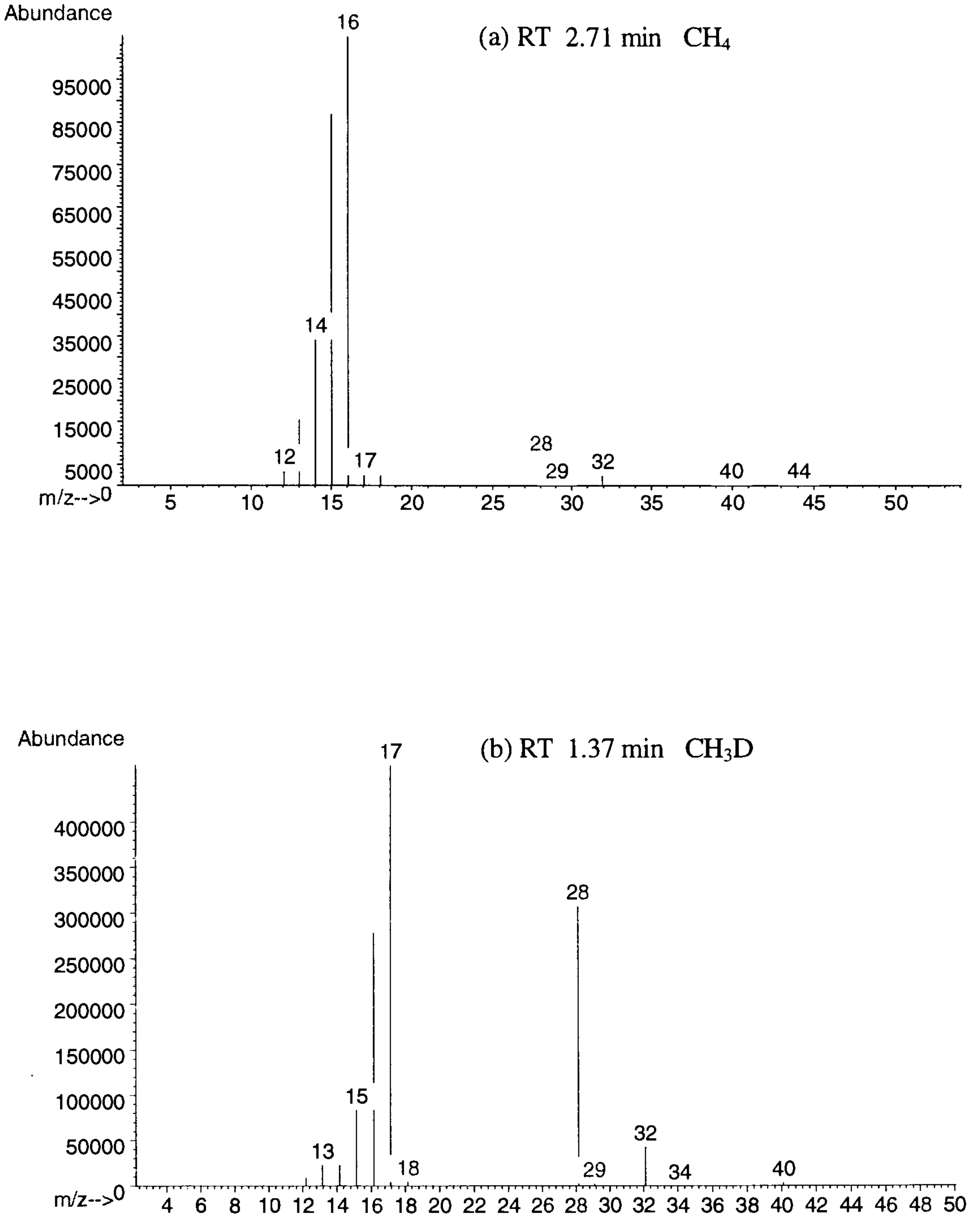
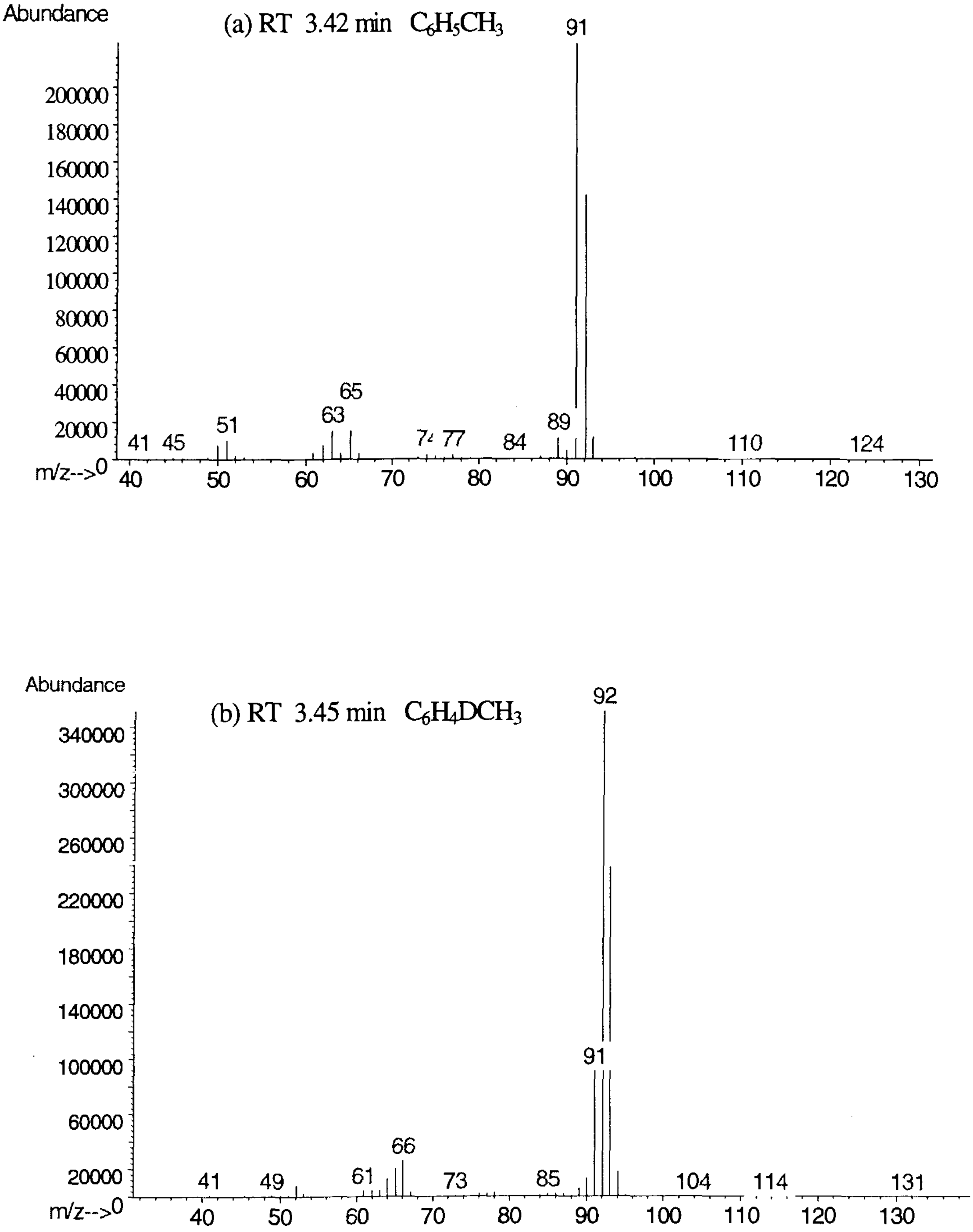


Figure 5.11 GC/MS of (a) methane and (b) methane-d_1.



(a) RT 3.42 min $C_6H_5CH_3$

(b) RT 3.45 min $C_6H_4DCH_3$

Figure 5.12 GC/MS of (a) toluene and (b) toluene-d_1.

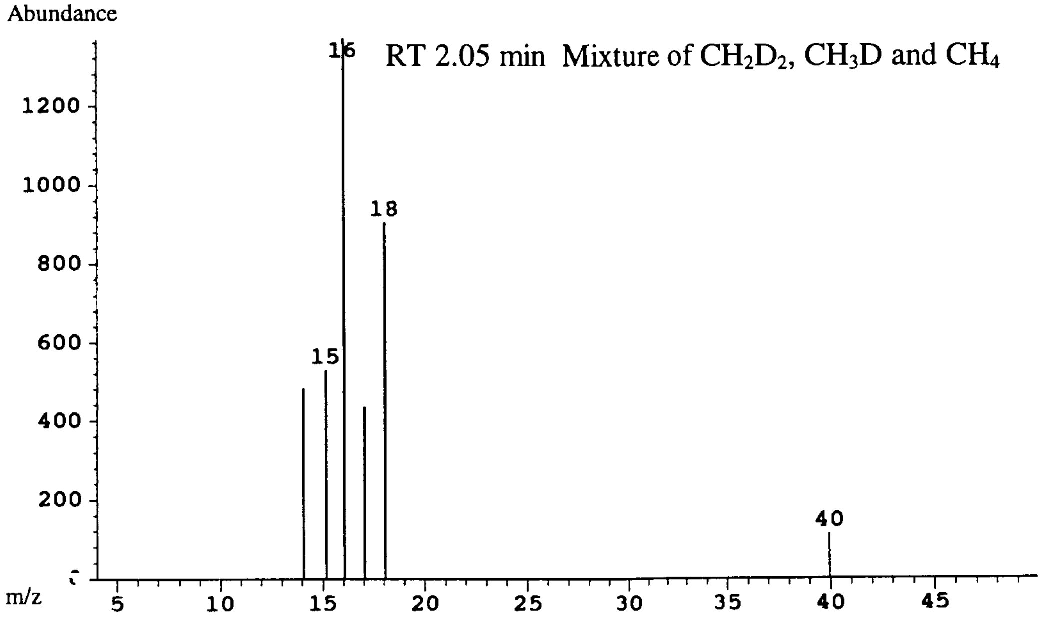


Figure 5.13 GC/MS of the volatile product of the reaction of **5.3** in benzene-d_6 under CO at room temperature.

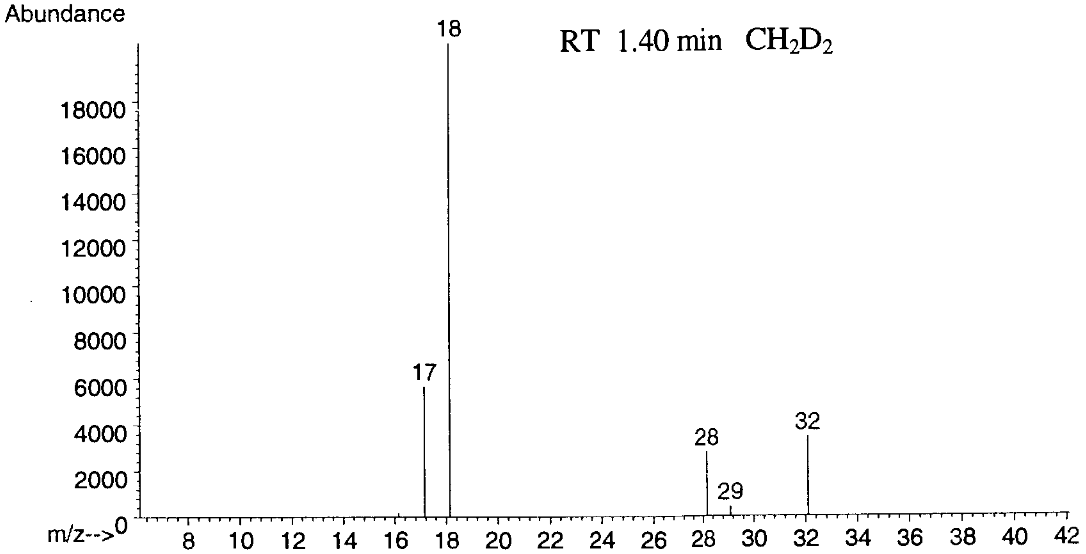


Figure 5.14 GC/MS of methane-d_2

5.3 Discussion

Photolysis of *trans*-Cp*Re(CO)$_2$Me(Tolyl) (**5.1**) under CO in cyclohexane leads to the initial production of Cp*Re(CO)$_3$, toluene and methane (Equation 5.3). The identification of the tricarbonyl complex was based on the $\nu_{(CO)}$ frequencies in the IR and on the ^{1}H NMR spectrum when compared with the literature values.[113]

$$\text{Cp*Re(CO)}_2\text{Me(Tolyl)} \xrightarrow[\text{1 atm CO}]{h\nu \;\; C_6H_{12}} \text{Cp*Re(CO)}_3 + CH_4 + C_6H_5CH_3 \quad \text{Eq 5.3}$$

The formation of toluene was confirmed by the ^{1}H NMR in cyclohexane and the analysis of the organic fraction by GC and GC/MS. The generation of methane was confirmed by the GC/MS of the gas phase. One possible mechanism to explain these products is homolytic cleavage of a rhenium-carbon bond to give the methyl or tolyl radical followed by hydrogen abstraction from the solvent (Figure 5.15). It has been observed that photolysis of (diphenyl)bis(cyclopentadienyl) titanium[117], and zirconium[118] complexes in benzene led to the formation of benzene, biphenyl, and bis(cyclopentadienyl) derivatives of titanium and zirconium. They propose that the reaction goes by a free radical mechanism, and the biphenyl and benzene were produced via a radical coupling reaction, and hydrogen abstraction from the solvent, respectively.[117,118]

The evidence to support a homolytic cleavage of the metal-carbon bond was the presence of CH_3Cl in the photolysis of **5.1** in CCl_4 and the formation of toluene-4-d_1 and methane-d_1 in the photolysis of **5.1** in benzene-d_6. The evidence to support the formation of toluene-4-d_1 was based on a comparison of the parent peak (M^+) and the fragmentation observed for a synthetic sample of toluene-d_1. The result suggested that toluene-d_1 was one of the products in the reaction. We corroborated the presence of CH_3D by comparison of the MS of our sample with experimental and theoretical values reported in the literature.[119a-b] Also, from the photolysis of **5.1** in benzene-d_6, a small component of toluene-d_5 was observed in the GC/MS. We propose that the toluene-d_5 was formed from a radical coupling reaction rather than activation of a benzene-d_6 molecule via an oxidative-addition reaction. We rule out the possibility of the oxidative-addition reaction because, for this mechanism, it would be necessary to lose a CO ligand and produce a vacant site (16-electron intermediate) for the activation of the solvent.[108] In the photolysis of **5.1** in the presence of a large amount of PPh_3, we did not observe the formation of the triphenylphosphine rhenium complex [$Cp^*Re(CO)(PPh_3)MePh$]. This product would be expected if a primary photoprocess is photochemical loss of CO.

$$\mathrm{Cp^*Re(CO)Me(}p\text{-}\mathrm{Tolyl)} \xrightarrow[\text{solvent}]{h\nu} [\mathrm{Cp^*Re(CO)_2}] + \mathrm{C_6H_4CH_3^\bullet} + \mathrm{CH_3^\bullet} \quad \text{(dissociation)}$$

$$[\mathrm{Cp^*Re(CO)_2}] + \mathrm{CO} \longrightarrow \mathrm{Cp^*Re(CO)_3}$$

$$\mathrm{C_6H_4CH_3^\bullet} + \mathrm{CH_3^\bullet} + \text{Solvent} \longrightarrow \mathrm{C_6H_5CH_3} + \mathrm{CH_4} \quad \text{(abstraction)}$$

$$\mathrm{C_6H_5^\bullet} + \mathrm{CH_3^\bullet} \longrightarrow \mathrm{C_6H_5CH_3} \quad \text{(coupling)}$$

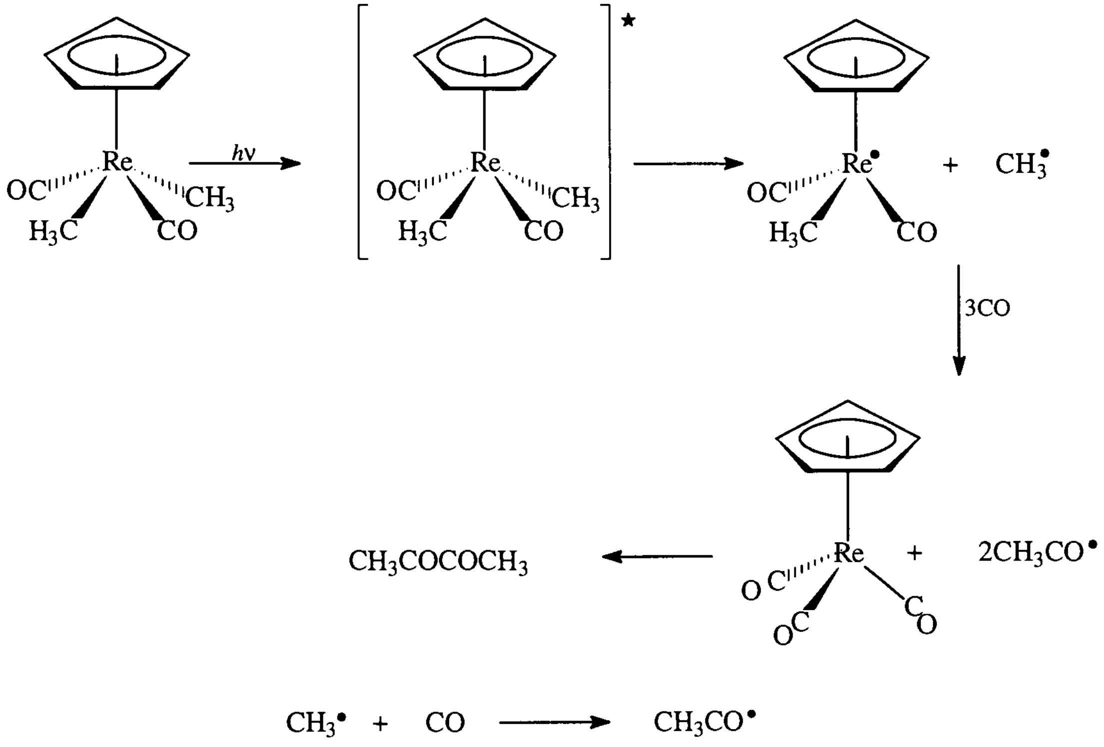
Figure 5.15 Proposed mechanism for the formation of methane or toluene.

No evidence of the reductive-elimination product (dimethyl benzene) was observed in the photolysis of **5.1** in cyclohexane, but when the reaction was carried out in benzene-d_6 traces of dimethyl benzene were detected. One explanation for the formation of dimethyl benzene would be a recombination of $CH_3^{\bullet}$ with $CH_3C_6H_5^{\bullet}$ and the formation of dimethyl benzene in the solvent cage (Equation 5.4).

$$C_6H_4CH_3^{\bullet} \quad + \quad CH_3^{\bullet} \longrightarrow CH_3C_6H_4CH_3 \qquad \text{Eq 5.4}$$

For the formation of benzene and methane in the photochemical reaction of **5.2**, we propose the same pathway discussed for **5.1**. Further evidence to support a radical recombination was the formation of toluene-d_5 in the photochemical reaction of **5.2** in benzene-d_6.

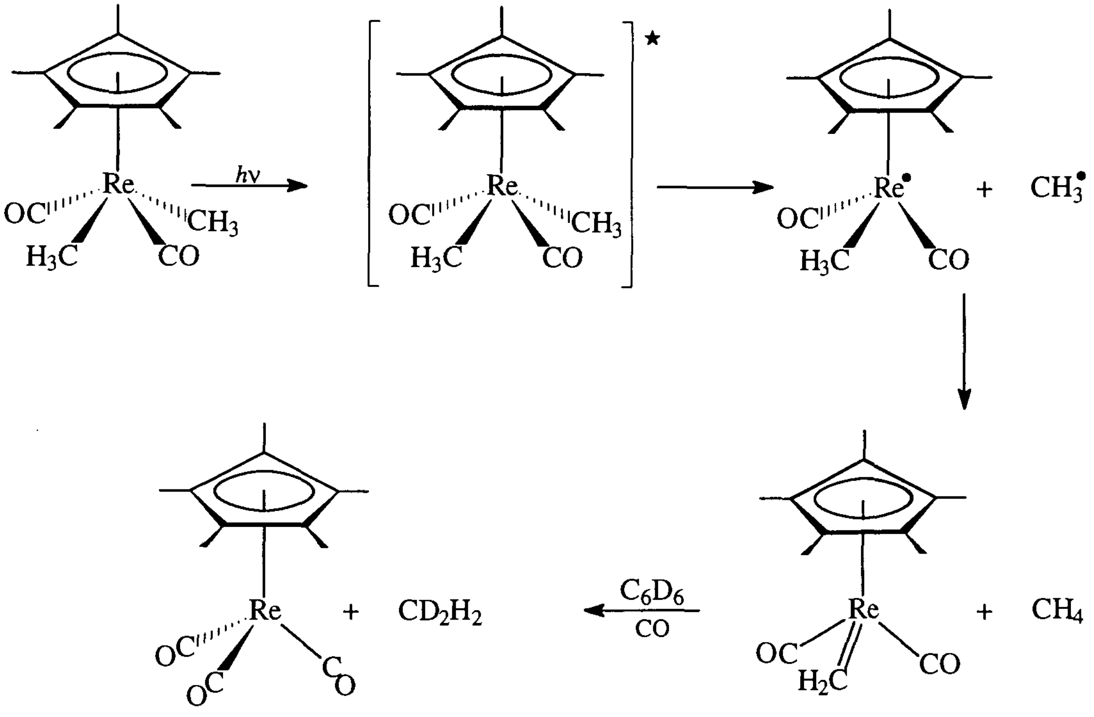
Bergman *et al.* have studied the photochemical decomposition of *trans*-$CpRe(CO)_2(Me)_2$ under CO (20 atm) at room temperature.[110] They observed that $CpRe(CO)_2Me_2$ gave a clean conversion to 2,3-butanedione and $Cp^*Re(CO)_3$ and small amounts of acetone. No evidence of methane or ethane was observed. They proposed that cleavage of rhenium-methyl bonds occurs and that the methyl radicals undergo carbonylation followed by combination of the acetyl radicals to yield the 2,3-butanedione (Scheme 5.1).[110]



Scheme 5.1 Proposed mechanism for the formation of 2,3-butanedione.[110]

In contrast with the above result the photochemical reaction of *trans*-Cp*Re(CO)$_2$Me$_2$ under CO (1 atm) in cyclohexane, led to the formation of CH$_4$ and Cp*Re(CO)$_3$ as the only products. No evidence of acetone or ethane was observed. We can conclude that the primary photoprocess was loss of CH$_3^•$ and hydrogen abstraction from the solvent. We did not observe a CO insertion reaction under these experimental conditions. We suggest that the formation of 2,3-butanedione observed by Bergman's group was dependent on the concentration of CO present in the system. It has been reported that the photochemical reaction of CpCo(PPh$_3$)Me$_2$ or [Me$_2$Co(bpy)$_2$]ClO$_4$ in toluene or benzene produced methane as a major product.[107a-b] Similar results have been reported for titanium and zirconium dimethyl complexes where methane was one of the major products obtained under photochemical conditions.[119c-d] In the cobalt, titanium or zirconium complexes, experimental results suggest that the source of hydrogen was the solvent in the formation of methane. There is an example in a titanium complex where the hydrogen source was the cyclopentadienyl ligand.[108,117a,118]

When the reaction of **5.3** was carried out in the presence of benzene-d_6, methane, methane-d_1, methane-d_2, and Cp*Re(CO)$_3$ were observed. The formation of methane-d_1 must therefore result from deuterium abstraction from the solvent. The formation of undeuterated methane may result from hydrogen abstraction from the other methyl group that remains coordinated to the metal center. The concurrent formation of CH_2D_2 is consistent with such a mechanism involving a methylene ligand intermediate (Scheme 5.2).



Scheme 5.2 Proposed mechanism for the formation of methane and methane-d_2.

Another possible mechanism that can explain the formation of methane in the photochemical reaction of $Cp^*Re(CO)_2Me_2$ is an α-disproportionation with the formation of a carbene intermediate (Figure 5.16). This mechanism has been proposed in manganese, cobalt, and tungsten alkyl complexes.[120] Our experimental results, however, suggested that the primary photoprocess was homolytic cleavage of the methyl-rhenium bond.

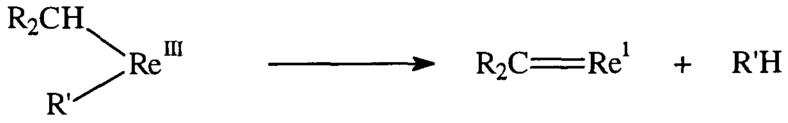
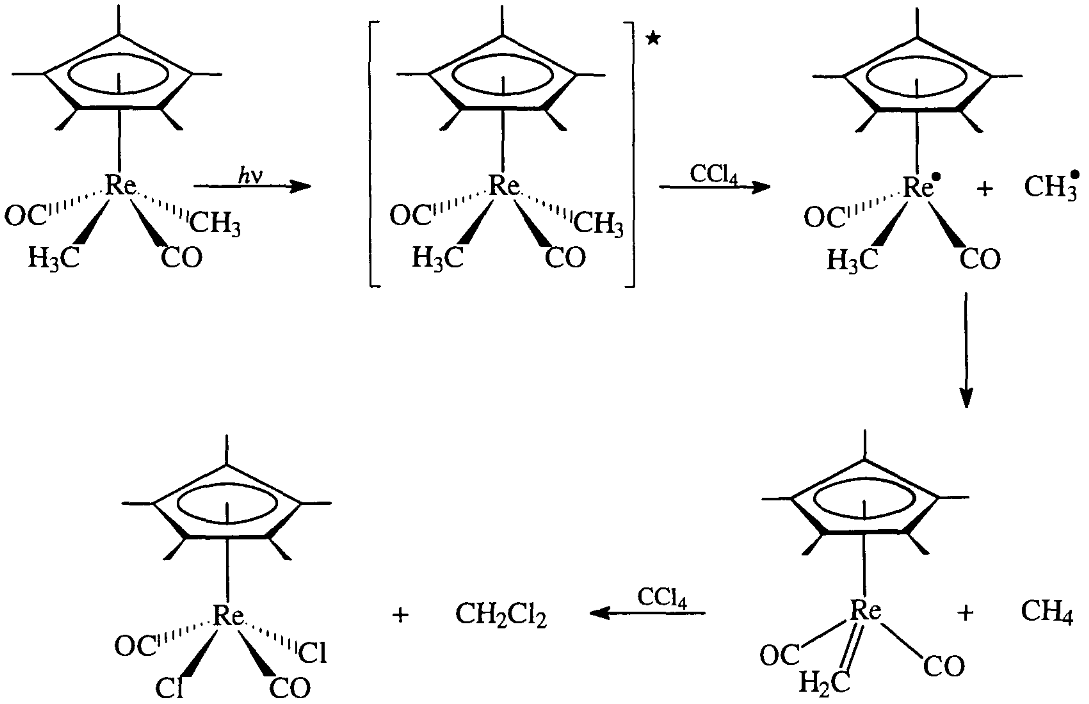


Figure 5.16 Alternative mechanism for the formation of methane.

The mechanism for the formation of methane and dichloromethane from the photolysis of $Cp^*Re(CO)_2Me_2$ (**5.3**) in CCl_4 can be explained in the same way as the formation of CH_4 and CH_2D_2 in the reaction with benzene-*d*$_6$ as shown in Scheme 5.3.



Scheme 5.3 Proposed mechanism for the formation of methane and dichloromethane

The formation of Cp*Re(CO)$_2$(η^2-C_6D_6), Cp*$_2$Re$_2$(CO)$_5$, and Cp*$_2$Re$_2$(CO)$_3$ complexes from the photolysis of Cp*Re(CO)$_2$MeR (R = *p*-Tolyl, Ph, and Me) (**5.1-5.3**) in benzene-d_6 can be explained as photoproducts of the concurrent photolysis of the initial photoproduct Cp*Re(CO)$_3$ in the presence of benzene. Similar rhenium complexes have been observed when a benzene solution of Cp*Re(CO)$_3$ was photolyzed at room temperature (Figure 5.17).[71a, 71c]

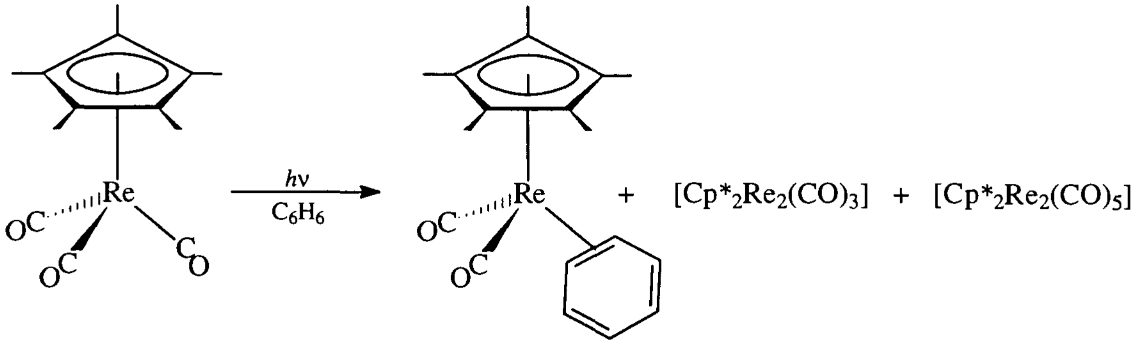


Figure 5.17 Photoproducts from the reaction of $Cp^*Re(CO)_3$ in benzene.[71a,71c]

5.4 Conclusion

Photochemical decomposition of the pentamethylcyclopentadienylrhenium alkyl complexes proceeds by a metal-carbon cleavage at both the metal-alkyl and the metal-aryl substituents, leading the formation of methyl and aryl radicals.

No evidence of reductive-elimination products or products of a CO insertion reaction was observed under these experimental conditions.

When the photochemical reactions were carried out in the presence of CCl_4, the final products for **5.1** or **5.2** were the aryl rhenium chloride complexes. This suggests that the first step is the homolytic cleavage of the methyl-rhenium bond. In contrast with this, when two alkyl ligands were coordinated to the metal center, the final product was the dichloride rhenium complex $Cp^*Re(CO)_2Cl_2$. This suggested that the aryl chloride rhenium complexes $Cp^*Re(CO)_2RCl$ (R = Ph, *p*-Tolyl) were photochemically stable compared with the alkyl chloride rhenium complex $Cp^*Re(CO)_2MeCl$.

When the photochemical reactions of **5.1-5.3** were carried out in the presence or absence of CO in CCl_4, we observed the same products. These results suggested that the products generated were independent of the CO concentration.

5.5 Experimental Section

5.5.1 General Methods

The complexes *trans*-Cp*Re(CO)$_2$MeR (R = *p*-Tolyl, Ph, and Me) were obtained from the laboratories of A. H. Klahn-Oliva. However, the complexes may be prepared by the published procedures.[25,121] The solvents, pentane, cyclohexane, hexane, diethylether, and CCl_4 were purified by standard methods and were freshly distilled under nitrogen. All reagents were obtained from Aldrich except where mentioned. The CO was purchased from Linde, D_2 was purchased from Matheson, and D_2O (99.9 %) was purchased from Isotec Inc. IR spectra were recorded on a Bomem Michelson-120 spectrophotometer. The samples were run in solution in a CaF_2 cell. ^1H NMR spectra were recorded on a Bruker WM-400 instrument operating at 400.13 MHz. The ^1H NMR spectra in non-deuterated solvents were carried out using a standard suppression program from the Bruker pulse program library. Gas chromatographic analysis was performed by using a Hewlett-Packard 5880A instrument equipped with a flame ionization detector and a fused silica, DB-1 coated column (15 m x 0.25 mm ID; 0.25 mm film). Mass spectra were obtained on a Hewlett-Packard 5985B and G1800A GC/MS instruments equipped with a DB-1 fused silica column (30m x 0.25 ID; 0.25 mm film) or on a GSQ column (30 m x 0.53 mm ID) (J & W Scientific) with a 100 μL sampling loop with a variable pressure, operating at 70 eV for electron impact (EI). The masses are reported for ^{12}C, ^{1}H, ^{2}H and ^{35}Cl. Photochemical reactions were carried out under CO (1 atm) at room temperature with a water-jacketed 200 watt Hanovia medium pressure mercury lamp as the UV source. The irradiation was conducted in a Pyrex tube which was placed adjacent to the lamp or in sealed 5 mm NMR tubes.

5.5.2 Gas Chromatography and GC/MS Control.

We analysed authentic samples of benzene, toluene, dimethylbenzene (*o*-, *m*-, *p*-position), acetone, chlorobenzene, *p*-chlorotoluene, and biacetal by GC and GC/MS. We repeated the same analysis in a different solvent if we changed the experimental conditions. The same analysis was repeated in a gas head space for CO, N_2, CH_4, CH_3Cl, CH_2Cl_2, CCl_4, benzene-d_6, cyclohexane, and hexane.

5.5.3 Room Temperature Photolysis

All the experiments were conducted in a similar manner. Therefore, a typical procedure will be described. A solution of *trans*-Cp*Re(CO)$_2$Me(*p*-Tolyl) (**5.1**) (20 mg, 0.041 mmol) in cyclohexane (5 mL) was transferred to a Pyrex Carius tube (fitted with a Teflon valve) and subjected to three cycles of freeze-pump-thaw. The vessel was then filled with CO (1 atm) and sealed. The solution was irradiated for approximately 20 min in a water bath at room temperature. After photolysis the crude sample was analysed by IR, ^{1}H NMR spectroscopy, gas chromatography (GC) and GC/MS.

5.5.4 Synthesis of Toluene-4-d_1.

The aryl magnesium bromide (a Grignard reagent) was prepared by standard methods.[122] A 2 mL sample was transferred into a Schlenk tube under N_2, and D_2O (99.9%) was slowly added dropwise until no further reaction was observed. An exothermic reaction was observed; therefore, to prevent solvent evaporation, the reaction vessel was kept in a water bath. The compound was extracted with hexane (2 x 2 mL). The GC showed a peak with a RT 4.44 min. The GC/MS showed a peak with a RT 3.45 with *m/z* 93 (M^+, 65), 92 (M^+-H, 100), and 91 (M^+-2H, 25). A toluene sample was run under the same experimental conditions to aid in the identification. The GC showed a peak with a RT 4.47 min. The GC/MS showed a peak with RT 3.45 with a *m/z* 92 (M^+, 55), and 91 (M^+-H, 100).

5.5.5 Synthesis of Methane-d_1.

The methyl magnesium bromide (a Grignard reagent) was prepared by standard methods.[122] A 6 mL sample was transferred into a Schlenk tube under N_2, subjected to three cycles of freeze-pump-thaw and D_2O (99.9%) was slowly added by syringe until no further reaction was observed. An exothermic reaction was observed and to prevent solvent evaporation, the reaction vessel was kept in a water bath. The mass spectrum was run by taking a headspace sample in a gas syringe and injecting the sample into the GC/MS. The GC/MS showed a peak with a RT 1.37 with *m/z* 17 (M^+, 100), 16 (M^+-H, 61) and 15 (M^+-2H, 22).

5.5.4 Synthesis of Methane-d_2.[123]

Raney nickel was prepared by standard methods.[124] The Raney nickel was washed several times with D_2O (99.9 %) to remove any ethanol present. A D_2O solution of 1,3-dithiane was added to the Raney nickel under N_2 and at room temperature. The mixture was subjected to three cycles of freeze-pump-thaw and was slowly warmed to room temperature. D_2 gas was bubbled into the closed system for 3 min. The mass spectrum was run by taking a headspace sample in a gas syringe and injecting into the GC/MS. The GC/MS showed a peak with a RT 1.40 with *m/z* 18 (M^+, 100), 17 (M^+-H, 28) and 15 (M^+-2H, 3).

5.5.7 Characterization of $Cp^*Re(CO)_2$(*p*-Tolyl)Cl.

A solution of $Cp^*Re(CO)_2Me$(*p*-Tolyl) (**5.1**) (25 mg, 0.05 mmol) in 3 mL of freshly distilled CCl_4 was degassed twice from liquid nitrogen and then irradiated for 15 min at room temperature. During the photolysis, a slow flux of N_2 was maintained. The IR spectrum after the photolysis reaction indicated the disappearance of the methyl tolyl complex **5.1**. The solvent was removed and the residue was dissolved in *ca* 2 mL of hexane and transferred to an air-free neutral alumina column prepared in hexane. The complex was eluted with a mixture of hexane:ether (5:1). A yellow band was collected and the solvent was removed under vacuum to give a yellow-orange powder. IR (hexane): $\nu_{(CO)}$ 2041, 1966 cm^{-1}. ^1H NMR ($CDCl_3$): 1.70 (s, 15H, Cp*), 2.28 (s, 3H, Me), 6.92 (d, 2H, C_6H_4Me, $J_{H\text{-}H} = 8.0$ Hz), 7.50 (d, 2H, C_6H_4Me, $J_{H\text{-}H} = 8.0$ Hz). EIMS (*m/z*): 504 (M^+), 476 (M^+-CO), 446 (M^+-2CO-2H).

5.5.6 Characterization of $Cp^*Re(CO)_2MeCl$.

A solution of $Cp^*Re(CO)_2Me_2$ **5.3** (20 mg, 0.05 mmol) in 3 mL of freshly distilled CCl_4 was degassed twice with liquid nitrogen and then irradiated for 10 min at room temperature. During the photolysis a slow flux of N_2 was maintained. The IR spectrum after the photolysis exhibited carbonyl bands associated with the starting material **5.3**, $Cp^*Re(CO)_2Cl_2$ and $Cp^*Re(CO)_2MeCl$. The solvent was removed and the residual solid was dissolved in *ca.* 2 mL of hexane and transferred to an air-free neutral alumina column prepared in hexane. The starting material **5.3** was eluted with hexane and a yellow band was eluted with a mixture of hexane:diethylether (5:1). The solvent was removed under vacuum and a yellow-orange powder was obtained. The IR spectrum of the yellow-orange product in hexane showed two different species. One species was identified as *trans*-$Cp^*Re(CO)_2Cl_2$ as the major product. IR (hexane): $\nu_{(CO)}$ 2066, 2000 cm^{-1}. ^1H NMR ($CDCl_3$): 1.88 (s, Cp*). EIMS (12 eV) (*m/z*): 448 (M^+), 420 (M^+-CO), 392 (M^+-2CO). The minor species present was identified as $Cp^*Re(CO)_2MeCl$. IR (hexane): $\nu_{(CO)}$ 2033, 1960 cm^{-1}. ^1H NMR ($CDCl_3$): 0.74 (s, 3H, Me), 1.80 (s, 15H, Cp*). EIMS (12 eV) (*m/z*): 428 (M^+), 400 (M^+-CO), 372 (M^+-2CO).

CHAPTER 6

Synthesis of Pyrazolylborate Rhenium Complexes

6.1. Introduction

The interest in aryldiazenido (N_2Ar) complexes of transition metals in organometallic chemistry can be viewed from two different aspect. They are models of a possible intermediate formed in the reduction of dinitrogen catalysed by the enzyme nitrogenase,[125] and they can exhibit different coordination modes, which makes them chemically[126] and structurally attractive.[127]

Previously, our group has reported the synthesis and chemical properties of dinitrogen (N_2) and aryldiazenido (N_2Ar) ligands in transition metal complexes.[128] From these studies, aryldiazenido ligands (N_2Ar) can be easily stabilised and are capable of transformations to give aryldiazene (NHNAr) or substituted arylhydrazido (2^-) (NNHAr) intermediates and subsequently, the substituted arylhydrazido (1^-) (NHNHAr) derivatives.[129] The focus of this work was to investigate the structural and chemical transformation of N_2Ar as a model of a possible sequence of steps $MNNH \rightarrow MNNH_2 \rightarrow MNHNH_2$ for the reduction and protonation of dinitrogen bound to a transition metal. So far, reactions in which the N_2H ligand has formed a complex are rare, and the characterization is far from complete.[130-132]

Structural studies have demonstrated that aryldiazenido ligands in mononuclear complexes can adopt different coordination geometries. There have been observed three different modes and it has been suggested that the geometry of the ligand depends on the electronic requirements of the metal (Figure 6.1).

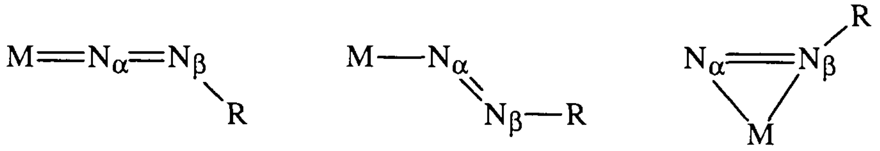


Figure 6.1 Coordination modes of the aryldiazenido ligand in mononuclear complexes.

The work reported in this chapter, resulted from attempts to synthesize the new aryldiazenido pyrazolylborate rhenium complexes with the general formula [TpRe(CO)L(*p*-$N_2C_6H_4OMe$)][BF_4] (L = PMe_3, PPh_3, $P(OMe)_3$, $P(OEt)_3$)) so as to study their reactivity with different nucleophiles. Previously, related cyclopentadienyl aryldiazenido complexes of the type [Cp'Re(CO)(L)(*p*-$N_2C_6H_4OMe$)][BF_4] (Cp' = C_5H_5 or C_5Me_5; L = CO, PMe_3, $P(OMe)_3$) had been successfully synthesized in our laboratory and were found to transform to the dinitrogen complexes Cp'Re(CO)(L)(N_2) under appropriate conditions. Furthermore, as reported in earlier chapters of this thesis and elsewhere, the phosphine dinitrogen complexes undergo photochemical C-H activation reactions. Therefore, as an extension of this study, we were interested to see whether similar chemistry resulted when Cp' is replaced by pyrazolylborate ligand (Tp = $HB(C_3H_3N_2)_3$).

6.2. Attempts to Synthesize Pyrazolylborate Rhenium Diazenido Complexes.

6.2.1 Results and Discussion

Direct substitution of a carbonyl group in $TpRe(CO)_3$[133] (**6.1**) is very difficult unless it is via UV-vis irradiation. Reactions of **6.1** or $TpRe(CO)_2PPh_3$[133] with the diazonium salt $[p\text{-}N_2C_6H_4OMe][BF_4]$ did not afford the pyrazolylborate rhenium aryldiazenido complex. These results are in agreement with the chemistry of Cp or Cp* rhenium complexes.[134]

Irradiation of the complex $TpRe(CO)_3$ (**6.1**) in the presence of the diazonium salt $[p\text{-}N_2C_6H_4OMe]^+$ cannot be used because it causes decomposition of the salt, generating nitrogen. However, previous workers in our laboratory have synthesized the complexes $[Cp'Re(CO)_2(N_2R)]^+$ (Cp' = C_5H_5 or C_5Me_5; R = $p\text{-}C_6H_4OMe$,) via the THF derivative $Cp'Re(CO)_2THF$,[135] which reacted *in situ* with the diazonium salt (Equation 6.1). The desired product can be isolated in better than 60% yield.[134]

$$Cp'Re(CO)_3 \xrightarrow[90\ min]{h\nu,\ THF} Cp'Re(CO)_2(THF) \xrightarrow[acetone]{[N_2R]^+} [Cp'Re(CO)_2(N_2R)]^+ \quad \text{Eq. 6.1}$$

$(R = C_6H_4OMe)$

A similar procedure was therefore used in an attempt to synthesize the pyrazolylborate rhenium aryldiazenido complex $[TpRe(CO)_2(p\text{-}N_2C_6H_4OMe)]^+$. The complex $TpRe(CO)_2THF$ (**6.2**) was generated by photolysis of $TpRe(CO)_3$ (**6.1**) in THF and then reacted *in situ* with diazonium salt $[p\text{-}N_2C_6H_4OMe][BF_4]$. The solution became red and it was stirred for 1 h at room temperature. The IR spectrum showed only the carbonyl bands $\nu_{(CO)}$ that corresponded to unreacted **6.1** at 2025, and 1913 cm^{-1} and $TpRe(CO)_2THF$ (**6.2**) at 1908, and 1823 cm^{-1}.[133] The solution was stirred for an extra 30 min and no change was observed in the IR spectrum.

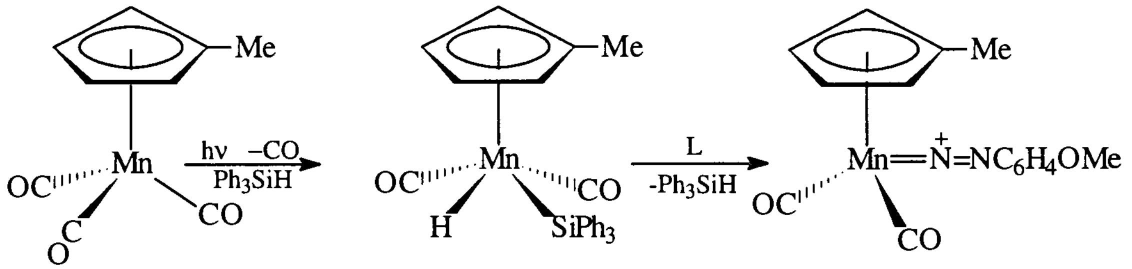
No evidence of the desired aryldiazenido rhenium complex was observed also when the reaction was carried out with a different ratios of the diazonium salt versus **6.2** (2:1 and excess). The IR spectrum showed the carbonyl bands associated with **6.1** and the complete loss of $\nu_{(NN)}$ at 2253 cm^{-1} for $[p\text{-}N_2C_6H_4OMe]^+$ indicated decomposition of the diazonium salt.

In an effort to increase the reactivity, the $TpRe(CO)_2THF$ (**6.2**) and diazonium salt were heated to 333 K in acetone for 15 min. This reaction was monitored by IR spectroscopy and no change was observed in the carbonyl region but the $\nu_{(N2)}$ at 2253 decreased in intensity. The reaction mixture was heated for further 30 min, 1 and 2 h, but the IR spectrum still showed only unreacted **6.1** and a decrease in the intensity of the carbonyl stretching bands of the THF derivative **6.2**. The same procedure was repeated with different ratios of the diazonium salt and **6.2** (2:1 and excess). The same result was observed. The reactions were repeated at low temperature (273 K) in case the problem was to prevent thermal decomposition of our target compound. The IR spectrum, however, again showed the bands associated with only **6.1** and **6.2** and no evidence of new carbonyl bands.

We concluded from this that the THF ligand in the pyrazolylborate rhenium complex $TpRe(CO)_2THF$ (**6.2**) was not labile enough to be replaced by the N_2R^+ ligand, in contrast to the chemistry of the Cp or Cp* rhenium analogues.[126a,134] It is well known in the field of rhenium diazenido chemistry, that the ligand MeCN is a very good leaving group and it can be replaced by a two electron donor ligand such as PR_3 (R = Me, OMe, Ph, Et).[134] We synthesized the acetonitrile derivative $TpRe(CO)_2(NCMe)$ by photolysis of $TpRe(CO)_3$ in MeCN.[133] The irradiation was carried out for 30 min and two new carbonyl bands ($\nu_{(CO)}$) were observed at 1913 and 1833 cm^{-1}, identified as those of $TpRe(CO)_2(NCMe)$ by comparison with literature values,[133] plus residual **6.1**. The solvent was removed and the crude acetonitrile complex $TpRe(CO)_2(NCMe)$ was dissolved in acetone and the diazonium salt $[p\text{-}N_2C_6H_4OMe]^+$ was added (1.0:1.0 ratio). The reaction was monitored by IR spectroscopy and after 15 min, the IR spectrum showed only the bands associated with unreacted **6.1** and the acetonitrile complex $TpRe(CO)_2(NCMe)$. The reaction was stirred overnight at room temperature, under N_2 and after 12 h there was no evidence of complex $TpRe(CO)_2(NCMe)$ and the IR spectrum showed only the unreacted $TpRe(CO)_3$ (**6.1**).

After all the attempts to synthesize our target compound $[TpRe(CO)_2(N_2C_6H_4OMe)][BF_4]$ were unsuccessful, we tried to change the electrophilic properties of the diazonium salt (better or poorer electrophile), by changing the substitutent on the phenyl ring. The complex $TpRe(CO)_2THF$ (**6.2**) was treated with $[N_2C_6H_4X][BF_4]$ (X = *o*-OMe, *o*-CF_3, *p*-Me); $[N_2C_6H_3X_2][BF_4]$, (X_2 = 3,5 dimethyl, 2,6 dimethyl); or $[N_2C_6H_2X_3][BF_4]$, (X_3 = 2,4,5-trifluoro) (1.0:1.0 ratio) *in situ* at room temperature and the reaction was followed by IR spectroscopy. The spectrum after 2 h showed a decrease in the intensity of carbonyl bands of **6.2** and decomposition of the diazonium salt. These reactions were also repeated at 273 and 333 K, and the results were similar to those at room temperature (see previously in the text).

It has been reported in the literature that $(MeCp)Mn(CO)_2(THF)$ produced instantaneous decomposition of the diazonium salt (N_2R^+) when the reaction was carried out *in situ.*[126a] An alternative route for the synthesis of $[(MeCp)Mn(CO)_2(N_2R)][BF_4]$ was the photolysis of $(MeCp)Mn(CO)_3$ and Ph_3SiH in *n*-hexane. The complex $(MeCp)Mn(CO)_2(H)(SiPh_3)$ so produced reacted with the diazonium salt (N_2R^+) to give the aryldiazenido manganese complex (Equation 6.2).[126a]



$L = [N_2C_6H_4OMe][BF_4]$

Eq. 6.2

Initially, the aryldiazenido rhenium complexes were prepared in low yields by reaction of the diazonium salt $[N_2R][BF_4]$ (R =*o*-C_6H_4OMe, *o*-$C_6H_4CF_3$, *p*-C_6H_4Me, 3,5-$C_6H_3Me_2$, 2,6-$C_6H_3Me_2$, 2,4,5-$C_6H_2F_3$) with $Cp'Re(CO)_2(SiPh_3)H$ (Cp' = C_5H_5 or C_5Me_5).[134] We followed the same procedure reported for manganese[136a] and rhenium[136b] silyl complexes in an attempt to synthesize $TpRe(CO)_2(SiPh_3)H$. Photolysis of a benzene solution of $TpRe(CO)_3$ with Ph_3SiH (1.0:0.6 ratio) was carried out for 45 min. The reaction was followed by IR spectroscopy, sampling every 15 min, and after 45 min the IR spectrum did not show any evidence of a new species in solution. The irradiation was extended for an extra 40 min, and the solution become brown and the intensity of the bands of **6.1** were reduced but no new bands were observed in the carbonyl region. The same reaction was carried out with a 1:1 ratio of $TpRe(CO)_3$ and Ph_3SiH and no evidence of the silyl derivative $TpRe(CO)_2(SiPh_3)H$ was observed. However, when the reaction was carried out with a 25 fold excess of Ph_3SiH, the IR spectrum showed two new carbonyl bands at 1962 and 1823 cm^{-1}. The ^1H NMR (acetone-*d*$_6$, 100.13 MHz) of the crude sample did not show a resonance in the metal hydride region and attempts to isolate this product were unsuccessful. The reaction was repeated, and the crude product was dissolved in acetone and reacted *in situ* with the diazonium salt ($[p\text{-}N_2C_6H_4OMe]^+$) in excess. The IR spectrum showed only the carbonyl bands of unreacted **6.1**; the carbonyl bands associated with the new species had disappeared, and no evidence of any other species was observed. The position of the carbonyl bands for the new species were compared with literature values for the complex $CpRe(CO)_2(SiPh_3)H$. Our values for the carbonyl stretching ($\nu_{(CO)}$ 1962 and 1832 cm^{-1}) were not in agreement with those observed for $CpRe(CO)_2(SiPh_3)H$, which were at $\nu_{(CO)}$ 1999 and 1932 cm^{-1} and at $\nu_{(CO)}$ 2004 and 1940 cm^{-1} in cyclohexane for cis and trans isomers, respectively.[136b] This suggests that the complex formed in the photolysis of $TpRe(CO)_3$ in excess of Ph_3SiH was not the silyl complex $TpRe(CO)_2(SiPh_3)H$.

The molybdenum pyrazolylborate aryldiazenido complex $TpMo(CO)_2(p\text{-}N_2R)$ (R = C_6H_4Me) can be obtained by reaction of the anion $[TpMo(CO)_3]^-$ with the diazonium salt ($N_2C_6H_4Me^+$). However, the bis(aryldiazenido) molybdenum complex can not be prepared with an excess of $[N_2C_6H_4Me][BF_4]$ unlike the Cp or Cp* molybdenum analogues.[137] An indirect synthesis for the pyrazolylborate molybdenum bis(aryldiazenido) complex $[TpMo(N_2R)_2PPh_3]^+$ (R = C_6H_4Me) has been reported by Lalor's group.[138] The reaction was carried out by a route involving the treatment of $[CpMo(p\text{-}N_2C_6H_4Me)_2(PPh_3)][BF_4]$ with $Tl[HB(N_2C_3H_3)_3]$ (TlTp) (Equation 6.3).[138]

$$[CpMo(N_2R)_2(PPh_3)]^+ + Tl[HB(N_2C_3H_3)_3] \longrightarrow [TpMo(N_2R)_2(PPh_3)]^+ + CpTl \qquad \text{Eq. 6.3}$$

$R = C_6H_4Me$

The reaction of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$[139a] with $Na[HB(N_2C_3H_3)_3]$ (NaTp) did not afford the complex $[TpRe(CO)_2(p\text{-}N_2C_6H_4OMe)]^+$. Moreover, the IR spectrum showed, in the carbonyl region, *five* new bands, which were identified as those of $Cp^*Re(CO)_2N_2$ ($\nu_{(N2)}$ 2125; $\nu_{(CO)}$ 1954 and 1902 cm^{-1}) and $Cp^*Re(CO)_3$ ($\nu_{(CO)}$ 2010 and 1913 cm^{-1}).[139b] In contrast to the result obtained with the molybdenum complex, the NaTp ligand reduced the diazenido rhenium complex to the known Cp* rhenium dinitrogen and Cp* rhenium tricarbonyl complexes (Equation 6.4). The corresponding Cp rhenium analogue was also reacted with NaTp and gave a similar result.[135,140]

$$[Cp^*Re(CO)_2(N_2R)]^+ \xrightarrow[\text{acetone}]{\text{NaTp}} Cp^*Re(CO)_2N_2 + Cp^*Re(CO)_3 + C_6H_5OMe \qquad \text{Eq. 6.4}$$

$R = C_6H_4OMe$; $Tp = HB(N_2C_3H_3)_3$

In the early work in the field of aryldiazenido chemistry, it was recognized that the nitrosyl ligand (NO^+) is isoelectronic with the diazonium ligand (N_2R^+), and synthesis of the related nitrosyl complexes facilitated the development of organodiazenido chemistry.[141]

While we were unable to synthesize an aryldiazenido complex, we were nevertheless interested in studying the reactivity of $TpRe(CO)_2THF$ (**6.2**) with NO^+ in an attempt to coordinate a nitrosyl to the rhenium center, and produce the complex $[TpRe(CO)_2(NO)][BF_4]$ (**6.3**) (Figure 6.2).

The complex $TpRe(CO)_2THF$ (**6.2**) was generated by photolysis of $TpRe(CO)_3$ (**6.1**) in THF and reacted *in situ* the with nitrosonium salt $[NO][BF_4]$ (dissolved previously in acetone and kept in an ice-bath). A yellow precipitate was formed. The crude product was dissolved in acetone and diethylether slowly added to precipitate the product.

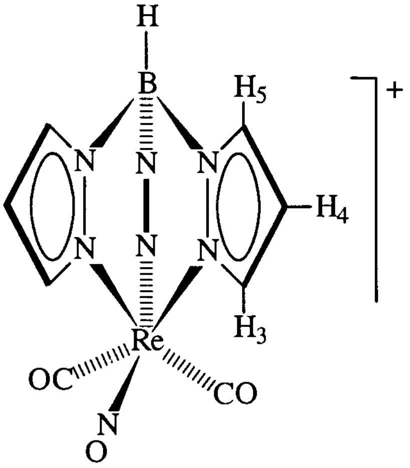


Figure 6.2 Structure of $[TpRe(CO)_2(NO)][BF_4]$ (**6.3**).

The nitrosyl complex $[TpRe(CO)_2(NO)][BF_4]$ (**6.3**) was characterized using IR, NMR and EIMS spectroscopies. The IR spectrum of **6.3** exhibited $\nu_{(CO)}$ bands at 2122 and 2058 cm^{-1} and $\nu_{(NO)}$ at 1832 cm^{-1}. These are in the typical regions for coordinated CO (terminal) and NO (linear) absorption in cationic rhenium compounds.[142] The values of the carbonyl and nitrosyl stretching frequencies of this complex are slightly lower than that reported for the corresponding cyclopentadienyl complex:[142c] this suggests that the pyrazolylborate ligand is a better donor than the Cp ligand. The positive-ion FABMS spectrum of **6.3** gave a strong parent M^+ peak at *m/z* 486 for the cation; this was also the base peak for this complex. A fragment at *m/z* 458 was consistent with loss of one coordinated CO. Another two fragments at *m/z* 430 and 400 correspond to loss of the second CO and then the NO ligand from the parent ion.

The ^1H NMR spectrum of **6.3** exhibited in the aromatic region the resonances corresponding to the protons of the $HB(N_2C_3H_3)_3$ ligand (Tp). The triplets at δ 6.58, and 6.65 were assigned to the two different H_4 environments in the Tp ligand and they integrated for 1H and 2H with a J_{H-H} = 2.3 Hz, respectively (See Figure 6.2). The doublet at δ 8.23 was assigned to the H_5 protons, and the resonance at δ 8.67 was assigned to H_3 protons. Both resonances integrated for 3H with a J_{H-H} = 2.3 Hz, (Figure 6.3). These assignments are in agreement with the literature values for the pyrazole ion[143] and pyrazolylborate ligand[133,144a], where H_4 typically exhibited an upfield resonance compared with the resonances for H_3 and H_5. It was observed in the ^1H NMR spectrum that H_3 and H_5 showed only one resonance for the Tp ligand. These results are in contrast with a C_s symmetry imposed by the nitrosyl ligand (NO), where the ^1H NMR spectrum

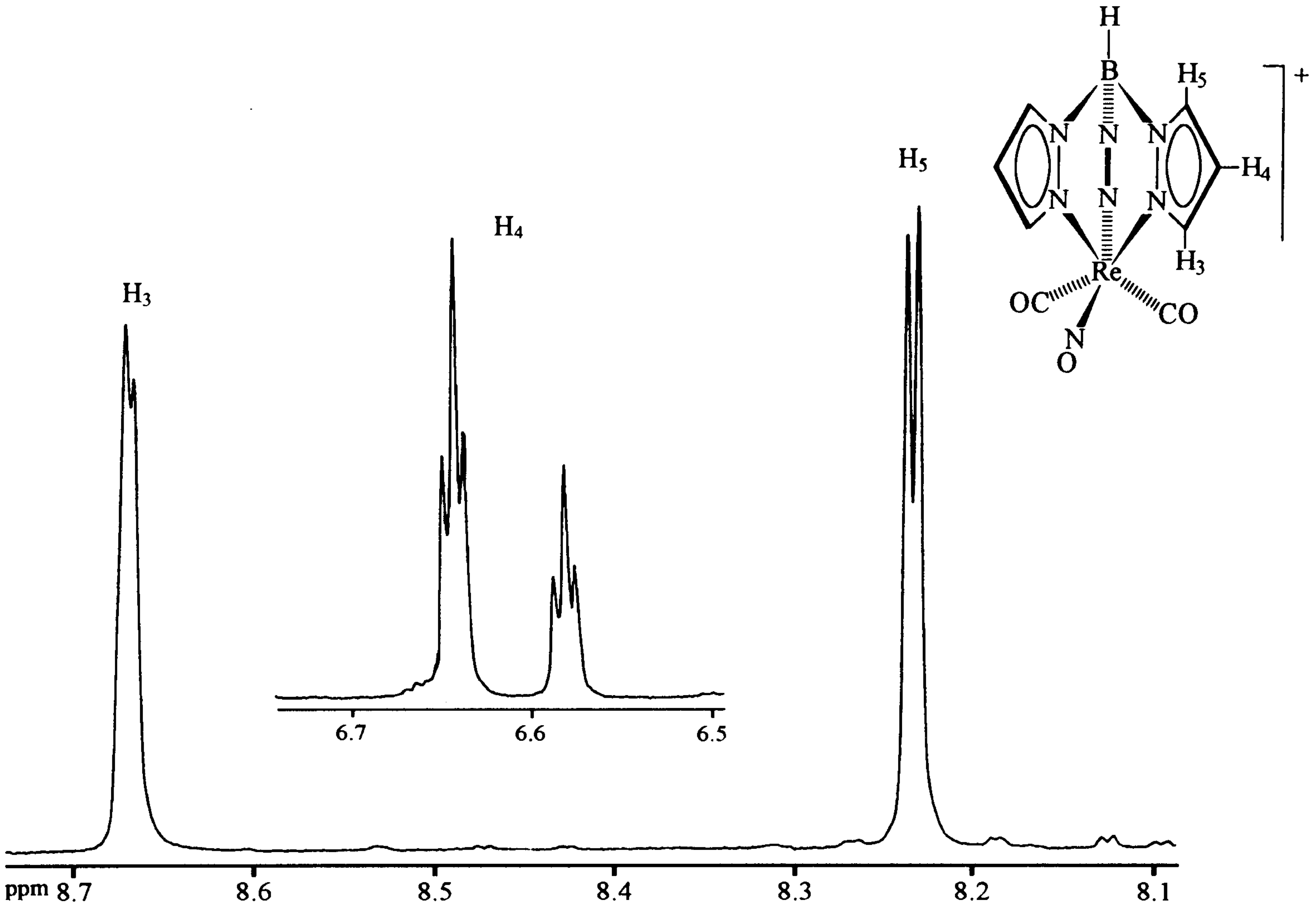


Figure 6.3 ^{1}H NMR spectrum of $[TpRe(CO)_2(NO)]^+$ (**6.3**) in acetone-d_6.

should show two signals (ratio 2:1) for each of the positions H_3, H_4 and H_5 of the pyrazolyl rings (see Figure 6.3).[133] We suggest that the chemical shift difference for the inequivalent H_3 (and H_5) protons is much smaller than for H_4, and appear coincident. If free rotation of the Tp ligand was occurring, the ^{1}H NMR should show only one signal for each of the different protons on three equivalent pyrazolyl rings (*i.e.* a single doublet for H_3, a single triplet for H_4 and a single doublet for H_5).

The $^{13}C\{^1H\}$ NMR showed *six* resonances for the Tp ligand (Figure 6.4), and the resonance for the Re-CO was not observed due to the very small intensity of the CO peak (not due to the signal overlapping with the solvent). Attempts to run the $^{13}C\{^1H\}$ NMR in $CDCl_3$ was unsuccessful due to the poor solubility of **6.3** in this solvent, but the presence of the carbonyl ligands was confirmed by IR spectroscopy. The $^{13}C\{^1H\}$ NMR spectrum was sensitive to the *two* different ring environments in the pyrazolylborate ligand. The upfield resonances at δ 109.1, and 109.3 (1:2) were assigned to carbons C_4, the resonances at δ 139.2, and 140.1 (2:1) were assigned to C_5 carbons and those at δ 147.3, and 147.4 (2:1) were assigned to C_3 carbons, respectively. These assignments of the different carbons in the pyrazolylborate ligand (Tp) are consistent with literature values for the pyrazolyl ion[143a] and the pyrazolylborate ligand.[144]

A possible explanation of the reactivity of NO^+ versus N_2R^+ could be that the nitrosonium (NO^+) is a better Lewis acid compared with the diazonium ions (N_2R^+).[141] A difference in the reactivity of the diazonium ion versus the nitrosonium ion has been observed previously in the synthesis of the Cp rhenium complexes. The nitrosonium ion

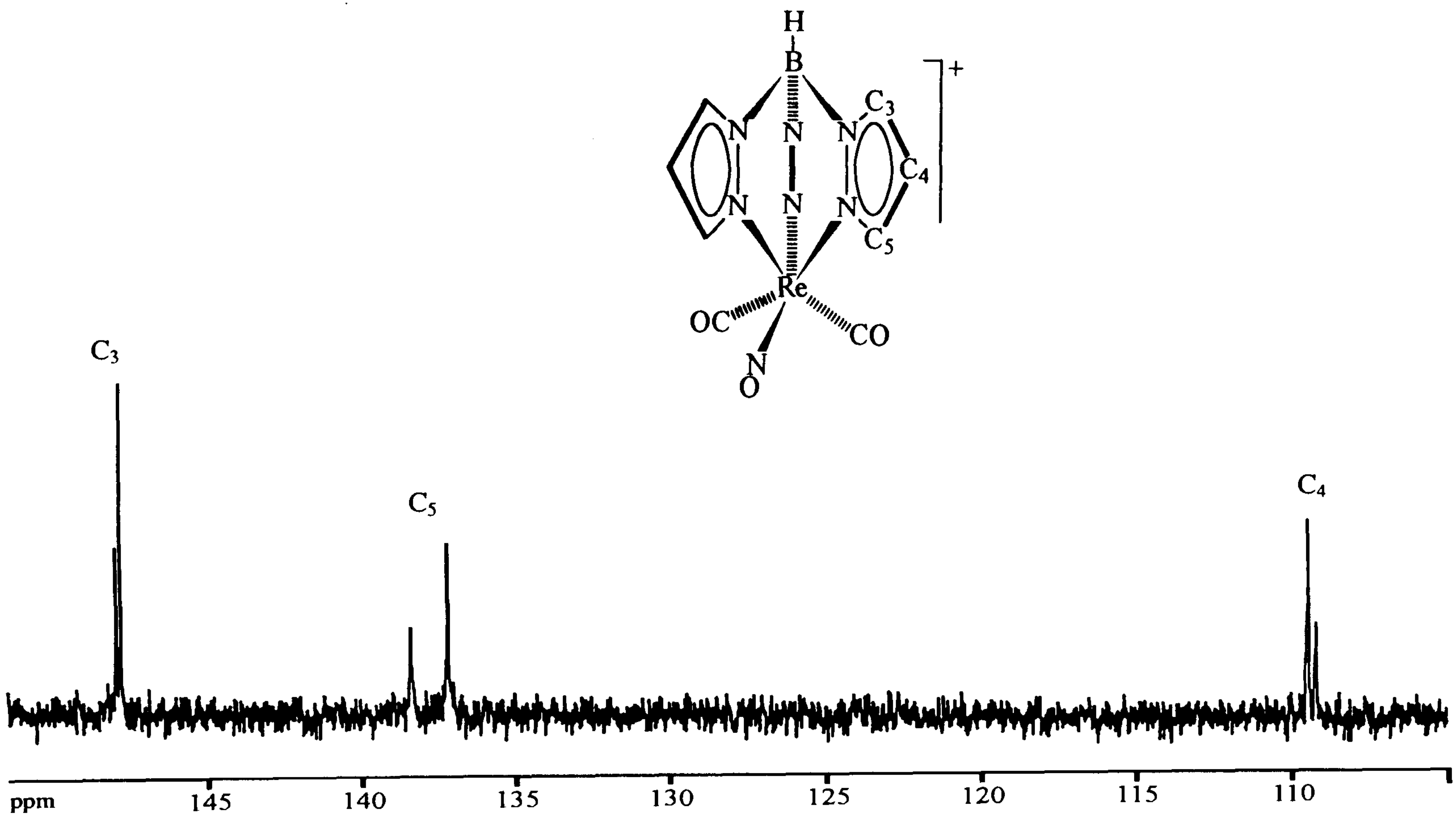


Figure 6.4 $^{13}C\{^{1}H\}$ NMR Spectrum of $[TpRe(CO)_2(NO)]^+$ (**6.3**) in acetone-d_6.

reacts with $CpRe(CO)_3$ at 258 K in $MeNO_2$ to form rhenium nitrosyl analogues,[142c] while the diazenido rhenium analogues needed to be synthesized from N_2R^+ via $Cp^*Re(CO)_2(THF)$[139a] or $CpRe(CO)_2(SiPh_3)(H)$.[126a]

Another possible explanation is the nature of the Tp ligand. $TpRe(CO)_3$ has a pseudo-octahedral geometry whereas $Cp'Re(CO)_3$ ($Cp' = C_5H_5$ or C_5Me_5) complexes form a "piano stool" geometry. However, both aryldiazenido and nitrosyl complexes with pyrazolylborate ligands (and substituted pyrazolylborate) have been reported in the literature in molybdenum chemistry.[137,138,145] We can summarise that the $TpRe(CO)_2(THF)$ (**6.2**) reacts with the nitrosyl ligand (NO^+) and produces $[TpRe(CO)_2NO]^+$ (**6.3**) but the routes used to synthesize the aryldiazenido analogues were not successful. We think that this lack of formation of the rhenium aryldiazenido complex was not due to steric interactions,[137,138] but it is possible that it could be due to an electronic effect. At the present, we can not conclude that this complex does not exist. It may just be that we have not found the right synthetic method.

6.3 Reactivity of $[TpRe(CO)_2(NO)][BF_4]$ (6.3) with Various Nucleophiles

The chemistry of Cp rhenium nitrosyl complexes has been studied by several groups[146] and it has been observed that when the rhenium nitrosyl cation [*i.e.* $CpRe(CO)_2(NO)]^+$ reacts with nucleophiles, it does not appear that the nitrosyl ligand is transformed. Instead, the nitrosyl complexes are remarkable for their ability to react with nucleophiles at the carbonyl carbon groups and yield stable products in which a new organic functionalization has resulted.[142c,146,147] It has been suggested that the tendency of a CO ligand to react with nucleophiles depends upon the electron density on the carbon atom.[148] The purpose of this work is to explore the pyrazolylborate rhenium nitrosyl chemistry that was, until now, completely unknown and compare its reactivity with the Cp nitrosyl analogues.

6.3.1 Results

6.3.1.1 Reaction of $[TpRe(CO)_2(NO)][BF_4]$ (6.3) with NaOMe

The reaction of **6.3** with NaOMe was carried out at room temperature in MeOH for 1 h. The IR spectrum showed $\nu_{(CO)}$ 1994, $\nu_{(COOMe)}$ 1632 and $\nu_{(NO)}$ 1751 cm^{-1} for TpRe(CO)(NO)(COOMe) (**6.4**) in benzene (Figure 6.5).

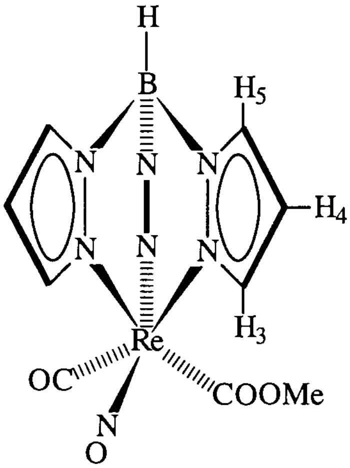


Figure 6.5 Structure of TpRe(CO)(NO)(COOMe) (**6.4**).

The mass spectrum of the complex **6.4** gave a parent peak at *m/z* 517. A fragment at *m/z* 486 is consistent with loss of the methoxy group (OMe); this was also the base peak for this complex.

The ^1H NMR spectrum of **6.4** in benzene-d_6 (Figures 6.6 and 6.6a) showed a OMe resonance at δ 3.80, and the aromatic region showed three inequivalent pyrazolyl rings. Three sets of triplets were observed at δ 5.58, 5.69, and 5.73 with a coupling constant ~2.3 Hz. These resonances were assigned to H_4 in the Tp ligand. The doublet of doublets at δ 6.97 (integral 1H) with a coupling constant of 2.3 Hz, and 0.7 Hz is assigned to H_5 and a multiplet at δ 7.15 (integral 3H) is assigned to the protons H_5 and H_3. The two doublets at δ 8.21, and 8.31 with a coupling constant of ~2.3 Hz were assigned to H_3. The assignments for the different protons and the coupling constant in the Tp ligand were confirmed by comparison of our data with the data reported in the literature for pyrazolyl ion and for other Tp complexes.[133,143,144]

When **6.3** was dissolved in MeOH, *two* extra bands were observed in the IR spectrum at 1994 and 1751 cm^{-1} (Figure 6.7). This product was identified as **6.4** which presumably was produced by nucleophilic attack of one molecule of MeOH on the carbonyl ligand in **6.3**. When NaOMe was added, the IR absorption bands of the starting material further decreased until undetectable and the only absorption bands observed were those that corresponded to **6.4** (see Figure 6.7).

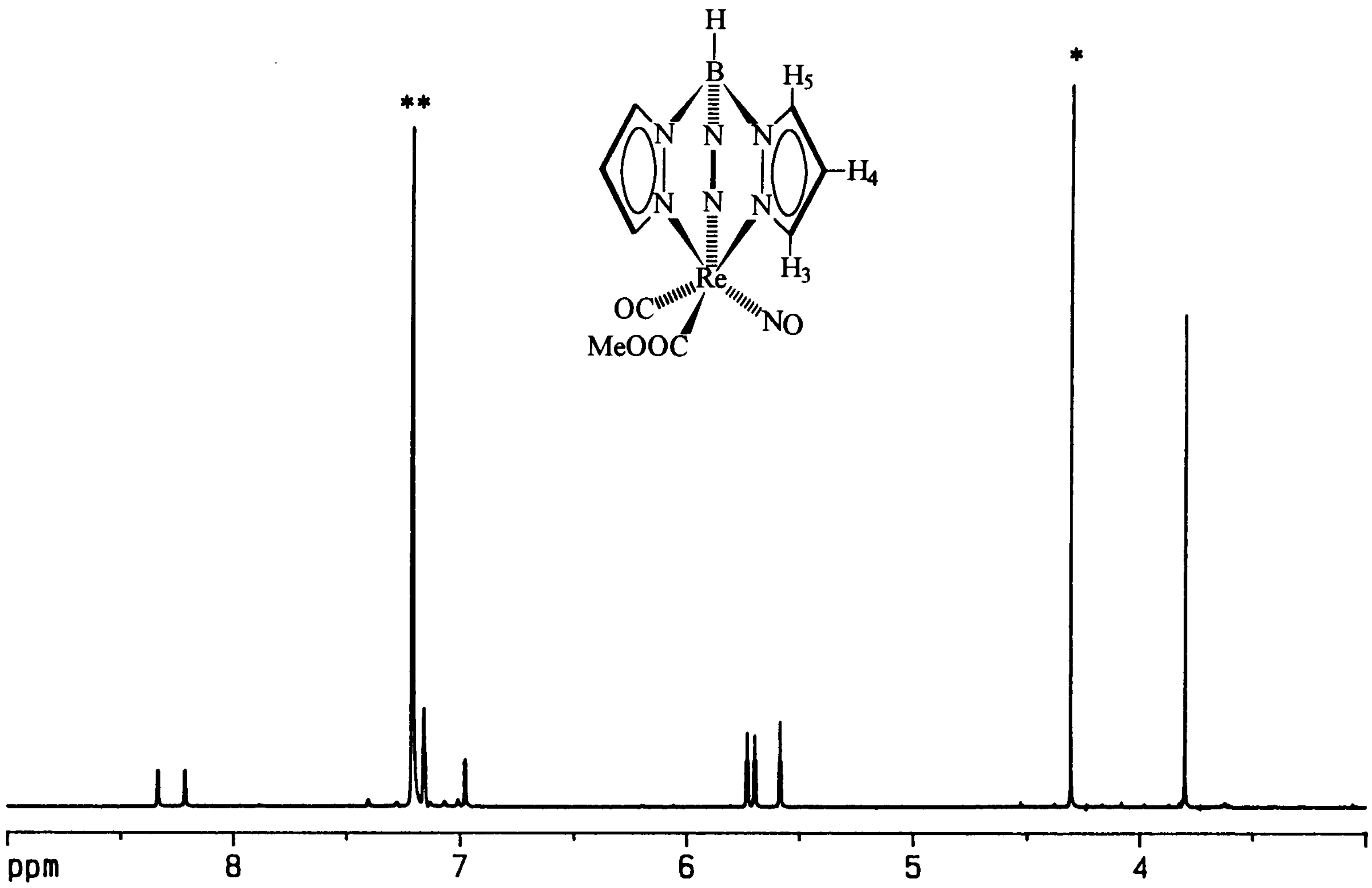


Figure 6.6 ^{1}H NMR spectrum of TpRe(CO)(NO)(COOMe) (**6.4**) in benzene-d_6.

* MeOH ** C_6H_6. An expanded spectrum is shown in Figure 6.6a.

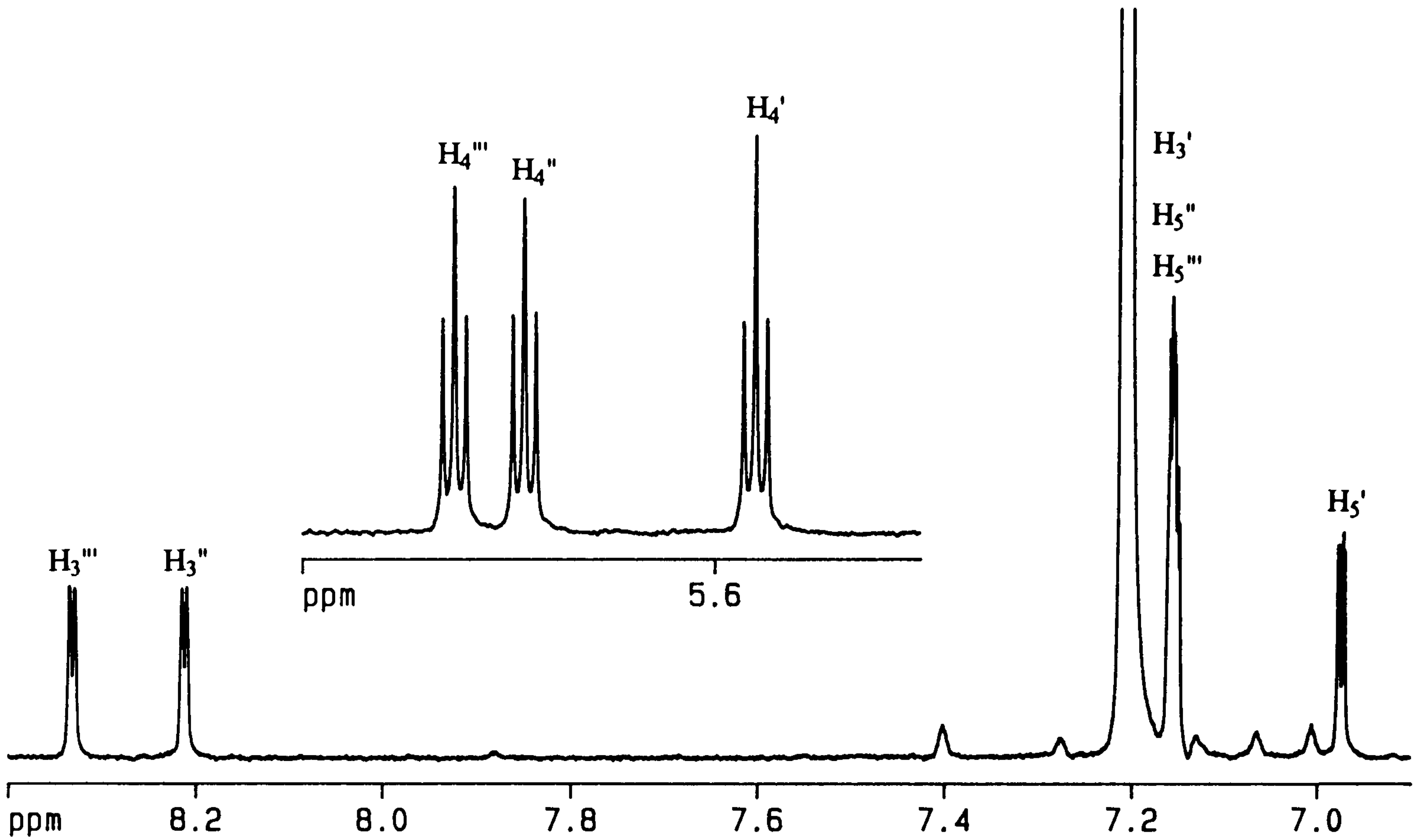


Figure 6.6a ^{1}H NMR spectrum of TpRe(CO)(NO)(COOMe) (**6.4**) in benzene-d_6. **Downfield resonances have been expanded for** clarity.

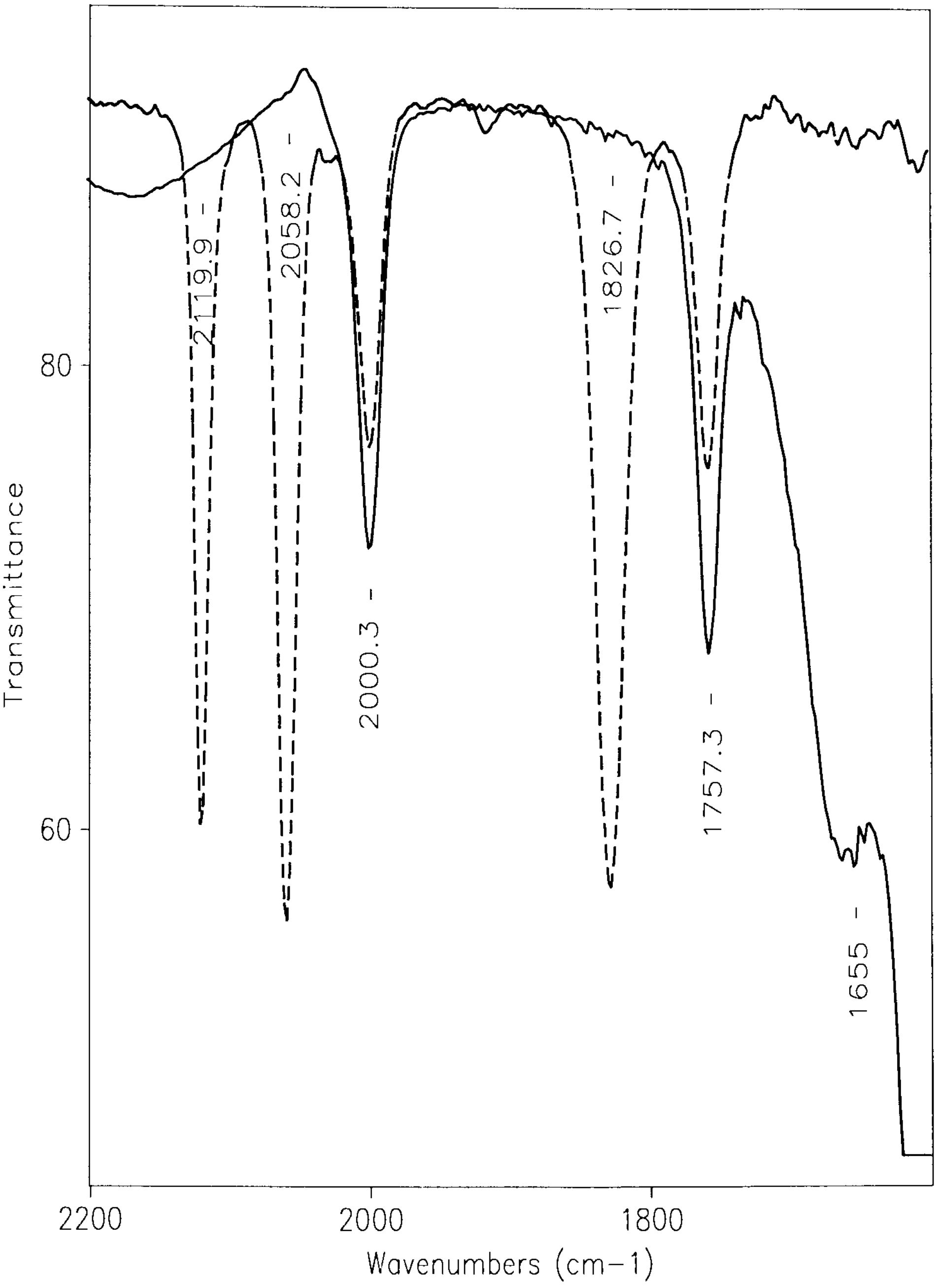


Figure 6.7 IR spectra of $[TpRe(CO)_2(NO)]^+$ (**6.3**) --- in MeOH — after added NaOMe.

6.3.1.2 Reaction of [TpRe(CO)$_2$(NO)][BF$_4$] (6.3) with NaN$_3$

The azide ion (N_3^-) is a common nucleophile in addition reactions of cationic transition metal complexes to form isocyanate complexes.[148a,149] Reaction of **6.3** with NaN$_3$ at room temperature in CH$_2$Cl$_2$ resulted in the complex TpRe(CO)(NO)(NCO) (**6.5**) (Equation 6.5).

$$[\mathrm{TpRe(CO)_2(NO)}]^+ \ + \ \mathrm{NaN_3} \ \xrightarrow[\text{room temp}]{\mathrm{CH_2Cl_2}} \ \mathrm{TpRe(CO)(NO)(NCO)} \ + \ \mathrm{N_2} \qquad \text{Eq. 6.5}$$

The IR spectrum of **6.5** showed the $\nu_{(CO)}$ absorption band at 1998 cm^{-1}, and absorption at 1751 $\nu_{(NO)}$ and at 2253 cm^{-1} $\nu_{(NC)}$ for the NCO ligand in CH$_2$Cl$_2$. This is an indication of the nucleophilic attack on one of the carbonyl ligands in the nitrosyl complex.

The ^{1}H NMR spectrum of **6.5** in acetone-d_6 showed the expected *three* inequivalent proton resonances of the pyrazolyl rings in the Tp ligand. The H_4 protons were observed at δ 6.52 and 6.50 as a triplet and two overlapping triplets integrating for 1H and 2H, respectively. The H_5 protons were observed at δ 7.99 (integral 1H) as a doublets of doublets, and at δ 8.01 (integral 2H) as a two overlapping doublet of doublets. Finally, the resonances for H_3 were observed at δ 8.05 (integral 1H) as a doublet, and at δ 8.07 (integral 2H) as a multiplet.

The EIMS of **6.5** gave a weak parent peak at *m/z* 500; the base peak was observed at *m/z* 472, which corresponds to the loss of CO from M$^+$. A fragment at *m/z* 442 and one at *m/z* 414 are consistent with loss NO and futher CO, presumably from the NCO ligand.

6.3.1.3 Reaction of [TpRe(CO)$_2$(NO)][BF$_4$] (6.3) with NaOH or Et$_3$N

Metallocarboxylic acids or hydroxycarbonyl complexes have been proposed as key intermediates in the reactions of metal carbonyls with water or base to give the corresponding metal hydrides.[139a,142c,150] We used the same method in an attempt to synthesize a pyrazolylborate rhenium hydride nitrosyl complex TpRe(CO)(NO)H. When complex **6.3** was dissolved in acetone and NaOH 6M (4 drops) was slowly added at room temperature, the colour of the solution changed from yellow to pale orange and the IR spectrum showed two new bands at 1994 and 1763 cm^{-1}. We assigned the higher frequency band to a carbonyl ligand and the lower band to the NO stretch of the nitrosyl group. We analyzed the IR spectrum in the range 1750-1600 cm^{-1} for a possible absorption band associated with the COOH group for evidence of the formation of TpRe(CO)(NO)(COOH).[147] The IR spectrum did not exhibit the corresponding band in this area.

The ^{1}H NMR spectrum (acetone-d_6) showed no evidence of a proton resonance in the range 12-8 ppm expected for the OH group in the complex TpRe(CO)(NO)(COOH) nor a metal hydride resonance attributable to the formation of TpRe(CO)(NO)H. However, the aromatic region showed characteristic resonances of the three inequivalent pyrazolyl rings of the Tp ligand. The resonances at δ 6.33 and 6.43 were assigned to H_4 nuclei (integral 1:2) in the pyrazolyl ring. The resonances at δ 7.91, 7.98, and 8.00 were assigned to protons H_5 and finally the resonances at δ 8.07, 8.14 and 8.16 were assigned to protons H_3. A resonance was observed at δ 3.55 which was assigned to a deshielded methyl group.

The mass spectrum of this product gave a weak peak of highest mass at *m/z* 517. This corresponds to $[TpRe(CO)(NO)(COOMe)]^+$. A fragment at *m/z* 484 is consistent with the M^+ of a $[TpRe(CO)_2(NO)]^+$ fragment resulting from OMe loss; this was also the base peak. The fragment *m/z* 458 corresponded to loss of a CO ligand (Figure 6.8). Indeed, the complete mass spectrum is essentially identical in position and intensity to that of **6.4**. Unaccountably, the evidence suggests the product to be the methoxycarbonyl complex **6.4**.

The reaction was repeated under milder conditions (0.6M NaOH) in case the result was due to possible decomposition of an initial product. Complex **6.3** was dissolved in acetone and NaOH (0.6M, 4 drops) was added dropwise to the solution. The IR spectrum after the addition showed the disappearance of the nitrosyl complex at $\nu_{(CO)}$ 2120, 2058, and $\nu_{(NO)}$ 1829 cm^{-1}, and two new bands were observed at 2021 and 1913 cm^{-1}. The complex formed was analyzed by MS. The mass spectrum showed a peak at *m/z* 484 (M^+). A fragment at *m/z* 456 and one at *m/z* 428 are consistent with loss CO and a second CO from M^+. The complex was identified as $TpRe(CO)_3$ (**6.1**) by comparison with the $\nu_{(CO)}$ in the IR and the mass spectrum obtained from our starting material **6.1**.[133]

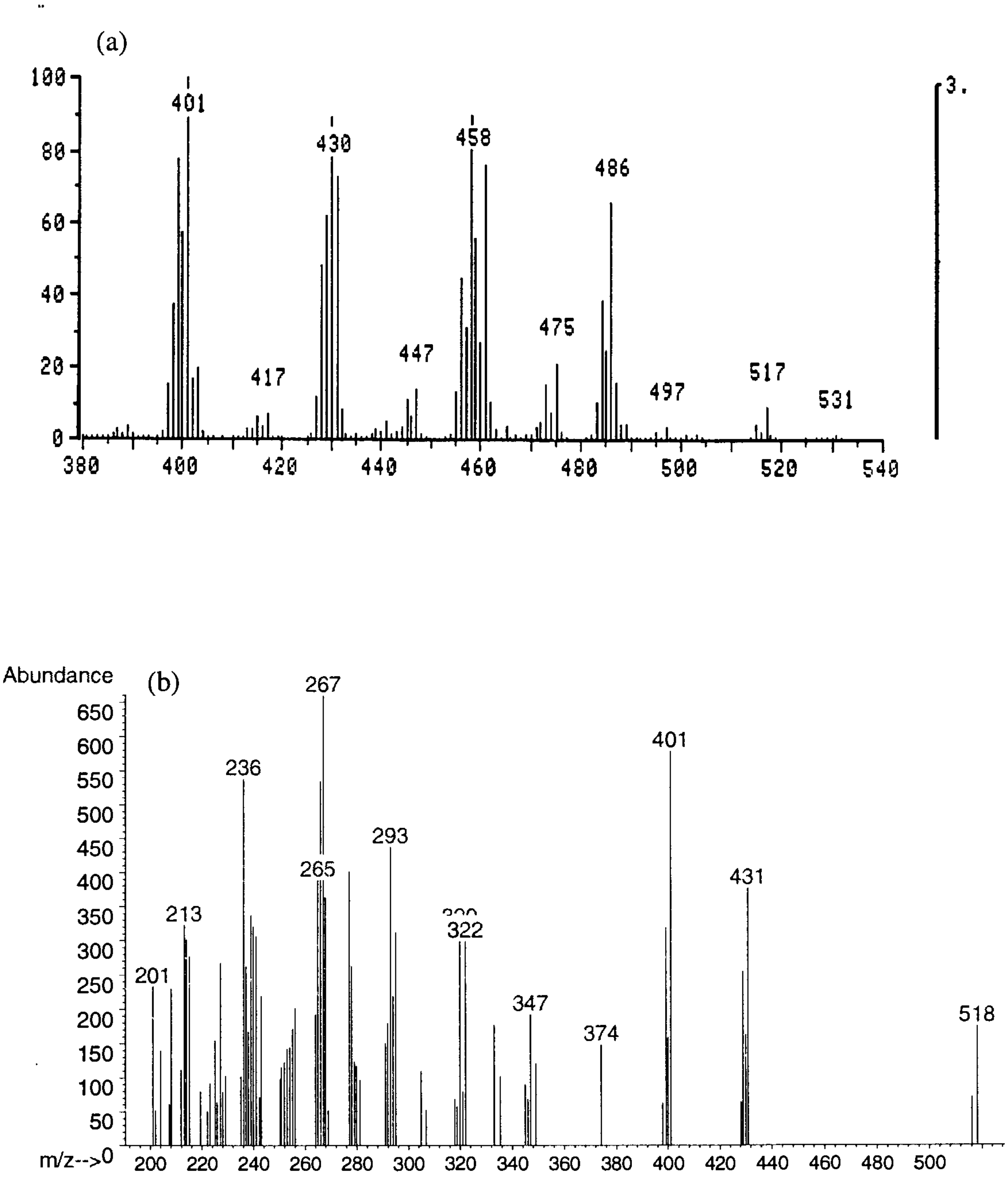


Figure 6.8 MS of the reaction between $[TpRe(CO)_2(NO)]^+$ (**6.3**) and (a) NaOH 6M (b) Et_3N (1% H_2O) in acetone.

The reaction was repeated using acetonitrile as a solvent. The complex **6.3** was dissolved in MeCN and slowly 4 drops of NaOH (6M) were added. The colour of the solution changed from yellow to colourless and a precipitation of a white solid was observed. The IR spectrum of the supernate did not show any carbonyl stretch(es) or a $\nu_{(NO)}$ in the range of 2200-1600 cm^{-1}. The supernate was discarded and the remaining solid was dissolved in hexane, diethylether, acetone, CH_2Cl_2, and ethanol. The IR spectra in the different solvents did not show a carbonyl absorption associated with an organometallic material. The solid dissolved in H_2O but no evidence of a carbonyl complex was observed in the IR spectrum.

It can be concluded from these results, that the OH^- did not attack the coordinated CO to give TpRe(CO)(NO)(COOH), which might have led to a hydrido complex TpRe(CO)(NO)H by decarboxylation. Instead, a reaction was observed but the spectroscopic data suggested that the product formed was TpRe(CO)(NO)(COOMe). However, we can not propose any reasonable mechanism for the formation of this complex. In contrast with these results, when NaOH 0.6M was used, we observed the tricarbonyl complex $TpRe(CO)_3$ (**6.1**). This result suggested that the nucleophilic attack was at the nitrosyl ligand rather than at the expected carbonyl group.

An alternative possible pathway for the formation of a hydride complex is to react the complex $[TpRe(CO)_2(NO)]^+$ (**6.3**) in acetone with 1% H_2O in the presence of triethylamine (NEt_3).[146b,151] The mixture of acetone and triethylamine (1% H_2O) was added to the nitrosyl complex (**6.3**), which immediately reacted to give an orange-red solution. The IR spectrum exhibited only one band at $\nu_{(CO)}$ 1989 cm^{-1} in the solvent mixture. When solvent was removed and the solid remaining was dissolved in benzene, *three* bands were observed in the IR spectrum at 1992, 1750, and 1633 cm^{-1}. The ^{1}H NMR spectrum in benzene-d_6 did not exhibit a resonance in the metal hydride region. The spectrum showed resonances in the methyl and methylene regions and the aromatic region showed the resonances attributable to the Tp ligand (See Experimental Section 6.5.10). The mass spectrum gave a weak peak at *m/z* 546, and at *m/z* 518 which is consistent with loss of CO ligand (see Figure 6.8). The identity of this complex is unknown and with the spectroscopic evidence available we can not propose any formulation.

When a benzene solution was kept for 30 min at room temperature, an oily residue was observed in the reaction vessel. The solvent was removed and the sample was dissolved in acetone. The IR spectrum showed absorption bands of the new complex and the starting material (**6.3**) to be present.

6.3.1.4 Reaction of [TpRe(CO)$_2$(NO)][BF$_4$] (6.3) with Et$_4$NCl

Oxidative removal of coordinated CO using iodosobenzene (PhIO) was first reported by Gladysz *et al.*, who found that the reaction of the dicarbonyl nitrosyl cation [CpRe(CO)$_2$NO]$^+$ in acetonitrile with PhIO resulted in the formation of the acetonitrile substituted complex [CpRe(CO)(NCMe)(NO)]$^+$ in good yield.[152]

Using a similar approach, we attempted to simulate the Cp nitrosyl rhenium chemistry in order to produce a labile complex and then by replacing the ligand by Cl$^-$ to obtain our target molecule TpRe(CO)(NO)Cl. A solution of [TpRe(CO)$_2$(NO)]$^+$ in

CH_2Cl_2 was treated with iodosobenzene at room temperature. The reaction was followed by IR spectroscopy and after 3 min, the IR spectrum showed two new weak bands at 2020 and 1765 cm^{-1} (Figure 6.9). The higher absorption was assigned to a carbonyl stretching and the lower to the nitrosyl ligand. We propose that the *two* new bands observed in IR spectrum correspond to dichloromethane coordinated to the rhenium center and the mechanism for the formation of this intermediate is initiated by nucleophilic attack of PhIO at the carbonyl carbon atom followed by liberation of CO_2 and coordination of a dichloromethane molecule from the solvent (Figure 6.10).[153]

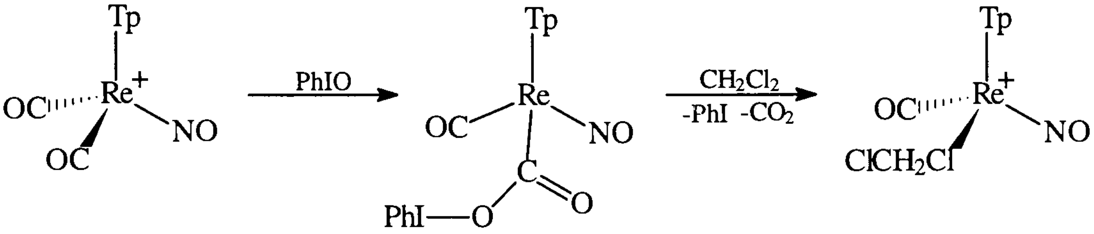


Figure 6.10 Oxidative removal of coordinated CO using PhIO.

Coordination of dichloromethane in the rhenium center has been observed by Gladysz *et al.* in the reaction of $CpRe(NO)(CH_3)(PPh_3)$ with $NaBH_4$ in CH_2Cl_2.[12] However, in the reaction of **6.3** with PhIO, iodobenzene (PhI) would be formed and this could instead react with the 16-electron intermediate [TpRe(CO)(NO)] and generate the complex $[TpRe(CO)(NO)(IPh)]^+$. According to the literature, alkyl and aryl iodides form stable complexes[99d] with $[CpRe(NO)(PPh_3)]$ fragment and we can not rule out the possible formation of the iodobenzene rhenium complex. When Et_4NCl was added the solution became purple and two new bands were observed at 2000 and 1751 cm^{-1} which were assigned to the carbonyl and nitrosyl ligand, respectively (see Figure 6.9).

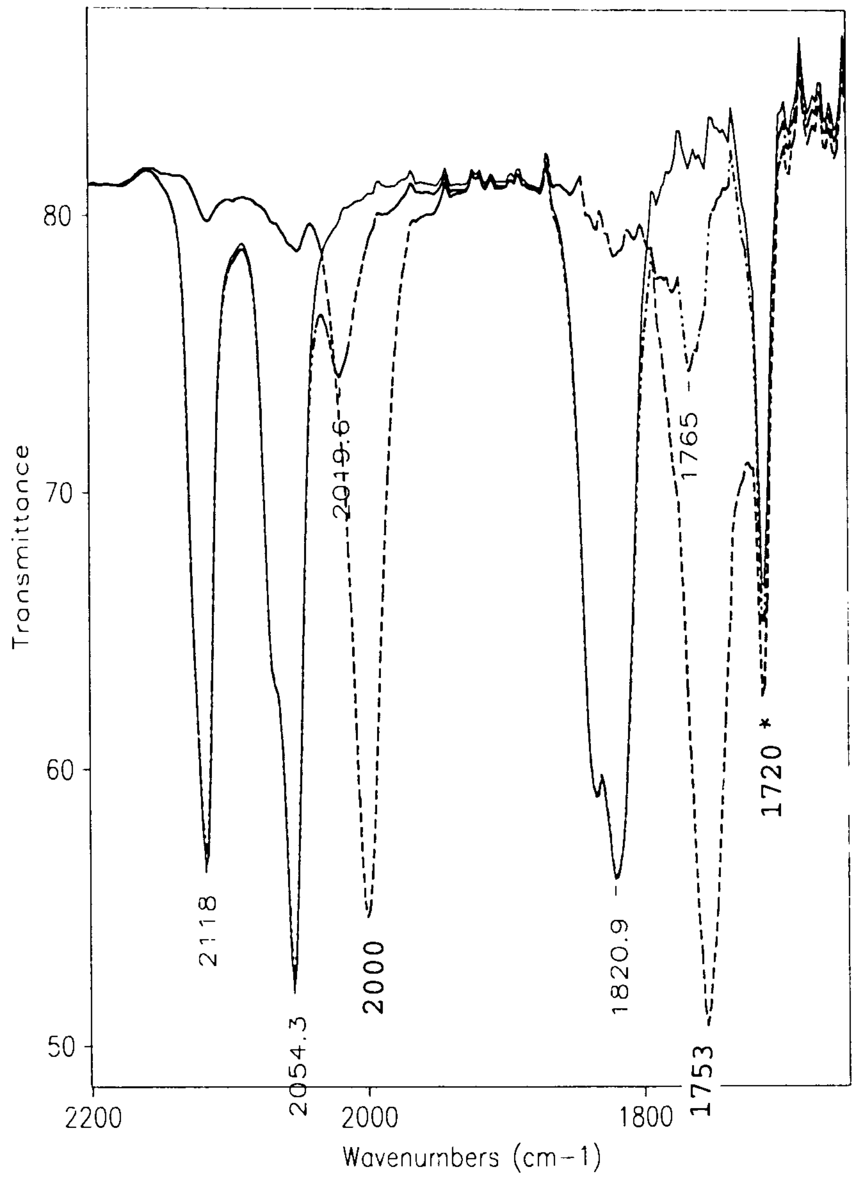


Figure 6.9 IR spectra of [TpRe(CO)$_2$(NO)][BF$_4$] (**6.3**) — in CH$_2$Cl$_2$; --- after 3 min of addition PhIO; — — — after 5 min of addition Et$_4$NCl. * Acetone as an impurity in the cell.

The new complex was identified as TpRe(CO)(Cl)(NO) (**6.6**) (Figure 6.11) using ^{1}H, ^{13}C{^{1}H} NMR and MS.

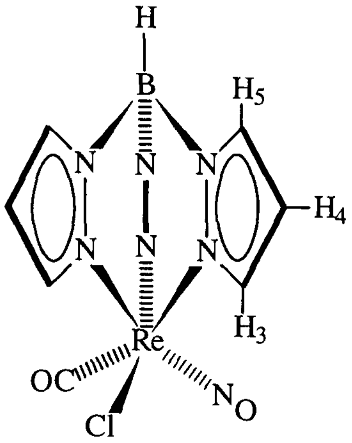


Figure 6.11 Structure of TpRe(CO)(Cl)(NO) (**6.6**)

The ^{1}H NMR spectrum of **6.6** showed three inequivalent environments for the pyrazolyl rings. Three sets of triplets were observed at δ 6.37, 6.47, 6.50 (integral 1H, respectively) with a coupling constant ~2.3 Hz. These resonances were assigned to H_4 in the Tp ligand (see Figure 6.11). A doublet and a multiplet at δ 7.93 and 7.97 (integral 1H and 2H, respectively) were assigned to H_5 and, finally, the three doublets at δ 8.04, 8.05 and 8.12 (integral 1H, respectively) with a coupling constant of ~2.3 Hz were assigned to H_3.

The ^{13}C{^{1}H} NMR showed *nine* resonances corresponding to the three inequivalent pyrazolyl groups in the Tp ligand. The number of resonances observed in the spectrum were in agreement with a C_1 symmetry in the rhenium center. The identification of the different carbons in the pyrazolylborate ligand was based on the literature values observed for the pyrazole ring.[143,144] The resonances at δ 107.5, 107.9, and 108.8 were assigned to the C_4 carbons, the resonances at δ 137.1, 137.2, and 138.2 were assigned to C_5 and finally the resonances at δ 144.1, 145.5, and 146.5 were assigned to C_3 in the pyrazolylborate ligand. The mass spectrum of the complex **6.6** gave a parent peak at *m/z* 493; the base peak at *m/z* 465 corresponds to the loss of CO from the parent ion. The fragment at *m/z* 435 is consistent with the loss of NO. The isotopic patters observed were comparable with simulated patters (Figure 6.12).

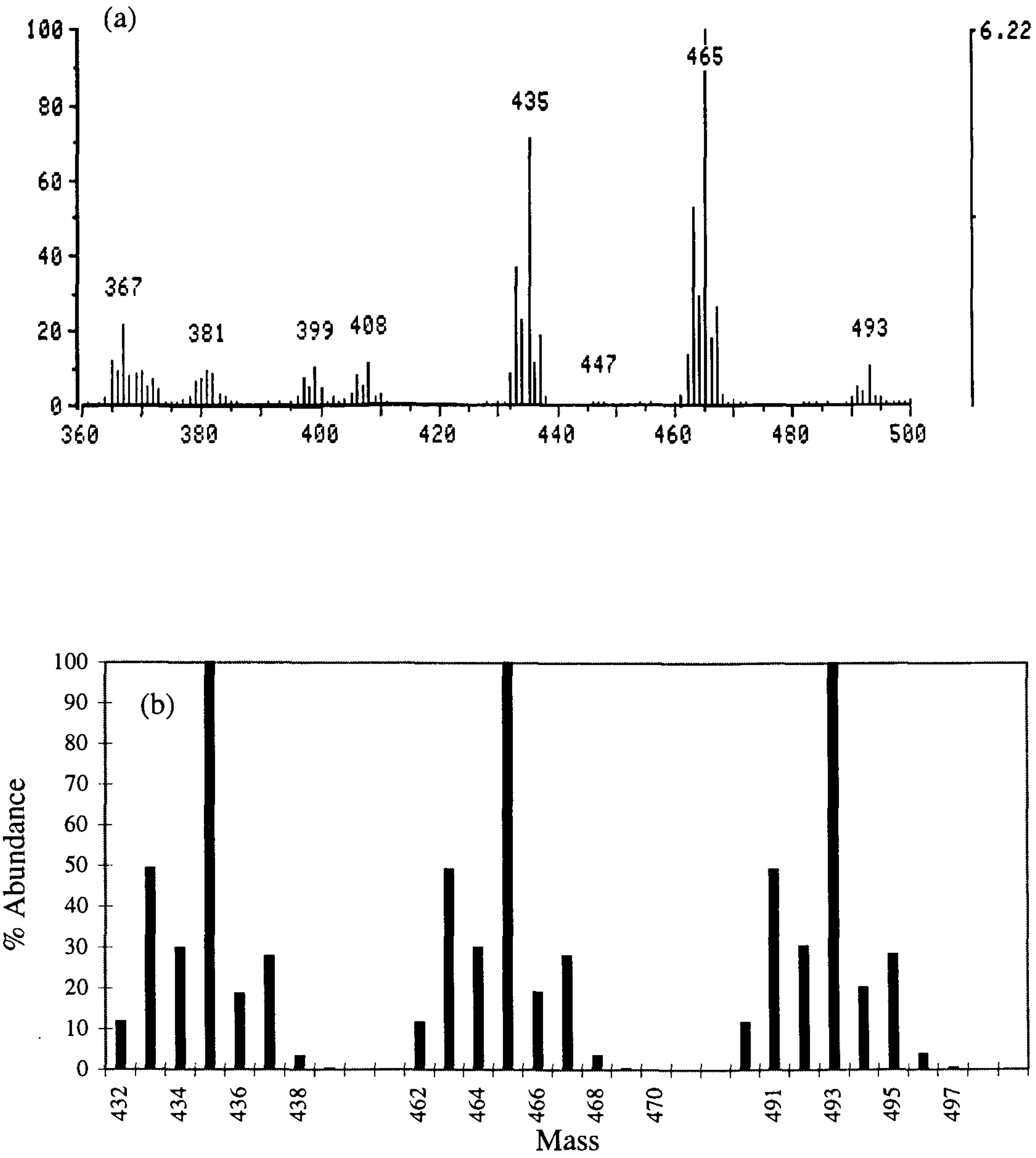


Figure 6.12 (a) Mass spectrum of TpRe(CO)(NO)Cl (**6.4**), (b) Simulation of the mass spectrum for **6.4**, M^+; (*m/z* = 493), for M^+-CO; (*m/z* = 465) and for M^+-CO-NO (*m/z* = 435)

6.3.2 Discussion

The reaction of **6.3** with nucleophiles OMe^-, N_3^-, and Cl^- are reported and all have similarities in that the products **6.4**-**6.6** are neutral monocarbonyl complexes of the general formula TpRe(CO)(NO)L (L = CO_2Me (**6.4**), NCO (**6.5**), Cl (**6.6**)). The reactions of **6.3** with NaOH and NEt_3 did not produce the desired products and they will be discussed further in this section.

The infrared spectra of **6.4**-**6.6** exhibit one $\nu_{(CO)}$ and one $\nu_{(NO)}$ absorption near 2000-1990 and 1751 cm^{-1}, respectively. The $\nu_{(CO)}$ absorptions are at a lower value than that of the nitrosyl dicarbonyl complex ($\nu_{(CO)}$ 2122, 2058 cm^{-1}) attributable to loss of the charge on the complex and to the fact that only one CO is competing for the backbonding now. The $\nu_{(NO)}$ are also lower than the corresponding band in $[TpRe(CO)_2NO]^+$ at $\nu_{(NO)}$ 1832 cm^{-1}. The IR absorption for the coordinated CO and NO ligands in the new complexes (**6.4**-**6.6**) did not show significant differences in position. This indicated that the electron density of the metal was not affected when the substitutent on the metal center was replaced.

The ^1H NMR spectra of the different nitrosyl complexes **6.4**-**6.6** can be summarized as follows: ***i)*** In all the complexes each pyrazole ring showed a different environment. This demonstrated that the Tp ligand does not show free rotation or that there is scrambling between the ligands at room temperature. ***ii)*** The resonance for H_4 was observed at an upfield chemical shift compared with the other protons in the Tp ligand (H_3, H_5). Similar observations have been reported for the pyrazolyl ion and pyrazolylborate ligand where H_4 was observed at an upfield compared with H_3 and H_5.

The differences in the chemical shift is attributable to the nitrogen atom (electron withdrawing group) in the Tp ligand.[143,144] ***iii)*** The identification of H_5 in the ^{1}H NMR spectrum was confirmed by an additional coupling ($J_{H\text{-}H}$ =~0.7 Hz). This coupling has been assigned to the hydrogen bound to the boron.[133] From our results, the small coupling was observed in only one of the pyrazolyl rings in the Tp ligand. The resonances for H_5 in the other rings overlapped with the other H_5 or with H_3 in the Tp ligand. ***iv)*** It has been observed in pyrazole ring complexes that $J_{H4\text{-}H5} > J_{H3\text{-}H4}$. The difference in the value of the coupling constant was a consequence of the delocalization of the π system in the pyrazole ring.[143] In our complexes we observed only a slight difference ΔJ = ~0.2 Hz between both values. This feature has been used as a way of distinguishing between H_3 and H_5 in pyrazolylborate complexes but in our system we did not observe differences in the values of the coupling constant or the values of the coupling constant were too close to be used as a means of identification of these hydrogens.

The mass spectra of **6.5** and **6.6** showed the parent ion peak in each case while complex **6.4** showed only the largest mass peak at *m/z* 484 which is consistent with a loss of OMe.

6.3.2.1 Discussion for the Reaction of 6.3 with NaOH and Et_3N.

The result obtained in the reaction of $[TpRe(CO)_2(NO)]^+$ (**6.3**) with NaOH depended on the reaction conditions; that is, the concentration of the hydroxide and the solvents present.

When complex **6.3** was treated with NaOH (6M, 4 drops) the solution changed from deep yellow to orange and the IR spectrum showed new absorption bands in the carbonyl region. The ^1H NMR spectrum of this product was run immediately after all **6.3** reacted. The spectrum exhibited the resonances corresponding to the pyrazolylborate ligand (Tp) but the expected resonances for the proton in the carboxylic acid group (8-10 ppm)[147] or a hydride (-8 - -11 ppm) were not observed.[62a] It is well known that $[CpRe(CO)_2(NO)]^+$ reacts with NaOH generating the complex CpRe(CO)(NO)(COOH) and this complex loses CO_2 to form a stable rhenium hydride complex CpRe(CO)(NO)H.[146b] Our experimental result showed no evidence for the formation of analogous product(s). The results from IR and ^1H NMR spectroscopies showed that Tp, one CO, and one nitrosyl ligand were coordinated in the metal center. The MS for the reaction of $[TpRe(CO)_2(NO)]^+$ (**6.3**) with NaOH (6M) showed a weak peak at *m/z* 517 which corresponded to the M^+ for the complex TpRe(CO)(NO)(COOMe) and a base peak at *m/z* 486 which corresponded to the "$TpRe(CO)_2(NO)$" fragment. Comparing our result with the Cp rhenium analogue we can conclude that the pyrazolylborate rhenium nitrosyl complex showed different reactivity compared with the Cp complex. The formation of the complex TpRe(CO)(NO)(COOMe) from the reaction of **6.3** with NaOH (6M) does not have an easy explanation and we can not propose a mechanism to explain the product observed.

In contrast with the result observed for **6.3** with NaOH (6M), when the concentration of NaOH was changed to 0.6M (4 drops), the complex $TpRe(CO)_3$ (**6.1**) was observed as the only reaction product. We propose that nucleophilic attack of the

OH^- occurs at the nitrosyl group rather than at the carbon of the carbonyl ligand. Evidence for nucleophilic attack on the nitrosyl ligand has been observed in Ru[154] and Ir[155] complexes, in which the NO is transformed to a NO_2 ligand (Equation 6.6).

$$[Ru(CN)_5(NO)]^{2-} \quad + \quad 2OH^- \quad \rightleftharpoons \quad [Ru(CN)_5(NO_2)]^{4-} \quad + \quad H_2O$$

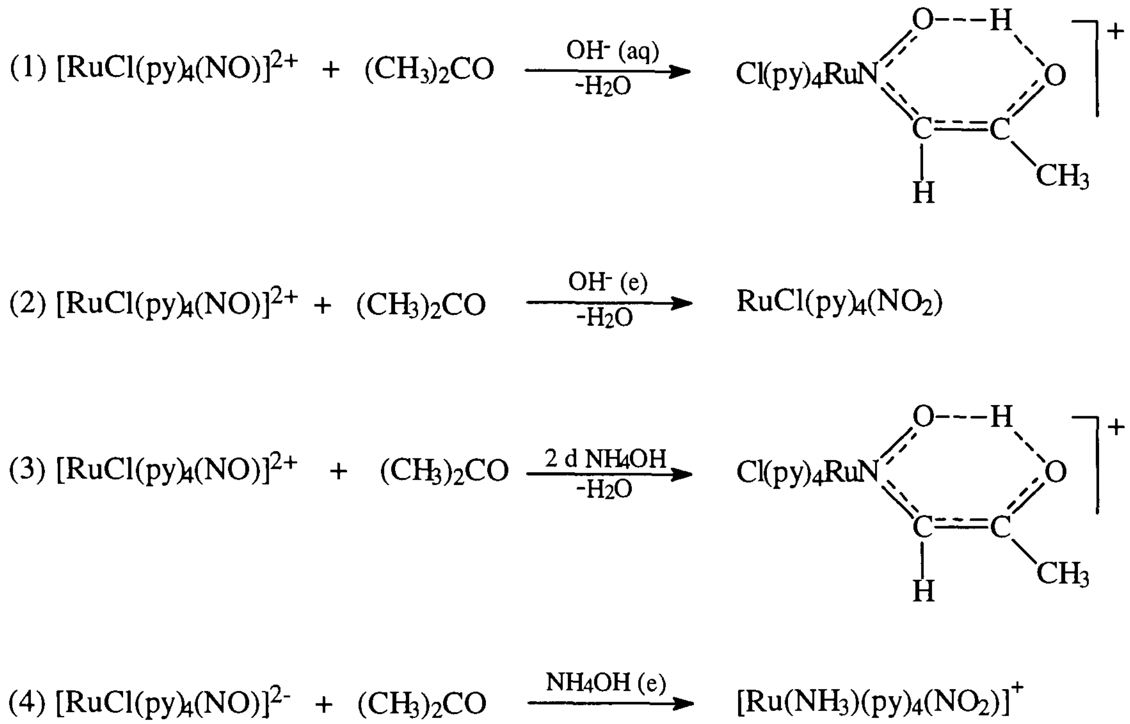
$$[Ir(X)_5(NO)]^- \quad + \quad 2OH^- \quad \rightleftharpoons \quad [Ir(X)_5(NO_2)]^{3-} \quad + \quad H_2O$$

(X = Cl or Br) Eq 6.6

It has been proposed that complexes containing NO having $\nu_{(NO)}$ greater than *ca.* 1886 cm^{-1} would be susceptible to nucleophilic attack at the nitrosyl nitrogen atom.[156] The $TpRe(CO)_2(NO)$ complex exhibited $\nu_{(NO)}$ 1832 cm^{-1} and at this frequency it might be expected that the nitrosyl ligand would not be susceptible to nucleophilic attack. (It has also been observed that some complexes which showed a nitrosyl band *higher* than 1886 cm^{-1} in the IR spectrum do not undergo nucleophilic attack of OH^-).[156]

As explained in the results section (Section 6.3.1.3), complex **6.3** was dissolved in MeCN and NaOH (6M, 4 drops) was added dropwise. No evidence for any new carbonyl or nitrosyl rhenium complex was observed and no starting material (**6.3**) was recovered. This result suggests that the product formed depends on the nature of the solvent.

Bottomley *et al.* have studied ruthenium nitrosyl complexes and they found that upon changing the nature and the concentration of the base, different products are observed (Equation 6.7).[154b-c]



d = drops; e = excess; aq = aqueous

Eq 6.7[154b-c]

The IR spectrum of the reaction of $[TpRe(CO)_2(NO)]^+$ (**6.3**) with NaOH (6M) showed no evidence of coordinated NO_2 (nitrite ligand) or coordinated acetone. The NO_2 ligand should be easy to recognize by IR spectroscopy because this ligand shows a characteristic $\nu_{(N=O)}$ stretching in the region 1500-1200 cm^{-1}.[157]

Graham *et al.* reported in 1972 that $[CpRe(CO)_2(NO)]^+$ reacts with Et_3N-H_2O in acetone at 323 K to afford a thermally stable product, CpRe(CO)(NO)H in good yield, and the carboxylic acid CpRe(CO)(NO)(COOH) was formed when a solution of $[CpRe(CO)_2(NO)]^+$ was treated with a base (Et_3N or NaOH) in water.[146b] When $[TpRe(CO)_2NO]^+$ was treated with Et_3N-H_2O in acetone, the solution changed from yellow to deep orange immediately. The IR spectrum showed a new carbonyl band and the ^{1}H NMR spectrum exhibited the resonances attributable to the Tp ligand, but no evidence of a hydride or carboxylic proton resonance was observed. The ^{1}H NMR spectrum also showed resonances in the methyl and methylene region (see Experimental Section 6.5.10), but the integration of these resonances did not help in the identification of this product. The mass spectrum showed a peak of highest mass at *m/z* 518. A fragment at *m/z* 413 corresponded to loss of 84. It was observed that the complex formed converted to the starting material **6.3** when it was kept in benzene solution at room temperature.

These results are in contrast with those observed for the complex $[CpRe(CO)_2(NO)]^+$ where nitrosyl hydride and nitrosyl carboxylic acid rhenium complexes were observed.

6.4 Conclusion

In this chapter, all the attempts to synthesize our target complex $[TpRe(CO)_2(N_2C_6H_4OMe)][BF_4]$ were unsuccessful but the complex $TpRe(CO)_2(THF)$ (**6.2**) did react with NO^+ to form the complex $[TpRe(CO)_2(NO)][BF_4]$ (**6.3**). This allowed a preliminary study of the reactivity of this complex with different nucleophiles.

A series of neutral carbonyl nitrosyl complexes of the type TpRe(CO)(L)(NO) (L = CO_2Me (**6.4**), NCO (**6.5**), Cl (**6.6**) were spectroscopically and analytically characterized. However, the reaction of the complex $[TpRe(CO)_2(NO)]^+$ with NaOH or Et_3N-H_2O did not afford the expected carboxylic acid nitrosyl rhenium complex or the nitrosyl hydride complex.

In general, we can conclude that the pyrazolylborate ligand (Tp) showed different reactivity, and thus it may behave electronically differently compared with the analogous cyclopentadienyl ligand, when *rhenium* is the metal center. It has been proposed that the aryldiazonium ion is "isoelectronic" with the nitrosonium ion, but our results suggest that when a pyrazolylborate ligand is coordinated to the metal center, these ions exhibit different reactivity.

6.5 Experimental Section

6.5.1 General Methods

All the reactions were carried out under dry nitrogen in Schlenk apparatus. Solvents were thoroughly dried by standard methods and distilled before use. Irradiation was carried out by using a water-jacketed 200 W Hanovia Model 654A-0360 medium pressure mercury vapour lamp and the solution was irradiated under a constant nitrogen purge. All the reagents were obtained from Aldrich except where mentioned. FTIR spectra were recorded on a Bomem Michelson-120 instrument. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded using a Bruker WM-400 instrument operating at 400.13, and 100.06 MHz, respectively. Mass spectra were obtained on a Hewlett-Packard Model-5985 GC-MS instrument, equipped with a Phrasor Inc. fast atom bombardment accessory. Samples for FABMS were dispersed in *m*-nitrobenzyl alcohol (NOBA). Iodosobenzene was prepared from iodosobenzeneacetate by the published method[158] and was stored in the refrigerator. The diazonium salts, $[N_2Ar][BF_4]$ were prepared by diazotization of aniline or *p*-anisidine (Fisher Scientific Co) with $NaNO_2$ (BDH)[159] and were recrystallized from acetone-diethyl ether. The $[NO][BF_4]$ (Strem Chemical Co) was stored in the refrigerator. The complexes $[Cp'Re(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$ (Cp' = C_5H_5,[126a] C_5Me_5[150d]) were synthesised by the published methods. Commercial $Re_2(CO)_{10}$ (Strem Chemical Co) was converted to $Re(CO)_5Br$ in 98% yield by reaction with 1.1 equiv of bromine in CCl_4 solution at room temperature.[160] Sodium pyrazolylborate ligand was prepared by the reaction of $NaBH_4$ and pyrazole.[161]

6.5.2 Reaction of $TpRe(CO)_3$ with $[p\text{-}N_2C_6H_4OCH_3][BF_4]$

A solution of $TpRe(CO)_3$ (25 mg, 0.05 mmol) in acetone (5 mL) was stirred at room temperature with $[p\text{-}N_2C_6H_4OCH_3][BF_4]$ (11 mg, 0.05 mmol) for 1h. The color of the solution changed from pale yellow to red. The solution was concentrated under vacuum at room temperature to ca. 2 mL. Addition of diethyl ether precipitated a great amount of unreacted diazonium salt. The IR spectrum of the clear filtrate showed only the presence of the starting tricarbonyl complex.

Similar reactions were carried out at higher temperature (up to 323 K), changing the ratio of tricarbonyl:diazonium salt to 1:2, using excess diazonium salt, or using the substituted tris-pyrazolylborate rhenium triphenylphosphine complex ($TpRe(CO)_2PPh_3$)[133], but no spectroscopic evidence for the formation of aryldiazenido complexes was obtained.

6.5.3 Reaction of $TpRe(CO)_2(THF)$ with $[p\text{-}N_2C_6H_4OCH_3][BF_4]$

A solution of $TpRe(CO)_2(THF)$ (**6.2**) in THF (60 mL) was stirred at room temperature with $[p\text{-}N_2C_6H_4OCH_3][BF_4]$ (15.5 mg, 0.07 mmol) dissolved in acetone for

1h. The color of the solution changed from yellow-brown to red. The solvent was removed and the residue was dissolved in THF. The IR spectrum showed the THF complex (**6.2**) and the unreacted starting material (**6.1**).

Similar reactions were carried out at higher temperature (up to 333 K), changing the ratio of tricarbonyl:diazonium salt to 1:2, using excess, or using different diazonium salts $[N_2C_6H_4X][BF_4]$; ($X = o\text{-}CF_3$, *p*-Me), $[N_2C_6H_3X_2][BF_4]$; (X_2 = 3,5-dimethyl, 2,6-dimethyl), and $[N_2C_6H_2X_3][BF_4]$; (X_3 = 2,4,5-trifluoro), but no spectroscopic evidence for the formation of aryldiazenido complexes was obtained.

6.5.4 Reaction of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ with NaTp

A solution of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (50 mg, 0.08 mmol) in acetone was stirred at room temperature with $Na[HB(N_2C_3H_3)_3]$ (19.6 mg, 0.08 mmol) for 5 min. The IR spectrum of the solution showed the presence of $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)]^+$ and *five* new bands. The IR spectrum of the same solution after 1 h, showed the complete disappearance of the cationic diazenido rhenium complex $[Cp^*Re(CO)_2(p\text{-}N_2C_6H_4OMe)]^+$ and the increase in intensity of the *five* bands observed previously. The assignment of the reaction products were: $Cp^*Re(CO)_3$ IR (hexane): $\nu_{(CO)}$ 2010, 1913 cm^{-1} and $Cp^*Re(CO)_2N_2$. IR (hexane): $\nu_{(N2)}$ 2125, $\nu_{(CO)}$ 1954 and 1902 cm^{-1}.

6.5.5 Synthesis of $TpRe(CO)_3$ (6.1)

The synthesis of $TpRe(CO)_3$ has been reported previously by Angaroni *et al.* by reaction of $[Re_2(\mu\text{-}Cl)_2(CO)_8]$ with $K[HB(C_3H_3N_3)_3]$.[133] A solution of $Re(CO)_5Br$[160] (0.50 g, 1.2 mmol) in toluene (60 mL) was refluxed with $Na[HB(C_3H_3N_3)_3]$[161] (0.42 g, 1.5 mmol) under N_2. After 2h the solution was filtered and evaporated under reduced pressure. The residual oil was washed with cold methanol and a white solid was obtained (0.46 g, 80 %). IR (THF): $\nu_{(CO)}$ 2025, 1913 cm^{-1}. ^{1}H NMR (acetone-d_6): 6.35 (t, 3H, H_4, Tp, $J_{H\text{-}H}$ = 2.4 Hz), 7.92 (d, 3H, H_5, Tp, $J_{H\text{-}H}$ = 2.2 Hz), 8.03 (d, 3H, H_3, Tp, $J_{H\text{-}H}$ = 2.0 Hz). ^{13}C{^{1}H} NMR (acetone-d_6): 107.6 (C_4, Tp), 136.9 (C_5, Tp), 146.1 (C_3, Tp). EIMS (*m/z*): 484 (M$^+$), 456 (M$^+$-CO), 428 (M$^+$-2CO), 400 (M$^+$-3CO). Anal. Calc^d. for $C_{12}H_{10}N_6BO_3Re$: C, 29.75; H, 2.10; N, 17.00. Found: C, 29.80; H, 2.05; N, 17.40.

6.5.6 Preparation of [TpRe(CO)$_2$(NO)][BF$_4$] (6.3)

A solution of TpRe(CO)$_3$ (600 mg, 1.2 mmol) in THF (60 mL) in a quartz tube, was irradiated under UV light for ~90 min. The IR spectrum showed the carbonyl bands due to the THF derivative at $\nu_{(CO)}$ 1908 and 1823 cm^{-1} and the unreacted starting material at $\nu_{(CO)}$ 2025 and 1913 cm^{-1}. The conversion of the THF complex was estimated at around ~60%. This conversion was estimated from the intensity of the carbonyl bands associated to this complex. The nitrosonium salt ([NO][BF$_4$]) was dissolved in acetone and was kept in an ice bath to prevent decomposition. The solution was then added to the THF solution until no more precipitation was observed. Solvents were pumped off under vacuum, the residue was dissolved in acetone, and the nitrosyl complex was obtained by precipitation with diethylether. The pure complex was obtained as a yellow powder in 65% yield. IR (acetone): $\nu_{(CO)}$ 2122, 2058; $\nu_{(NO)}$ 1832 cm^{-1}. ^{1}H NMR (acetone-d_6): 6.58 (t, 1H, H_4, Tp, $J_{H\text{-}H}$ = 2.3 Hz), 6.65 (t, 2H, H_4, Tp, $J_{H\text{-}H}$ = 2.3 Hz), 8.23 (d, 3H, H_5, Tp, $J_{H\text{-}H}$ = 2.3 Hz), 8.67 (d, 3H, H_3, Tp, $J_{H\text{-}H}$ = 2.3 Hz). ^{13}C{^{1}H} NMR (acetone-d_6): 109.1 (C_4, Tp), 109.3 (C_4, Tp), 139.2 (C_5, Tp), 140.1 (C_5, Tp), 147.3 (C_3, Tp), 147.4 (C_3, Tp).

FABMS (*m/z*): 486 (M^+), 458 (M^+-CO), 430 (M^+-2CO). Anal. Calc^d. for $C_{11}H_{10}N_7B_2F_4O_3Re$: C, 25.05; H, 1.75; N, 17.11. Found: C, 25.12; H, 1.74; N, 17.05.

6.5.7 Preparation of TpRe(CO)(COOMe)(NO) (6.4)

$NaOCH_3$ (10 mg, 0.19 mmol) was added to a solution of complex **6.3** (12 mg, (0.021 mmol) in MeOH (3 mL) at 273 K and the solution was stirred for 1 h. New $\nu_{(CO)}$ absorptions were observed in the IR spectrum at 1998 and 1757 cm^{-1}. The solvent was pumped off and the residue was extracted with benzene (1 mL x 3), and filtered through Celite. The solvent was removed and a pure pale orange solid was obtained. IR (benzene): $\nu_{(CO)}$ 1994 (s), $\nu_{(NO)}$ 1751 (s), $\nu_{(COOMe)}$ 1632 (br) cm^{-1}. ^1H NMR (benzene-d_6): 3.80 (s, 3H, OMe), 5.58 (t, 1H, H_4, Tp, $J_{H\text{-}H}$ = 2.3 Hz), 5.69 (t, 1H, H_4, Tp, $J_{H\text{-}H}$ = 2.2 Hz), 5.73 (t, 1H, H_4, Tp, $J_{H\text{-}H}$ = 2.2 Hz), 6.97 (dd, 1H, H_5, Tp, $J_{H\text{-}H}$ = 2.2 Hz, $J_{H\text{-}H}$ = 0.7 Hz), 7.15 (m, 3H, H_5, H_3, Tp), 8.21 (d, 1H, H_3, Tp, $J_{H\text{-}H}$ = 2.1 Hz), 8.31 (d, 1H, H_3, Tp, $J_{H\text{-}H}$ = 2.2 Hz). EIMS (*m/z*): 517 (M^+), 486 (M^+-OMe). Anal. Calc^d. for $C_{12}H_{13}N_7BO_4Re$: C, 27.92; H, 2.54; N, 18.99. Found: C, 27.78; H, 2.54; N, 18.69.

6.5.8 Preparation of TpRe(CO)(NCO)(NO) (6.5)

Complex **6.3** (20 mg, 0.035 mmol) and NaN_3 (20 mg, 0.31 mmol) were dissolved in CH_2Cl_2 (2 mL) in a Schlenk tube, then stirred at room temperature for 2 h. By this time, the IR showed the disappearance of the $\nu_{(CO)}$ and $\nu_{(NO)}$ for **6.3**, and new $\nu_{(CO)}$ bands at 1998 and 1725, $\nu_{(NO)}$ 1751, and at $\nu_{(NC)}$ 2253 cm^{-1} appeared. The sample was filtered through a short column of Celite, and then the solvent was removed. The product obtained was a pale red powder and it was insoluble in hydrocarbons and $CDCl_3$. IR (CH_2Cl_2): $\nu_{(NC)}$ 2253, $\nu_{(CO)}$ 1998, $\nu_{(NO)}$ 1751 cm^{-1}. ^1H NMR (acetone-d_6): 6.52 (t, 1H, H_4, Tp, $J_{H\text{-}H}$ = 2.3 Hz), 6.50 (m, 2H, H_4, Tp), 7.99 (dd, 1H, H_5, Tp, $J_{H\text{-}H}$ = 2.3 Hz, $J_{H\text{-}H}$ = 0.6 Hz), 8.01 (broad d, 2H, H_5, Tp), 8.05 (m, 2H, H_3, Tp,), 8.07 (d, 1H, H_3, Tp, $J_{H\text{-}H}$ = 2.1 Hz). EIMS (*m/z*): 500 (M^+), 472 (M^+-CO), 442 (M^+-CO-NO), 414 (M^+-2CO-NO). Anal. Calc^d. for $C_{11}H_{10}N_8BO_3Re$: C, 26.46; H, 2.02; N, 22.45. Found: C, 34.33; H, 3.86; N, 18.40.

6.5.9 Reaction of [TpRe(CO)$_2$(NO)][BF$_4$] (6.3) with NaOH

Complex **6.3** was dissolved in acetone and slowly was added 4 drops of NaOH (6 M) at room temperature. The solution changed from yellow to pale orange and two new bands were observed in the IR spectrum. The reaction was stirred for 30 min and the solvent was evaporated to dryness. The residue was dissolved in acetone and filtered through a short column of Celite. The volume was reduced to 1 mL and hexane was added to precipitated the product. The product was obtained as slightly orange powder. The spectroscopy properties are identical to those of **6.4**. IR (acetone): $\nu_{(CO)}$ 1994, $\nu_{(NO)}$ 1763 cm^{-1}. ^{1}H NMR (acetone-*d*$_6$): 6.33 (t, 1H, H_4, Tp, $J_{H\text{-}H}$ = 2.3 Hz), 6.43 (m, 2H, H_4, Tp), 7.91 (dd, 1H, H_5, Tp, $J_{H\text{-}H}$ = 2.2 Hz, $J_{H\text{-}H}$ = 0.6 Hz), 7.98 (dd, 1H, H_5, Tp, $J_{H\text{-}H}$ = 2.2 Hz, $J_{H\text{-}H}$ = 0.6 Hz), 8.00 (dd, 1H, H_5, Tp, $J_{H\text{-}H}$ = 2.4 Hz, $J_{H\text{-}H}$ = 0.6 Hz), 8.07 (d, 1H, H_3, Tp, $J_{H\text{-}H}$ = 2.1 Hz), 8.14 (d, 1H, H_3, Tp, $J_{H\text{-}H}$ = 1.8 Hz), 8.16 (d, 1H, H_3, Tp, $J_{H\text{-}H}$ = 2.0 Hz) 3.55 (s, OCH_3). EIMS (*m/z*): 517 (M^+), 486 (M^+-31), 458 (M^+-31-CO).

6.5.10 Reaction of [TpRe(CO)$_2$(NO)][BF$_4$] (6.3) with NEt$_3$

Complex **6.3** was dissolved in a mixture of wet acetone (1 mL, 1% water) and triethylamine (1 mL) at room temperature. The nitrosyl complex reacted immediately and the solution became pale red and a new absorption in the IR was observed at 1989 cm^{-1}.

The reaction was stirred for 15 min and the solvents were evaporated to dryness. The residue was extracted with benzene (2 mL x 3) and the solvent was reduced to 1 mL and the IR showed three bands at 1992, 1750 and 1633 cm^{-1}. The solvent was removed and the sample was dissolved in benzene-d_6. The ^{1}H NMR spectrum was taken immediately. IR (benzene): $\nu_{(CO)}$ 1992, $\nu_{(NO)}$ 1750, and an extra band at 1633 cm^{-1}. ^{1}H NMR (benzene-d_6):) 0.85 (t, Me, $J_{H\text{-}H}$ = 7.2 Hz), 0.93 (t, Me, $J_{H\text{-}H}$ = 7.1 Hz), 3.01 (m, 1H, CH_2), 3.32 (m, 1H, CH_2), 5.56 (t, 1H, H_4, Tp, $J_{H\text{-}H}$ = 2.3 Hz), 5.68 (m, 2H, H_4, Tp), 6.98 (dd, 1H, H_5, Tp, $J_{H\text{-}H}$ = 2.3 Hz, $J_{H\text{-}H}$ = 0.6 Hz), 7.14 (m, 3H, H_3, H_5, Tp), 8.17 (d, 1H, H_3, Tp, $J_{H\text{-}H}$ = 1.8 Hz),), 8.19 (d, 1H, H_3, Tp, $J_{H\text{-}H}$ = 2.1 Hz). EIMS (*m/z*): 518 (M^+-CO), 413 (M^+-CO-87), 401 (M^+-CO-87-NO).

6.4.11 Preparation of TpRe(CO)(Cl)(NO) (6.6)

[TpRe$(CO)_2$(NO)][BF_4] (**6.3**) (21 mg, 0.037 mmol) was dissolved in CH_2Cl_2 (3 mL) at room temperature and PhIO (17 mg, 0.075 mmol) was added to the solution. The solution become green and two new bands were observed in the IR spectrum at 2018 and 1761 cm^{-1} (3 min). Et_4NCl (13 mg, 0.12 mmol) was added to the solution which turned immediately to purple and the IR spectrum after 5 min showed two new bands at 2000 and 1751 cm^{-1}. The mixture was stirred for 30 min and the solution was filtered through a Celite column prepared in prepared in CH_2Cl_2. The solvent was evaporated to dryness and the residue was dissolved again in the minimum amount of CH_2Cl_2. Hexane was added slowly to the CH_2Cl_2 and the sample was stored at 273 K for recrystallization. The complex was obtained as a deep purple solid. IR (CH_2Cl_2): $\nu_{(CO)}$ 2000, $\nu_{(NO)}$ 1751 cm^{-1}. ^{1}H NMR (acetone-d_6): 6.37 (t, 1H, H_4, Tp, $J_{H\text{-}H}$ = 2.3 Hz), 6.47 (t, 1H, H_4, Tp, $J_{H\text{-}H}$ = 2.3

Hz), 6.50 (t, 1H, H_4, Tp, J_{H-H} = 2.3 Hz), 7.93 (d, 1H, H_5, Tp, J_{H-H} = 2.3 Hz), 7.97 (m, 2H, H_5, Tp), 8.04 (d, 1H, H_3, Tp, J_{H-H} = 2.3 Hz), 8.05 (d, 1H, H_3, Tp, J_{H-H} = 2.3 Hz), 8.12 (d, 1H, H_3, Tp, J_{H-H} = 2.3 Hz). $^{13}C\{^1H\}$ NMR (acetone-d_6): 107.5, 107.9, 108.8 (C_4, Tp) 137.1, 137.2, 138.2 (C_5, Tp) 144.1, 145.5, 146.9 (C_3, Tp). EIMS (*m/z*): 493 (M^+), 465 (M^+-CO), 435 (M^+-CO-NO). Anal. Calc^d. for $C_{10}H_{10}N_7BClO_2Re$: C, 24.38; H, 2.05; N, 19.90. Found: C, 28.87; H, 3.21 ; N, 17.55.

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