# SYNTHESIS AND REACTIVITY
# OF PENTAMETHYLCYCLOPENTADIENYL RHENIUM
# ALLYL COMPLEXES

by

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ii

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# ABSTRACT

The thesis describes the synthesis, characterization, and reactivity investigation of the new rhenium pentamethylcyclopentadienyl allyl complexes of the general formula $[Cp*Re(\eta^3-C_3H_5)LL'][BF_4]$ (L = L' = CO, $CH_3CN$, $CH_3CH_2NH_2$; L = CO, L' = $CH_3CN$, $CH_3CH_2NH_2$; L = $PMe_3$, L' = $CH_3CN$, $CH_3CH_2NH_2$) and $Cp*Re(\eta^3-C_3H_5)(CO)L$ (L = Cl, H, and alkyl group). $[Cp*Re(\eta^3-C_3H_5)(CO)_2][BF_4]$ (**2.1**) was successfully synthesized in a photochemical reaction by irradiating $Cp*Re(CO)_3$ in the presence of allyl alcohol and $HBF_4$ in ether solution. Its derivatives, the mono- and bis- pentamethylcyclopentadienyl acetonitrile allyl rhenium complexes $[Cp*Re(\eta^3-C_3H_5)(CO)(NCCH_3)][BF_4]$ (**2.2**) and $[Cp*Re(\eta^3-C_3H_5)(NCCH_3)_2][BF_4]$ (**2.3**) have been made, and the X-ray crystal structures of these compounds have been obtained.

The reactivity of complex **2.1** with various nucleophiles has been studied. $C_2H_5S^-$, $C_6H_5S^-$, $^-SCH_2CH_2CH_2S^-$, $NH_2^-$, $N_3^-$, $CH_3COO^-$, and $Me_2CHMgBr$ reacted with **2.1** at 0 -20 °C by attacking the allyl ligand to give substituted propene compounds. When **2.1** was treated with PhLi, or $CH_3O^-$ at 0 °C, both the allyl and the CO ligands were attacked to give complexes $Cp*Re(CO)_2(\eta^2-CH_2CHCH_2R)$ and $Cp*Re(CO)(\eta^3-C_3H_5)(COR)$, but the substituted propene product is thermodynamically preferred.

The reactions of complexes **2.2** and **2.3** with $NaBH_4$, $PMe_3$ and NaOMe (or NaOH) were investigated. For complexes **2.2** and **2.3**, $NaBH_4$ reduced the coordinated acetonitrile ligand to ethylamine; $PMe_3$ underwent nucleophilic attack on the allyl group in **2.2** to generate the corresponding phosphonium compound, or substituted one acetonitrile ligand in **2.3** to produce the $PMe_3$ complex.

Irradiation of $Cp*Re(CO)_3$ under UV light with allyl chloride was investigated in order to discover a method of synthesizing $Cp*Re(\eta^3-C_3H_5)(CO)Cl$ (**5.1**). Complex **5.1** was also obtained by treating complex **2.1** with PhIO in $CH_2Cl_2$ in the presence of $Me_4NCl$, and this is an efficient method compared with the photochemical reactions of

Cp*Re(CO)$_3$ with allyl chloride. Complex **5.1** reacted with C$_6$H$_5$Li or RMgX (R = CH$_3$, C$_2$H$_5$, C$_3$H$_5$, X = Br; R = C$_4$H$_9$, X = Cl) to give complexes Cp*Re($\eta^3$-C$_3$H$_5$)(CO)R (**5.8 - 5.12**). The reactivities of these rhenium allyl alkyl compounds have also been studied.

Complex **5.1** reacted with LiBEt$_3$H in dry ether to provide an alternative convenient route for the synthesis of the rhenium hydrido compound Cp*Re($\eta^3$-C$_3$H$_5$)(CO)H (**5.7**). The reactions of this complex towards H$^+$, ArN$_2$$^+$, NO$^+$, Ph$_3$C$^+$, PMe$_3$, CH$_3$C≡CC$_6$H$_5$, CH$_3$CN, C$_2$H$_4$, C$_6$H$_{10}$, C$_6$H$_{12}$ and CO have been investigated. The protonation of complex **5.7** with CF$_3$CO$_2$H and CF$_3$SO$_3$H in various solvents occurred at the metal center to give the dihydride intermediates, followed by a migration of H$^-$ to the coordinated allyl to give the propene complexes Cp*Re(CO)(H)($\eta^2$-C$_3$H$_6$)L (L = CF$_3$CO$_2$ or CF$_3$SO$_3$). A variable temperature NMR study of these protonation reactions indicated the existence of the dihydride intermediates.

# DEDICATION

To my parents, my husband Daqing and my daughter Karina Bo

# ACKNOWLEDGMENTS

# TABLE OF CONTENTS

Chapter I: Transition Metal Allyl Complexes and Their Applications in

       Organic Synthesis

x

Chapter IV: Reactivity of Mono- and Bis-Acetonitrile Complexes [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(NCMe)][BF$_4$] **(2.2)** and [Cp*Re($\eta^3$-C$_3$H$_5$)(NCMe)$_2$][BF$_4$] **(2.3)** Towards Hydride, Trimethylphosphine and Hydroxide

Chapter V: Photochemical Reactions of Cp*Re(CO)$_3$ with Allyl Halides. Synthesis, Characterization and Reactivity of the Rhenium Allyl Chloride Complex Cp*Re($\eta^3$-C$_3$H$_5$)(CO)Cl and Its Alkyl Derivatives

Chapter VI: Reactivity Investigation of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (**5.7**)

xv

# LIST OF ABBREVIATIONS AND SYMBOLS

| | |
|---|---|
| Ar | aryl or aromatic |
| t-Bu | t-butyl |
| CI | chemical ionization |
| Cp | cyclopentadienyl ($\eta^5$-$C_5H_5$) |
| Cp* | pentamethylcyclopentadienyl ($\eta^5$-$C_5Me_5$) |
| DBU | 1,8-diazabicyclo [5.4.0] undec-7-ene |
| DMF | N,N-dimethylformamide |
| DPPE | 1,2-bis(diphenylphosphino)ethane ($PPh_2CH_2CH_2PPh_2$) |
| EI | electron impact |
| Et | ethyl ($CH_3CH_2$) |
| FAB | fast atom bombardment |
| HMPA | hexamethylphosphoramide $[(CH_3)_2N]_3PO$ |
| i-Pr | isopropyl |
| IR | infrared |
| M | central transition metal in complex |
| $M^+$ | parent ion |
| Me | methyl ($CH_3$) |
| MS | mass spectroscopy |
| NMR | nuclear magnetic resonance |
| NOE | nuclear Overhauser enhancement |
| OMe | methoxy ($OCH_3$) |
| Ph | phenyl ($C_6H_5$) |
| R | alkyl |
| THF | tetrahydrofuran ($C_4H_8O$) |

# LIST OF COMPLEXES

# LIST OF FIGURES

Page Number

# LIST OF SCHEMES

# LIST OF TABLES

Page Number

# Chapter I

# Transition Metal Allyl Complexes and Their Applications in Organic Synthesis

## 1.1. Introduction

Transition metal $\eta^3$-allyl complexes are considered to be important for at least three reasons: **i.** they can be synthesized by using a wide variety of strategies, such as the reaction of a metal halide with an allyl Grignard, the oxidative addition of an allyl halide to a low valent metal complex, the protonation of a metal diene complex, or from an olefin complex by either base abstraction of an allylic proton, or by insertion of the transition metal into the allylic C-H bond; **ii.** the reactions of $\eta^3$-allyl complexes with either nucleophiles or electrophiles at the terminal or the central carbon of the allyl can lead to the formation of various new C-C or C-X bonds (where X can be N, P, O, S and halides); **iii.** transition metal $\eta^3$-allyl complexes are the key intermediates in the metal-catalyzed coupling of alkenes to dienes.[1] Especially, the (bis-$\eta^3$-allyl)nickel complex is of both practical and historical significance. This complex, as well as a variety of other nickel complexes, catalyzes the cyclotrimerization of butadiene to cyclododecatriene.[1a] This reaction was one of the first organometallic reactions mechanistically studied by Wilke (Scheme 1.1).[1b]

The allyl group can be either a $\sigma$ or a $\pi$ ligand by donating one or three electrons to the metal, and is one of the most widely studied ligands in transition metal organometallic chemistry. A great variety of both homoleptic and mixed ligand $\eta^3$-allyl complexes have been synthesized, and their properties studied.[1] The synthesis, structure and development of $\eta^3$-allyl complexes have been systematically summarized by Green and Nagy in their review paper in 1964, which is a basis for the later review papers on transition metal allyl chemistry.[1a,c] Among numerous transition metal allyl complexes in the literature, only a relatively few rhenium allyl compounds have been reported. The study of

Scheme 1.1. Nickel catalyzed cyclotrimerization of butadiene.

rhenium allyl chemistry is a quite undeveloped area compared with other transition metals.

In previous work, our group reported in 1989 a pentamethylcyclopentadienyl rhenium allyl hydrido complex Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (**5.7**), which was isolated as a C–H activation product from the irradiation of Cp*Re($\eta^2$-C$_3$H$_6$)(CO)$_2$ (**3.1**) (Scheme 1.2).[1d-e] Treatment of complex **3.1** with [Ph$_3$C][BF$_4$] produced the rhenium cationic allyl compound [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] (**2.1**) (Scheme 1.2). For both of these two rhenium allyl complexes, no study of their reactivity was undertaken at that time. However, for a future comparison, the iridium allyl hydride Cp*Ir($\eta^3$-C$_3$H$_5$)(H), an analogue of complex **5.7**,[1f] and the manganese analog [Cp*Mn($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] of **2.1** had both been extensively studied.[1g] Therefore, these two rhenium allyl complexes

2

provide the basis of an attempt to investigate the chemistry displayed by rhenium allyl compounds, which forms the project of this thesis.



Scheme 1.2. Synthesis of **2.1** and **5.7** from complex **3.1**. * Both of these complexes were obtained as the mixture of *endo* and *exo* isomers.

In order to give the necessary background review of transition metal allyl chemistry, so as to be able to place in context the contribution to the study of the allyl complexes made in this work, the thesis begins with a discussion of the coordination

modes of the allyl ligand, and some examples of the synthesis, reactions and applications of transition metal $\eta^3$-allyl complexes in organic synthesis. This is followed by a description of the known rhenium allyl complexes obtained in a search of the literature, that form a background to the present work. Finally, a brief description of the principal results obtained in this work is presented as a guide to the content of subsequent chapters of this thesis.

## 1.2. Allyl-Metal Bond

As indicated in the introduction, the allyl group $C_3H_5$ may behave as a one electron donor ligand, which forms a $\sigma$ bond with the metal center (**a**), or it may behave as an $\eta^3$ ($\pi$) ligand, which donates three electrons to the metal center to form metal $\eta^3$-allyl complexes. Furthermore, when $\eta^3$-allyl coordinates to the metal center, it can be in a symmetrical fashion (**b**), with equivalent terminal carbon atoms, or it may bond in an unsymmetrical way, which gives two inequivalent terminal carbon atoms (**c**).[1-5]



Figure 1.1. Coordination modes of the allyl ligand in a mononuclear complex.

Examples of $\sigma$ coordination of the allyl in (**a**) are $(\eta^1\text{-}C_3H_5)Co(CN)_5^{3-}$ [5c] and $(\eta^1\text{-}C_3H_5)Mn(CO)_5$.[5d] The occurrence of metal-$\sigma$-allyl in the case of transition metal compounds is mainly due to the absence of empty coordination sites. However, upon irradiation in solution, the $\sigma$-allylcobalt and manganese complexes were converted into the $\pi$-allyl compounds respectively.[5] The symmetrical coordination of the $\eta^3$-allyl ligand (**b**) is the dominating fashion in most of the $\eta^3$-allyl transition metal complexes. For example, in

4

complexes $CpMo(\eta^3\text{-}C_3H_5)(CO)_2$, $CpW(\eta^3\text{-}C_3H_5)(CO)_2$ and $Mn(\eta^3\text{-}C_3H_5)(CO)_4$,[5b-d] and all the compounds reported in this work, no matter whether neutral or cationic, the $^1H$ NMR spectra of these complexes suggested that the $\eta^3$-allyl group is coordinated to the metal center in a symmetrical way. The unsymmetrical fashion (c) in mono-nuclear metal complexes is not very common.[5f,g]

In some polynuclear complexes, allyl can be a bridging ligand to two metal centers in a symmetrical way (Figure 1.2a), or in an unsymmetrical fashion in which it forms a $\sigma$ bond to one metal atom, and a $\pi$ olefin bond with another metal atom (Figure 1.2b).[6-9]



Figure 1.2. Coordination models of the allyl ligand in a polynuclear complex.

The symmetrical bridging (Figure 1.2a) $\eta^3$-allyl complex occurs in the palladium complex $(C_5H_5)\{PdP(^iPr)_3\}_2\{\eta^3\text{-}CH_2C(Me)CH_2\}$. In this complex, both the allyl and the cyclopentadienyl ligands are bridged to the two metal centers.[9a] The earliest example of the unsymmetrical bridging allyl (Figure 1.2b) was reported for the complex $Fe(C_3H_5)(CO)I$. The solution NMR study of this complex suggested that it is in a monomer-dimer equilibrium in solution, and the dimeric species involves a bridging allyl group (Figure 1.2c).[9b]



Figure 1.2c. The unsymmetrical bridging allyl in $[Fe(C_3H_5)(CO)I]_2$.

In $\eta^3$-allyl complexes, all the carbon atoms bond to the metal center. Free rotation about the carbon-carbon axes does not occur. Thus, if the allyl group has substituents (R) at the terminal carbon atoms, there will exist three possible isomers. They are: *syn-syn*, *syn-anti* and *anti-anti* (Figure 1.3).[10]



Figure 1.3. Isomers from the substitution of the allyl group.

Chemically, the $\eta^3$-allyl group often behaves as an electron rich ligand. In some cases, its reactions involve the dissociation of one terminus to form an $\eta^1$-allyl intermediate, followed by reformation of the $\eta^3$-allyl complex. A similar process in an $\eta^3$-allyl complex itself can occur, leading to a fluxional rearrangement, exchanging the *syn* and *anti* protons (Figure 1.4). The activation energy values of the *syn-anti* exchange are in a region of 34-80 kJ mol$^{-1}$.[11,12]

When the substituted allyl group is bonded to the metal center in an unsymmetrical environment, the *syn-syn*, *anti-anti* proton exchange can also be observed. One of the proposed mechanisms for this exchange process is through a dissociation mechanism as

Figure 1.4. *Syn-anti* proton exchange by a $\eta^3-\eta^1-\eta^3$ dissociation mechanism.



Figure 1.5. *Syn-syn anti-anti* exchange by a dissociation mechanism.

reported for $Pd(1\text{-}MeC_3H_4)(C_6Cl_5)(PPh_3)$ (Figure 1.5).[13] The *syn-syn, anti-anti* exchange can also be achieved by the rotation of the allyl ligand in the allyl $C_1C_2C_3$ plane about the allyl-metal axis.[1,2,14]

In half sandwich or piano-stool complexes, such as cyclopentadienyl allyl compounds, the $\eta^3$-allyl ligand may adopt two different orientations with respect to the remaining ligand environment. These are termed as *exo* or *endo* isomers (Figure 1.6).[15] Some complexes show a preference for either the *endo* or the *exo* isomer depending on both metal center and the ancillary ligand. In others, both isomers exist in equilibrium in solution. The rate of interconversion of *exo* and *endo* **5.7** is slow enough that each isomer has been isolated and crystallized, and the X-ray structures determined.[1d] However, the *endo* and the *exo* isomers of $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)_2][BF_4]$ [29a] undergo fast exchange in solution, and even in the solid state the crystal is a mixture of the two isomers. The factors influencing the population of *exo-endo* isomers and their diagnostic spectroscopic properties have been reported.[16-20]



Figure 1.6. Structures of the *endo* and the *exo* isomers.

## 1.3. Syntheses of $\eta^3$-Allyl Transition Metal Complexes.

### 1.3.1. Reactions of Metal Halide Compounds with Grignard Reagents

Transition metal $\eta^3$-allyl complexes can be prepared in several different ways, dependent on the specific starting material. For most of the transition metal halide

compounds, the common synthetic method is the reaction of the metal halide derivatives with Grignard compounds (Equations 1.1-1.3).[1,7,9,19-23]

$$NiCl_2 \ + \ 2CH_2{=}CHCH_2MgBr \ \longrightarrow \ Ni(\eta^3\text{-}C_3H_5)_2 \ + \ 2MgBrCl \quad (Eq.\ 1.1)^{23}$$

$$RhCl_3 \ + \ 3CH_2{=}CHCH_2MgCl \ \longrightarrow \ Rh(\eta^3\text{-}C_3H_5)_3 \ + \ 3MgCl_2 \quad (Eq.\ 1.2)^{23}$$

$$mer\text{-}[IrCl_3(PPh_3)_3] \ + \ (\eta^1\text{-}C_3H_5)MgCl \ \longrightarrow \ IrCl_2(\eta^3\text{-}C_3H_5)(PPh_3)_2 \quad (Eq.\ 1.3)^{23}$$

### 1.3.2. Oxidative Addition of Allyl Halides

Many $\eta^3$-allyl complexes can also be synthesized conveniently by reactions of allylic halides with a low oxidation state transition metal complex. The reaction involves the cleavage of the C–X bond and an increase of the formal oxidation state of the metal center. This is a typical example of the oxidative addition reaction (Equations 1.4-1.6).[24-26]



### 1.3.3. From Metal Olefin Complexes

An important method to prepare palladium allyl compounds is the elimination of HX from its olefin complex (Equation 1.7).[27]

(Eq. 1.7)

The cationic $\eta^3$-allyl complexes can be synthesized through a reaction of the neutral transition metal olefin compound with $Ph_3C^+$, which abstracts one $H^-$ from the coordinated olefin to generate the allyl derivatives (Equations 1.8-1.9).[28-29]



(Eq. 1.8)[28]



(Eq. 1.9)[29]

(*endo + exo*)

### 1.3.4. Reactions of 1,3-Diene Metal Complexes

Transition metal hydrido complexes react with 1,3-dienes leading to the formation of $\eta^3$-allyl compounds in which $H^-$ transfers from the metal to the terminal carbon atom of

the diene to give $\eta^3$-allyl. In cases where the nucleophile is not $H^-$ but other groups like OR, Cl, RCO, and CH$_3$COO, the reaction also occurs (Eq. 1.10).[29b-f]

$$HNi[P(OPh)_3]_4^+ + CH_2{=}CHCH{=}CH_2 \longrightarrow Ni(1\text{-}MeC_3H_4)[P(OPh)_3]_2^+ \quad (Eq.\ 1.10)^{29b}$$

The protonation of 1,3-dienes metal complexes also affords cationic $\eta^3$-allyl complexes (Eq. 1.11).[30-35]



(Eq. 1.11)[30]

## 1.3.5. Rearrangement of $\eta^1$ to $\eta^3$ Allyl Complex

The $\eta^1$-$\eta^3$ rearrangement is often a key step in the synthesis of $\eta^3$-allyl compounds. The reaction occurs under thermal or photochemical process (Equation 1.12). The equilibrium between tricarbonylcobalt-$\eta^3$-allyl and tetracarbonylcobalt-$\eta^1$-allyl has been studied.[36] The thermal decarbonylation of *cis* or *trans* $(\eta^1\text{-}C_4H_7)Mn(CO)_5$ by (dppe)$_2$IrCl at 90 °C gave $(\eta^3\text{-}C_4H_7)Mn(CO)_4$ as the *syn* isomer only.[37]

$$M(CO)(\eta^1\text{-allyl}) \longrightarrow M(\eta^3\text{-allyl}) + CO \quad (Eq.\ 1.12)$$

## 1.3.6. Other Reported Methods

As more and more transition metal allyl complexes have been synthesized and their properties investigated, the discovery of new synthetic routes for the formation of allyl transition complexes has been extensive. In addition to the common traditional methods mentioned above of preparing $\eta^3$-allyl metal complexes, some newly developed methods have been reported. For example, nucleophilic addition of LiBEt$_3$H at the coordinated

alkyne in a cationic compound (Equation 1.13),[38] or hydride abstraction by $Ph_3C^+$ in a neutral alkyne complex [39] both gave $\eta^3$-allyl complexes.

The irradiation of metal carbonyl complexes with allyl alcohol in the presence of a strong non oxidizing protonic acid also provides a convenient method for the synthesis of allyl compounds (Scheme 1.3).[40-43]

In this work, we have employed the last method, of utilizing allyl alcohol as



(Eq. 1.13)



Scheme 1.3. Proposed mechanism for the formation of the $\eta^3$-allyl complex.

reagent, for the preparation of our pentamethylcyclopentadienyl rhenium allyl complex [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] (**2.1**). The improvement of the method and the experimental details will be discussed in Chapter II.

## 1.4. Application of Transition Metal Allyl Complexes in Organic Synthesis

Transition metal complexes have been used extensively in industry and laboratory processes to catalyze a variety of chemical reactions. Transition metal allyl complexes have proven to be important intermediates in several catalytic processes. Among all the catalysts studied since the early 1950s when the famous Ziegler-Natta catalyst was discovered,[44-45] nickel and palladium complexes are the two leading metals for which the chemistry is very well established, both in synthetic methodology and applications in catalytic reactions, and this is particularly true of their allyl complexes.

There have been several review articles discussing the synthesis, characterization, and the importance of $\eta^3$-allyl metal derivatives in synthetic chemistry.[46-50] The chemistry of $\eta^3$-allyl nickel complexes as intermediates in catalytic reactions has been exhaustively summarized in the book "The Organic Chemistry of Nickel" by Jolly and Wilke.[51] The advantages of using nickel complexes in catalytic processes is in selective organic synthesis which clearly involves $\eta^3$-allyl nickel complexes. The synthetic ability of $\eta^3$-allylnickel halides has been shown in the synthesis of many natural products which include $\alpha$-santalene (Eq. 1.14),[52] coenzyme Q (Eq. 1.15),[53] and vitamin K.[54]

The reactions above have been proposed to proceed through the initial one-electron transfer from an $\eta^3$-allyl nickel complex to an organic halide.[55] Nickel $\eta^3$-allyl complexes as intermediates play an important role for the formation of new carbon-carbon bonds in organic synthesis. The mechanism proposed for the catalytic cycle when using the complex L$_2$NiR(MgX) (L = PPh$_3$) as a catalyst is shown in Scheme 1.4.[56,57]

Palladium-catalyzed nucleophilic replacement of an allylic acetate has become a standard reaction in organic synthesis.[58-61] Palladium $\eta^3$-allyl complexes also play an important role in C−C bond formation by reacting with various carbon nucleophiles.

(Eq. 1.14)

MeO

OAc

MeO

Br

OAc

hmpa

(Eq. 1.15)

MeO

MeO

Olefin

RMgX

Scheme 1.4. C–C bond formation via $\eta^3$-allyl nickel complex.

14

The reaction can be carried out as both stoichiometric and catalytic procedures. In the first case, an $\eta^3$-allyl palladium compound was isolated, then reacted with the carbon nucleophile to form allylated products. This kind of reaction was first reported by Tsuji and co-workers in 1965.[62] In catalytic reactions, $\eta^3$-allyl palladium complexes were obtained as intermediates from the reaction of various allylic compounds with palladium metal, followed by the reaction with carbon nucleophiles to give new carbon-carbon bonds (Equations 1.16-1.17).[63,64]

The chemistry mentioned above is only a sample of the many examples of the application of transition metal allyl complexes in organic synthesis. The achievements in this area have been reviewed.[46-51] The discovery of synthetic methods and the application of transition metal allyl complexes continues unabated.[65-67]



(Eq. 1.16)[63]

(Eq. 1.17)[64]

## 1.5. Research Background for the Thesis Project

In the early 1970s, allyl organometallic complexes were studied by only relatively few organometallic chemists. The complexes synthesized and characterized were mainly those of first row transition metals, such as Cr, Mn, Fe, Co, and Ni. Palladium allyl complexes were also extensively investigated since they are relatively stable, and have broad applications in various catalytic reactions. Some allyl complexes of Mo and W were

reported, but not as much allyl chemistry was developed for these as for the other metals mentioned.[68-71]

Starting from the late 1970s, a new emphasis reappeared in this field, because of the application of allyl organometallic complexes in stereocontrolled organic synthesis. Although allyl complexes of most transition metals were thoroughly investigated, not much was reported in the case of rhenium. In 1971, a rhenium $\eta^3$-allyl complex $Re(\eta^3$-$C_3H_5)(CO)_4$ was reported by Abel and Moorhouse, which is the earliest rhenium allyl complex we can find in the literature.[72a] The investigation of the reactivity of this complex and the $^{13}C$ NMR study were not reported until 1983.[72-74] An allyl-containing rhenium dimer $Re_2(C_3H_5)_4$ was reported in 1977.[75,76] Reaction of $Re_2(CO)_{10}$ with butadiene under irradiation afforded another $\eta^3$-allyl-containing dimer complex $(\eta^3$-allyl)$(CO)_4ReRe(\eta^1$-allyl)$(CO)_5$, in which the allyl is $\eta^3$- coordinated to one rhenium, and $\eta^1$- coordinated at the other rhenium center.[77,78] Irradiation of $(PPh_3)_2ReH_7$ with propene produced the bis-allyl rhenium hydrido complex $(PPh_3)_2Re(\eta^3$-$C_3H_5)_2H$ (Scheme 1.5).[79]



Scheme 1.5. Reaction of $(PPh_3)_2ReH_7$ with propene (L = $PPh_3$).

The synthesis and crystallographic characterization of a pentamethylcyclopentadienyl (Cp*) rhenium $\eta^3$-allyl bromide complex were reported in 1988 (Equation 1.18).[80]

16

Two years later, Casey and co-workers reported the synthesis of a pentamethylcyclopenta-dienyl rhenium $\eta^3$-allyl bis-carbonyl complex [CpRe($\eta^3$-C$_3$H$_5$)(CO)$_2$][PF$_6$] by using Ph$_3$C$^+$ to abstract one H$^-$ from the coordinated propene (Equation 1.8).[28]



$$\text{(Eq. 1.18)}$$
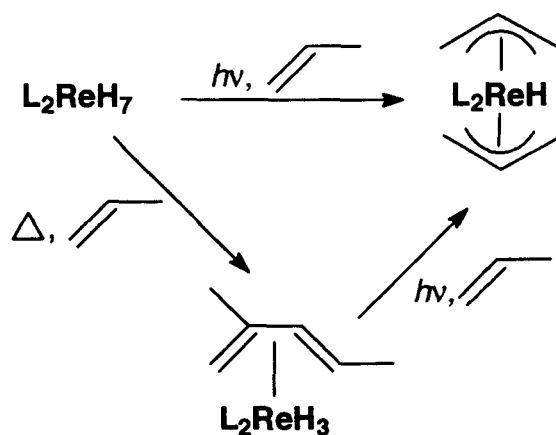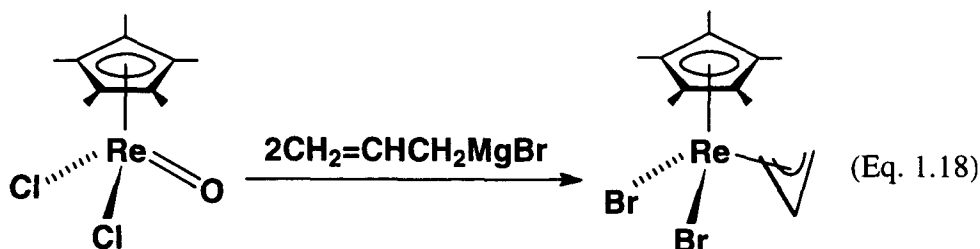
In 1989, the pentamethylcyclopentadienyl rhenium $\eta^3$-allyl hydrido complex Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (**5.7**) was reported from our group.[1d-e] The crystal structures of its two isomers, *endo* and *exo*, were also obtained. This is the first rhenium half sandwich $\eta^3$-allyl hydrido complex ever reported. The study of its chemistry is an untouched area, and became one of the subprojects of this research work.

## 1.6. Our Contributions to $\eta^3$-Allyl Rhenium Chemistry

With reference to Scheme 1.2, it was found in that work that the irradiation of Cp*Re(CO)$_3$ with propene did not completely convert Cp*Re(CO)$_3$ to complex Cp*Re($\eta^2$-C$_3$H$_6$)(CO)$_2$ (**3.1**), and the separation of **3.1** from the large amount of unreacted Cp*Re(CO)$_3$ is very difficult (both Cp*Re(CO)$_3$ and complex **3.1** are soluble in nopolar solvents); therefore, the syntheses of [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] (**2.1**) and Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (**5.7**) from **3.1** is not efficient. The first goal of this thesis research was to develop a new methodology to make complexes **2.1** and **5.7**, so as to provide material for subsequently investigating the chemistry initiated by these rhenium allyl complexes. This was successful. Both complexes were obtained by using different methodologies in comparison with the methods reported previously in our group. In fact, the best method for synthesizing **5.7** was from complex **2.1** from which it was obtained in a two step

reaction in fairly good yield. But, more importantly, while investigating possible new synthetic routes for preparing **5.7**, a series of rhenium $\eta^3$-allyl complexes were synthesized, and the properties of these new compounds were investigated, as will be described in Chapters II-VI.

More than forty new pentamethylcyclopentadienyl rhenium $\eta^3$-allyl or $\eta^2$-substituted propene complexes have been synthesized and characterized in this research. The $\eta^3$-allyl complexes were generated by ligand substitution of the $\eta^3$-allyl complex **2.1**, or from the reactions of its derivatives, such as the reduction of coordinated $CH_3CN$ to $CH_3CH_2NH_2$. Nucleophilic addition at the coordinated allyl group produced a series of $\eta^2$-substituted propene complexes, and provides an efficient method for the formation of a new C-X bond (where X can be C, N, P, S and O). The method of synthesis, as well as investigation of the properties of these complexes are described in detail in each Chapter, as summarized below.

In Chapter II, the synthesis, characterization, and determination of the *endo-exo* isomer distribution by $^1$H NMR NOE experiments of complexes [Cp*Re($\eta^3$-$C_3H_4R)L_1L_2$][BF_4] (R = H, $L_1$, $L_2$ = CO, $CH_3CN$, $CH_3CH_2NH_2$ and PMe_3; R = CH_3, $L_1$, $L_2$ = CO, $CH_3CN$) are described. The X-ray crystal structures of the mono and bis acetonitrile complexes [Cp*Re($\eta^3$-$C_3H_5)(CO)(NCCH_3)$][BF_4] (**2.2**) and [Cp*Re($\eta^3$-$C_3H_5$) ($NCCH_3)_2$][BF_4] (**2.3**) are included.

The nucleophilic addition of the carbon nucleophiles or heteroatom (X) to $\eta^3$-allyl in a cationic transition metal complex is a key step for the formation of a new C–C or C–X bond. We have therefore investigated the reactions of different nucleophiles, including $CH_3O^-$, $CH_3CO_2^-$, $C_2H_5S^-$, $C_6H_5S^-$, $^-SC_3H_6S^-$, $N_3^-$, $NH_2^-$, $C_6H_5^-$, $Me_2CH^-$, $H^-$, and PMe_3, with complex [Cp*Re($\eta^3$-$C_3H_5)(CO)_2$][BF_4] (**2.1**). The nucleophilic attack occurred on either the $\eta^3$-allyl (in most cases), or on the coordinated CO (at low temperature) depending on the specific nucleophile. The details will be discussed in Chapter III.

Acetonitrile is often used as an easily substituted ligand for the formation of desired complexes since it is usually labile. The results from our research work on the

acetonitrile complexes described in Chapters II and IV are different. Attempts were made to replace acetonitrile by hydride as an alternative method of synthesizing the allyl hydrido complex $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(H)$ (**5.7**). The fact is, however, that the acetonitrile ligand in $Cp^*$ rhenium $\eta^3$-allyl complexes (both the mono and the bis-acetonitrile complexes) is an active site for reaction. Nucleophilic attack occurred at the carbon atom of the coordinated acetonitrile to give an ethylamine complex when $NaBH_4$ was used as nucleophile. Base catalyzed hydrolysis reaction also occurred to afford an amide complex. Thus, the acetonitrile is even more active than the allyl ligand towards some nucleophiles. This reactivity study of mono and bis-acetonitrile $\eta^3$-allyl rhenium complexes will be discussed in Chapter IV.

As indicated, the application of nickel and palladium allyl halide complexes is very important in organic synthesis. No report on the reactivity study or application of the rhenium allyl halide complexes has appeared yet. Therefore, we have synthesized $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(Cl)$ (**5.1**) through both photochemical and thermal reactions. While researching the preparation of rhenium allyl halide complexes, the irradiation of $Cp^*Re(CO)_3$ with allyl halides under various conditions was studied, and the results are reported in Chapter V. Complex $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(Cl)$ (**5.1**) provides an important precursor for the further study of neutral rhenium allyl compounds. A series of rhenium allyl alkyl complexes have been synthesized from (**5.1**), and the characterization and reactivity of these complexes are also included in Chapter V.

Reaction of $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(Cl)$ (**5.1**) with $LiBEt_3H$ in ether gave the rhenium hydrido complex $Cp^*Re(\eta^3\text{-}C_3H_5)(CO)(H)$ (**5.7**), and provided an efficient method for the synthesis of this crucial compound in this project. The investigation of the reactivity of this rhenium allyl hydrido complex is still under study. Protonation of Re-H in this compound did not eliminate $H^-$ and release $H_2$ as often occurs for many transition metal hydride compounds.[81] The protonation occurred at metal center first, forming a dihydride intermediate, then one hydride migrated to the coordinated allyl to give a neutral propene hydrido complex $Cp^*Re(\eta^2\text{-}C_3H_6)(CO)(CF_3CO_2)(H)$ when $CF_3COOH$ was used

19

as the proton source. Attack of $NO^+$ at the metal center also occurred, indicating the nucleophility of the rhenium center in this complex. The exploration of the interesting properties of $Cp*Re(\eta^3\text{-}C_3H_5)(CO)(H)$ will be described in Chapter VI.

# Chapter II

# Synthesis and Characterization of Pentamethylcyclopentadienyl Rhenium Allyl Complexes [Cp*Re($\eta^3$-C$_3$H$_4$R)LL'][BF$_4$] (L, L' = CH$_3$CN, CO; R = H, CH$_3$)

## 2.1. Introduction

Transition metal allyl complexes can be synthesized in many different ways as mentioned in Chapter I. Previously, our group has reported the synthesis, characterization and X-ray crystal structure of the cationic pentamethylcyclopentadienyl rhenium dicarbonyl allyl complex [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] by using [Ph$_3$C][BF$_4$] to abstract a hydride from the coordinated propene in Cp*Re($\eta^2$-C$_3$H$_6$)(CO)$_2$ (Scheme 2.1).[1e,29a]
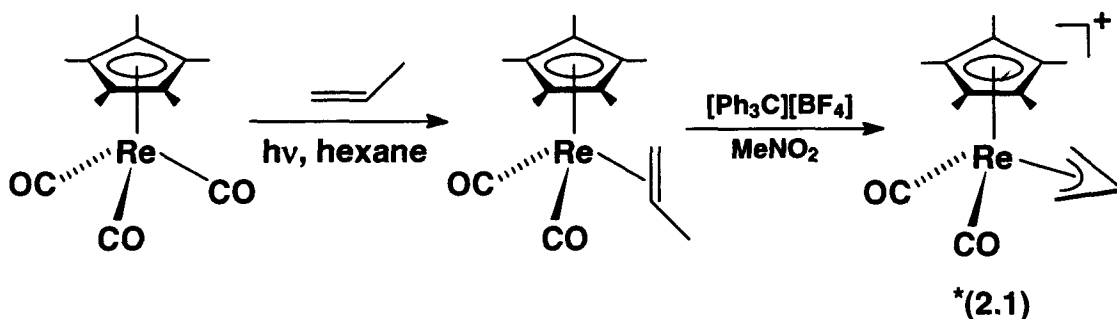


Scheme 2.1. Synthesis of complex **2.1**. * Mixture of both the *endo* and *exo* isomers.

The cationic allyl complex is of considerable interest with respect to (**a**) the barrier for *exo* —*endo* isomerization of the allyl group and (**b**) the possibility of further elaboration of the allyl group through reaction with nucleophiles including which of the central or terminal carbons is the preferred site of reaction.

In order to explore more widely the chemistry of the $\eta^3$-allyl ligand in half-sandwich rhenium complexes of this type, we have sought to replace the CO group in

complex $[Cp*Re(\eta^3-C_3H_5)(CO)_2]^+$ (**2.1**) to prepare derivatives of composition $[Cp*Re(\eta^3-C_3H_5)(CO)(L)]^+$ and $[Cp*Re(\eta^3-C_3H_5)(L)_2]^+$, where L is a 2e-donor ligand other than CO. This Chapter reports the results of our initial attempts in this direction. The synthesis, characterization and X–ray structure determination of the mono- and bis- acetonitrile allyl complexes $[Cp*Re(\eta^3-C_3H_5)(CO)(NCMe)][BF_4]$ (**2.2**) and $[Cp*Re(\eta^3-C_3H_5)(NCMe)_2]$ $[BF_4]$ (**2.3**) are described in this Chapter. The methyl allyl complex $[Cp*Re(\eta^3-C_3H_4Me)(CO)_2][BF_4]$ (**2.4**) and its mono and bis-acetonitrile complexes $[Cp*Re(\eta^3-C_3H_4Me)(CO)(NCMe)][BF_4]$ (**2.5**) $[Cp*Re(\eta^3-C_3H_4Me)(NCMe)_2][BF_4]$ (**2.6**) were also synthesized by using the same methodology as used in the synthesis of the allyl complexes.

## 2.2. Synthesis of Complexes 2.1-2.6

As mentioned in the Introduction, the $\eta^3$-allyl complex $[Cp*Re(\eta^3-C_3H_5)(CO)_2][BF_4]$ (**2.1**) can be generated by treating the propene complex $Cp*Re(\eta^2-C_3H_6)(CO)_2$ with $[Ph_3C][BF_4]$.[1e] This methodology has not been employed in this work because the propene complex is available in only low yield (ca 28%) and must be separated from secondary products (e.g., the hydrido(allyl) complex $Cp*Re(\eta^3-C_3H_5)(CO)(H)$ formed in the photolysis of $Cp*Re(CO)_3$ with propene).[1e] Instead, **2.1** was synthesized in good yield by photolysing $Cp*Re(CO)_3$ with allyl alcohol in diethyl ether in the presence of $HBF_4$ (Scheme 2.2).[41,42] The dicarbonyl complex **2.1** was obtained as an equilibrium mixture of both the *exo* and *endo* isomers.[29]

Complex **2.1** reacted with iodosobenzene (PhIO) in acetonitrile solution at 0 °C over 2 h to effect the oxidative removal of only one CO group to produce *endo* $[Cp*Re(\eta^3-C_3H_5)(CO)(NCMe)][BF_4]$ (**2.2**) in 80% yield after work up as a yellowish solid. By contrast, trimethylamine oxide, $Me_3NO$, in acetonitrile solution reacted at room temperature with **2.1** to oxidatively remove both CO groups to give *endo* $[Cp*Re(\eta^3-C_3H_5)(NCMe)_2][BF_4]$ (**2.3**) as a pale yellow solid in 90-94% yield after isolation (Scheme 2.2). Both **2.2** and **2.3** were obtained only as the *endo* $\eta^3$-allyl isomers in both solution and
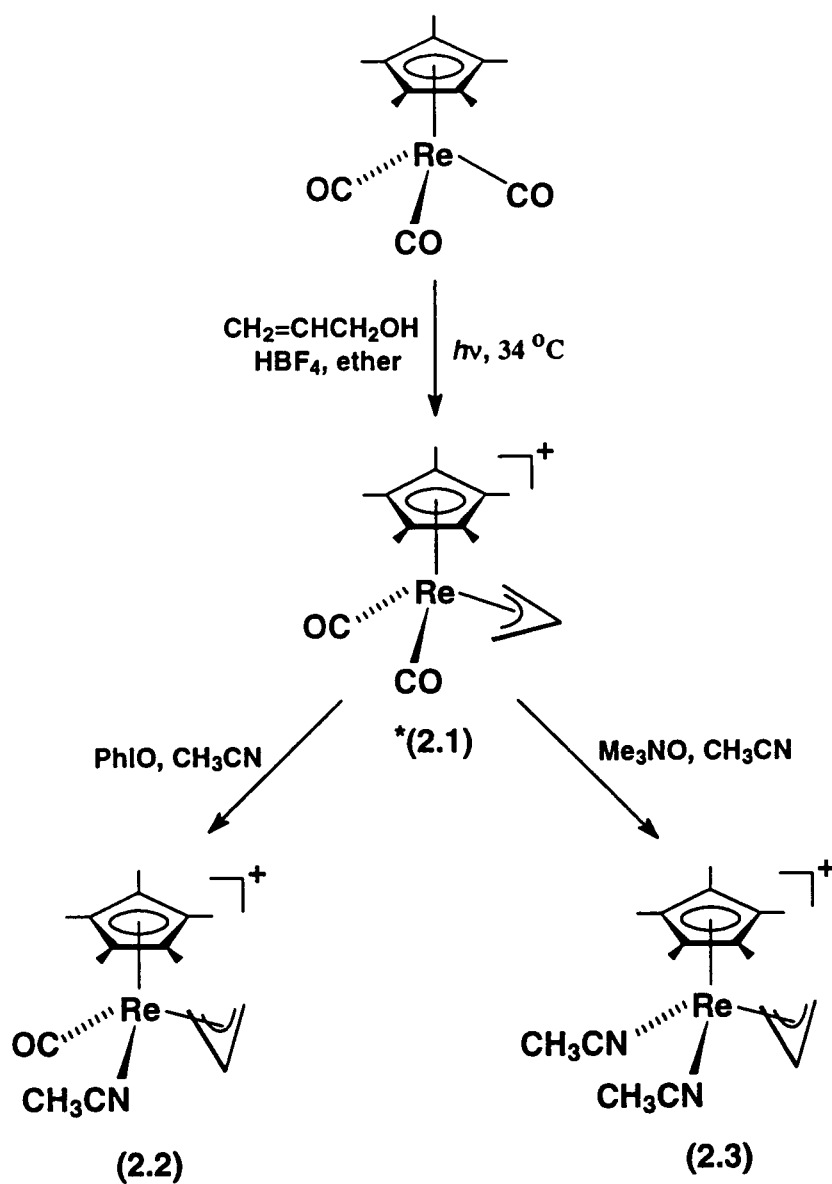
Scheme 2.2. Synthesis of the *mono* and *bis*-acetonitrile complexes 2.2 and 2.3. * Mixture of both the *endo* and *exo* isomers.

the solid state. These were identified on the basis of $^1$H NMR nuclear Overhauser enhancement (NOE) data and X-ray structure determinations (described below).

When allyl was replaced by methallyl, complex **2.4** was synthesized under the same procedure as used for the preparation of complex **2.1**. Theoretically, complex **2.4** should have four isomers: *endo-syn* or *endo-anti*, and *exo-syn* or *exo-anti* isomers (Scheme 2.3). The $^1$H NMR spectrum of complex **2.4** showed only two isomers. The major one is the *endo-syn* isomer, the minor one is the *exo-syn* isomer according to the $^1$H NMR nuclear Overhauser enhancement (NOE) data.

Upon treatment of complex **2.4** with PhIO in acetonitrile, one CO was substituted to give the mono acetonitrile complex **2.5**. When PhIO was replaced by Me$_3$NO, both CO groups were substituted by MeCN to give the bis-acetonitrile complex **2.6**. The $^1$H NMR spectra of **2.5** and **2.6** were consistent with only the *endo-syn* isomer.

## 2.3. Characterization of Complexes 2.2-2.6

### 2.3.1. IR Spectra of Complexes 2.2-2.6

Complexes **2.2-2.6** have been characterized by microanalysis, IR, $^1$H NMR and fast-atom bombardment (FAB) mass spectroscopy (Table 2.1). The IR spectrum of complex **2.2** exhibited the expected single $\nu$(CO) absorption at 1975 cm$^{-1}$ in CH$_2$Cl$_2$. This is shifted to lower wavenumber by comparison with the absorption for the dicarbonyl complex **2.1** (2053, 1999 cm$^{-1}$ in CH$_2$Cl$_2$),[29] because MeCN is a poorer $\pi$-acid compared with the CO ligand. Of course, no $\nu$(CO) absorption occurred for **2.3**, indicating complete replacement of the CO ligands and no contamination with **2.2**.

Complex **2.4** showed only two $\nu$(CO) absorptions at 2044, 1991 cm$^{-1}$ in CH$_2$Cl$_2$ solution. The two isomers of the *endo-syn* and *exo-syn* did not give well resolved $\nu$(CO) absorptions in the IR spectrum in CH$_2$Cl$_2$. Complex **2.5** showed one $\nu$(CO) absorption at 1962 cm$^{-1}$ in CH$_3$CN, while **2.6** showed no $\nu$(CO) absorption in agreement with substitution of both CO groups by the acetonitrile ligands. The $\nu$(CN) absorptions for the
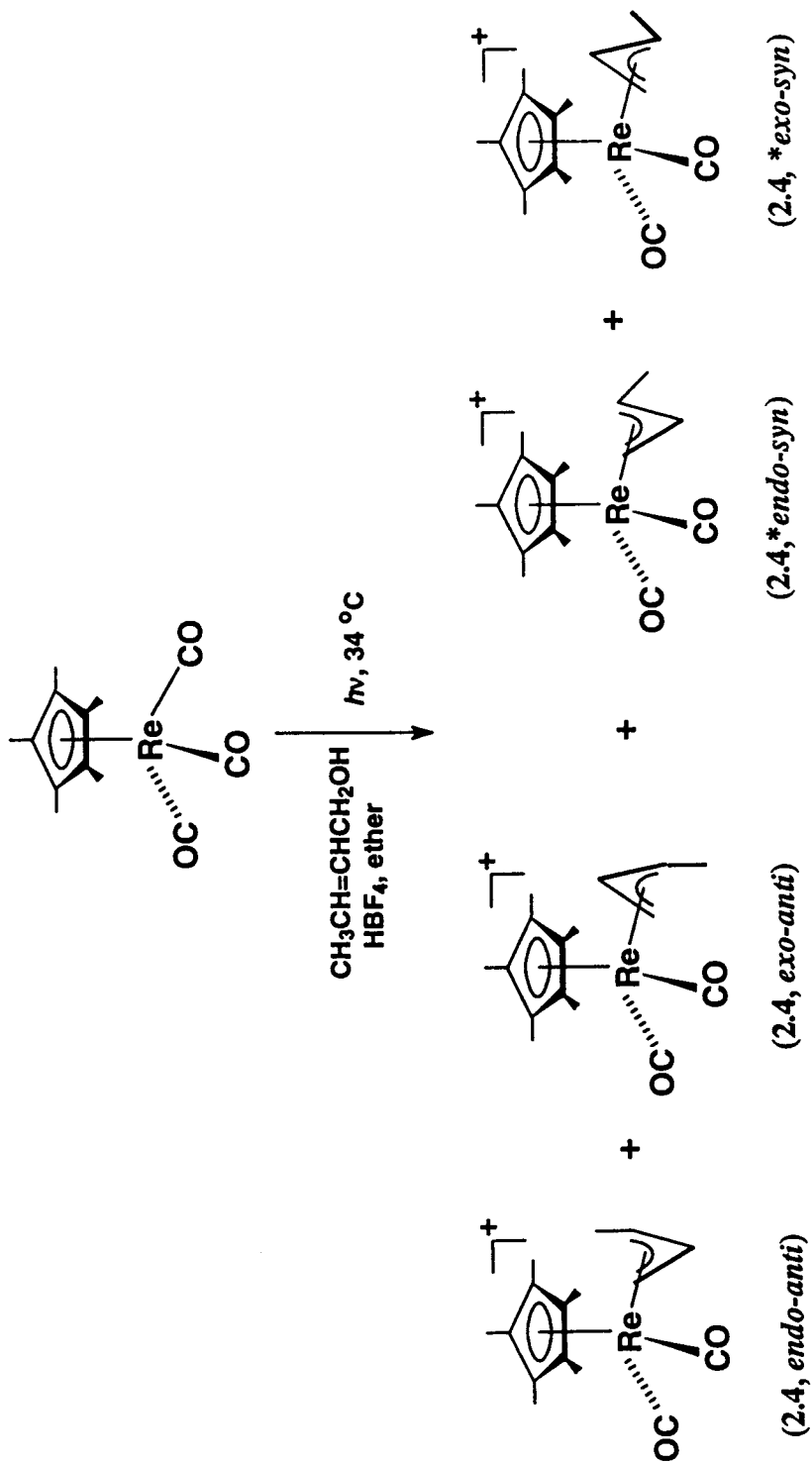
Scheme 2.3. Synthesis of complex 2.4. * Isomer observed in $^1$H NMR spectrum.

25

Table 2.1. Spectroscopic Data of Complexes **2.1-2.6**.

| Complex | IR $\nu(CO)$, cm$^{-1}$ | FABMS, m/z M$^+$ | Base | $^1$H NMR (CDCl$_3$, $\delta$ (ppm)$^a$. |
|---|---|---|---|---|
| **2.1**$^b$ | 2053, 1999$^c$ | 419 | 391 | 4.73 (m, H$_c$); 3.82 (d, J$_{sc}$ = 5.6, H$_s$); 2.21 (s, Cp*); 1.87 (d, J$_{ac}$ = 9.9, H$_a$). |
| **2.2** | 1975$^c$ | 432 | 389 | 4.85 (m, H$_c$); 3.21 (m, H$_s$); 3.16 (m, H$_{s'}$); 2.80 (s, CH$_3$CN); 2.04 (d, J$_{ac}$ = 11.6, H$_a$); 1.98 (s, Cp*); 1.33 (d, J$_{a'c}$ = 9.3, H$_{a'}$). |
| **2.3** | | 445 | 404 | 3.81 (m, H$_c$); 2.80 (s, CH$_3$CN); 2.47 (d, J$_{sc}$ = 5.0, H$_s$); 1.71 (s, Cp*); 1.47 (d, J$_{ac}$ = 6.3, H$_a$). |
| **2.4**$^d$ | 2044, 1991$^c$ | 433 | 433 | 4.62 (m, H$_c$); 3.69 (d, J$_{s'c}$ = 6.5, H$_{s'}$); 2.69 (m, H$_a$); 2.00 (d, J = 7.4, CH$_3$); 2.18 (s, Cp*); 1.70 (d, J$_{a'c}$ = 9.3, H$_{a'}$). |
| **2.5**$^d$ | 1962$^e$ | 446 | 405 | 4.78 (m, H$_c$); 3.07 (d, J$_{s'c}$ = 6.9, H$_s$); 2.78 (s, CH$_3$CN); 2.53 (m, H$_a$); 1.89 (s, Cp*); 1.86 (d, J = 6.7, CH$_3$); 1.32 (d, J$_{a'c}$ = 6.9, H$_{a'}$). |
| **2.6**$^d$ | | 459 | 375 | 3.86 (m, H$_c$); 2.86 (s, CH$_3$CN); 2.35 (d, J$_{s'c}$ = 6.0, H$_{s'}$); 2.00 (m, H$_a$); 1.67 (s, Cp*); 1.33 (d, J$_{a'c}$ = 6.6, H$_{a'}$); 1.12 (d, J = 6.0, CH$_3$). |

a. Coupling constants (J) in Hz;  b. Data for the *endo* isomer;  c. In CH$_2$Cl$_2$;  d. Data for the *endo-syn* isomer.  e. In CH$_3$CN.

coordinated acetonitrile ligand in complexes **2.2**, **2.3**, **2.5** and **2.6** were not observed in the IR spectrum. Although $\nu$(CN) in the IR spectrum for coordinated $CH_3CN$ in transition metal complexes normally occurs at a frequency lower than for the free $CH_3CN$,[82a] the failure to observe $\nu$(CN) in acetonitrile substituted complexes due to the very weak absorptions has been reported.[82b-d]

## 2.3.2. MS Spectra of Complexes 2.2-2.6

The positive–ion FABMS spectrum of **2.2** gave a strong parent $M^+$ peak at m/z 432 for the cation, and the base peak at m/z 389 corresponded to the loss of MeCN and 2H from $M^+$. The loss of two H atoms from the $C_5Me_5$ ligand in the fragmentation of pentamethylcyclopentadienyl rhenium compounds is well documented.[1e,83] Notably, there was no peak at m/z 404 corresponding to the loss of CO from $M^+$. This may indicate that the coordinated MeCN is more labile than the CO ligand in the MS experiment, since loss of CO is usually observed for most carbonyl complexes. The FABMS of **2.3** gave a parent $M^+$ peak at m/z 445, but the intensity was weak by comparison with the parent peak for **2.2**, presumably reflecting a greater lability of the second MeCN ligand. A peak at m/z 404 resulted from loss of one MeCN, and the base peak for **2.3** at m/z 361 corresponded to the loss of two MeCN ligands and 2H atoms from the parent ion.

The mass spectrum of the complex **2.4** gave a parent peak at m/z 433; this was also the base peak for this complex. A fragment at m/z 405 is consistent with loss of one coordinated CO, and loss of the second CO and two H atoms gave the fragment of m/z 375. For complex **2.5**, the parent peak is m/z 446; the base peak corresponds to the loss of $CH_3CN$ from the parent ion at m/z 405. The fragment m/z 375 is consistent with the loss of the CO, $CH_3CN$ and two H atoms from the parent ion. The parent peak of complex **2.6** (m/z 459) is much weaker compared with those of **2.4** and **2.5**; this indicates the lability of the second coordinated acetonitrile. This is the same as in the case of complex **2.3**. Another two fragments at m/z 418 and 375 correspond to loss of one or two acetonitrile ligands from the parent ion.

### 2.3.3. $^1$H NMR Spectra of Complexes 2.2-2.6

Complex **2.2** does not possess a plane of symmetry, so that in addition to the resonances for Cp* ($\delta$ 1.98) and MeCN ($\delta$ 2.80), all five protons of the allyl group give individual resonances. These were deduced from NOE data to have the assignments shown in Table 2.1, where $H_a$ and $H_s$ are the *anti* and *syn* protons on one terminal carbon atom and $H_{a'}$, $H_{s'}$ are on the other terminal carbon atom.

The interpretation of the $^1$H NMR spectrum for **2.3** is straightforward with singlets at $\delta$ 1.71 (Cp*) and 2.80 (MeCN), and because of the plane of symmetry, three resonances corresponds to the $H_c$ ($\delta$ 3.81 quintet), $H_s$ (doublet at $\delta$ 2.47) and $H_a$ (doublet at $\delta$ 1.47) protons of the allyl group. Notably, these resonances are all shifted upfield compared with the same resonances for **2.1** (*endo* isomer) (Table 2.1) as a result of the increased shielding by MeCN compared with CO. The assignments for $H_c$, $H_a$ and $H_s$ are straightforward, and were confirmed by NOE experiments (see below).

The $^1$H NMR spectrum of complex **2.4** indicated two isomers (Figure 2.1). The major one (83.5% according to the integration of the $^1$H NMR spectrum for the Cp* signal) was confirmed to be the *endo-syn* isomer by the $^1$H NMR NOE experiment. The minor one (16.5%) is the *exo-syn* isomer. The Cp* resonance for the *endo-syn* isomer occurred at $\delta$ 2.18. Substitution of the methyl group in the allyl reduces the symmetry of complex **2.4**; consequently, resonances of the four protons in the allyl ligand occur at different positions (Figure 2.1). The resonance at $\delta$ 4.62 was assigned to $H_c$, the doublet at $\delta$ 3.69 to $H_{s'}$, and the multiplet at $\delta$ 2.69 to $H_a$ which is on the same carbon terminus as the methyl group. The other $H_a$ resonance at $\delta$ 1.70 is a doublet with a coupling of $J_{ac}$ = 9.3 Hz. The methyl group gave a doublet at $\delta$ 2.00 with a coupling of 7.4 Hz to the center proton. From the expanded $^1$H NMR spectrum of **2.4**, the resonances for the *exo-syn* isomer of **2.4** can be clearly observed. The central proton $H_c$ at $\delta$ 4.20, $H_s$ at $\delta$ 3.35, and $H_a$ from the carbon terminus bearing the methyl at $\delta$ 2.80. The Cp* resonance occurred at $\delta$ 2.20, the methyl group at $\delta$ 1.98, and the other $H_a$ at $\delta$ 1.65.
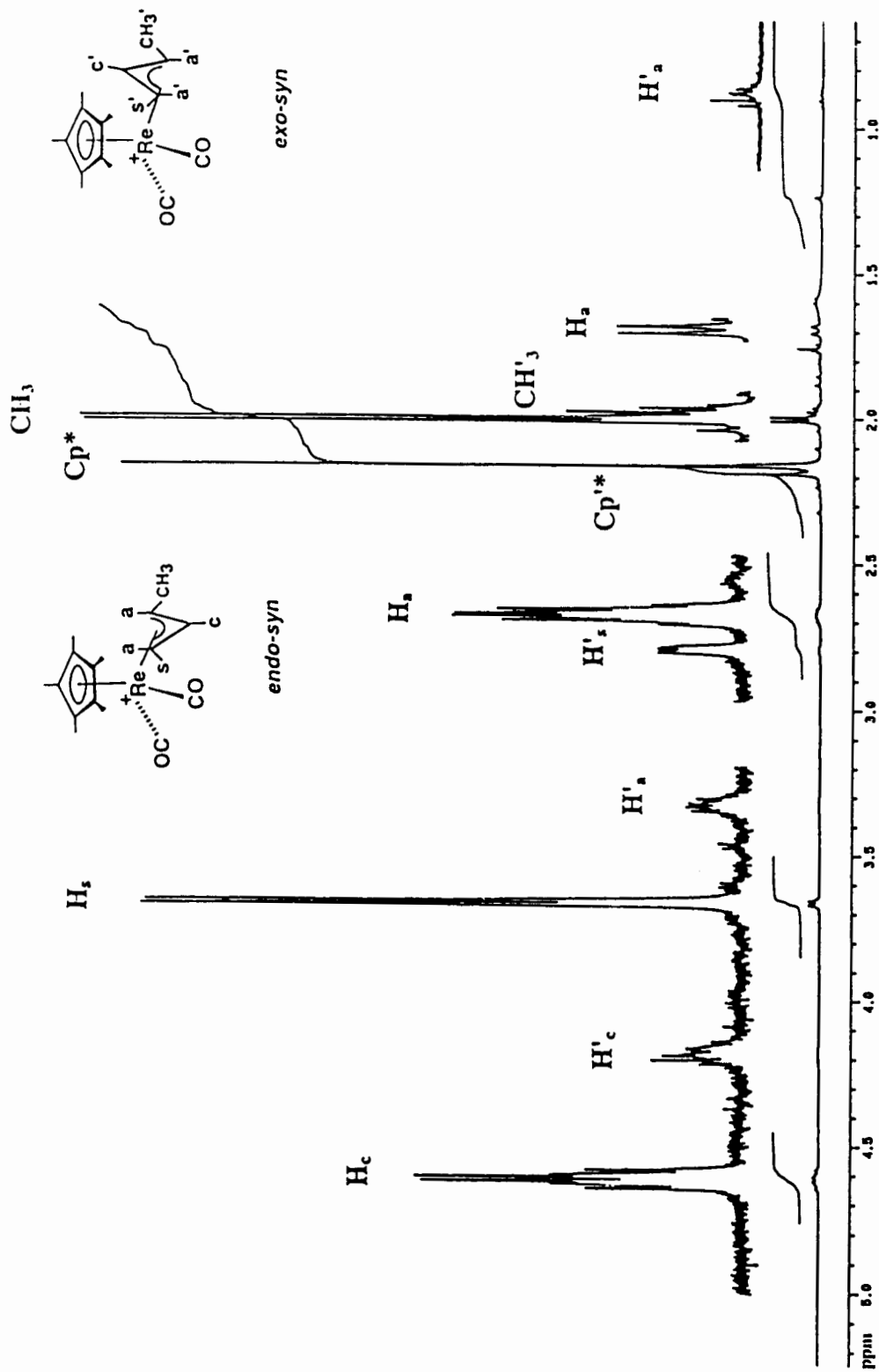
Figure 2.1. $^1$H NMR spectrum of complex [Cp*Re($\eta^3$-C$_3$H$_4$Me)(CO)$_2$][BF$_4$] (mixture of the *endo-syn* and the *exo-syn*) (2.4) in CDCl$_3$. The signals with (') assigned to the *exo-syn* isomer.

29

The $^1$H NMR spectrum of complex **2.5** showed resonances for only the *endo-syn* isomer. The resonance for the Cp* occurred at δ 1.89, which is high field shifted compared with the case of complex **2.4**. The resonance for the coordinated acetonitrile occurred at δ 2.78, which is in a similar position to that of complex **2.2**. The protons of the methyl group appeared as a doublet at δ 1.86, all the signals for the allyl protons occurred in the region of δ 4.78-1.32, these were assigned as: 4.78 to $H_c$; 3.07 to $H_s$; and 2.53, 1.32 to $H_a$.

Complex **2.6** showed resonances for only the *endo-syn* isomer; these are assigned as: multiplet at δ 3.86 to $H_c$; singlet at δ 2.86 to $CH_3CN$; the doublet at δ 2.35 to $H_s$; the two $H_a$ occurred at δ 2.00 and δ 1.33. The Cp* resonance was a singlet at δ 1.67, which is further high field shifted compared with the cases of complexes **2.4** and **2.5**; this can be attributed to the σ-donor ability of the acetonitrile ligand.

## 2.4. Discussion

### 2.4.1. $^1$H NMR NOE Experiments of Complexes 2.2-2.3

It is possible for the $\eta^3$-allyl ligand to adopt two different orientations with respect to the remaining ligand environment as mentioned in Chapter I. These are termed the *exo* and the *endo* isomers as illustrated for piano–stool complexes of the type considered here. In some cases only one of these isomers is observed, but often both isomers occur in solution and frequently there is rapid interconversion between them. Additionally, stereochemical non-rigidity in a given isomer may interconvert the $H_a$ and $H_s$ protons. In the case of the dicarbonyl complex **2.1**, it was demonstrated that rapid interconversion of the *exo* and *endo* isomers occurred in solution with no scrambling of the *syn* and *anti* protons, and the X–ray crystal structure indicated both isomers to be present in the solid state.[29] It was therefore of considerable interest to compare the properties of **2.1** with the new cationic complexes **2.2** and **2.3** to evaluate the effect of replacing CO by MeCN in the rhenium coordination sphere.

For complex **2.2**, irradiation of the Cp* resonance gave a strong enhancement of the $H_{a'}$ resonance at $\delta$ 1.33, indicating that the major form in solution is the *endo* isomer (Figure 2.2). The resonance for the other *anti* proton $H_a$ is very close to the methyl proton resonance of the Cp* ligand, so no enhancement could be observed for this signal. In fact, when irradiation of Cp* is conducted, $H_a$ is unavoidably irradiated also, and this gives rise to the observed enhancement of the geminal proton $H_s$ signal at $\delta$ 3.21; this indicated that these two protons are from the same carbon terminus. Similarly, irradiation of $H_{a'}$ at $\delta$ 1.33 results in enhancement of the $H_{s'}$ signal from the same carbon terminus at $\delta$ 3.16. Again, there is no indication of $H_a$-$H_s$ exchange, nor exchange of the two $H_a$ or the $H_s$ protons (i.e., no end-to-end interchange of the terminal allyl protons).

For complex **2.3**, irradiation of the methyl proton resonance of the Cp* resulted in a strong NOE enhancement of the $H_a$ resonance at $\delta$ 1.47, indicating that this is the *endo* isomer (Figure 2.3). Irradiation of the $H_s$ resonance at $\delta$ 2.47 caused an enhancement of the $H_c$ and $H_a$ signals and confirmed the correctness of the assignments. There was no indication of $H_a$-$H_s$ exchange.

It was hoped that irradiation of the MeCN methyl resonance in **2.2** would allow us to observe which terminal allyl proton signals are due to the protons closest in proximity to the MeCN ligand and therefore to uniquely assign all the allyl protons. Unfortunately, this assignment could not be made with any degree of certainty, because irradiation of the MeCN signal could not be achieved without also irradiating the adjacent $H_s$ signals, which inevitably produced NOE's to $H_a$ and $H_{a'}$. In the inverse NOE experiment, irradiation at $\delta$ 1.33 ($H_{a'}$) did not give any NOE enhancement of the MeCN methyl signal; however, neither did irradiation at Cp* and $H_a$ (combined ), so no specific assignment of the two sets of allyl terminus protons can be made. Irradiation of the $H_c$ resonance in complex **2.2** at $\delta$ 4.85 gave the expected enhancement of $H_s$ and $H_{s'}$ signals, confirming the assignment of the *syn* and *anti* protons.

These results indicated that both **2.2** and **2.3** are produced only as the *endo* isomers (in contrast to the dicarbonyl **2.1**) and that the allyl group in each case is
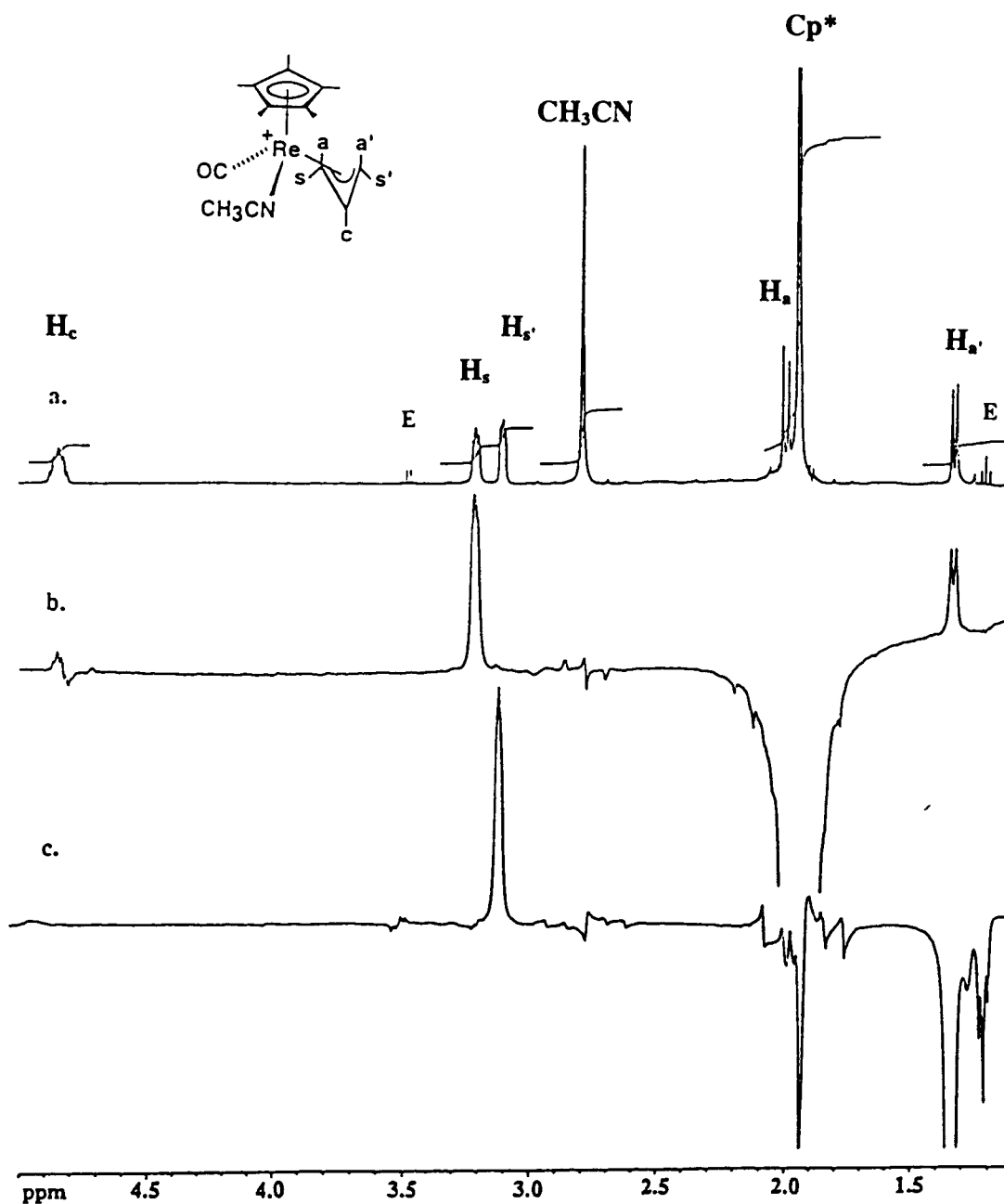
Figure 2.2. a. $^1$H NMR spectrum of $[Cp^*Re(\eta^3\text{-}C_3H_5)(CH_3CN)(CO)][BF_4]$ (2.2) in CDCl$_3$. b. NOE difference spectrum with irradiation of Cp$^*$ at $\delta$ 1.98 and H$_a$ at $\delta$ 2.04. c. NOE difference spectrum with irradiation of H$_{a'}$ at $\delta$ 1.33. E. ether signal.
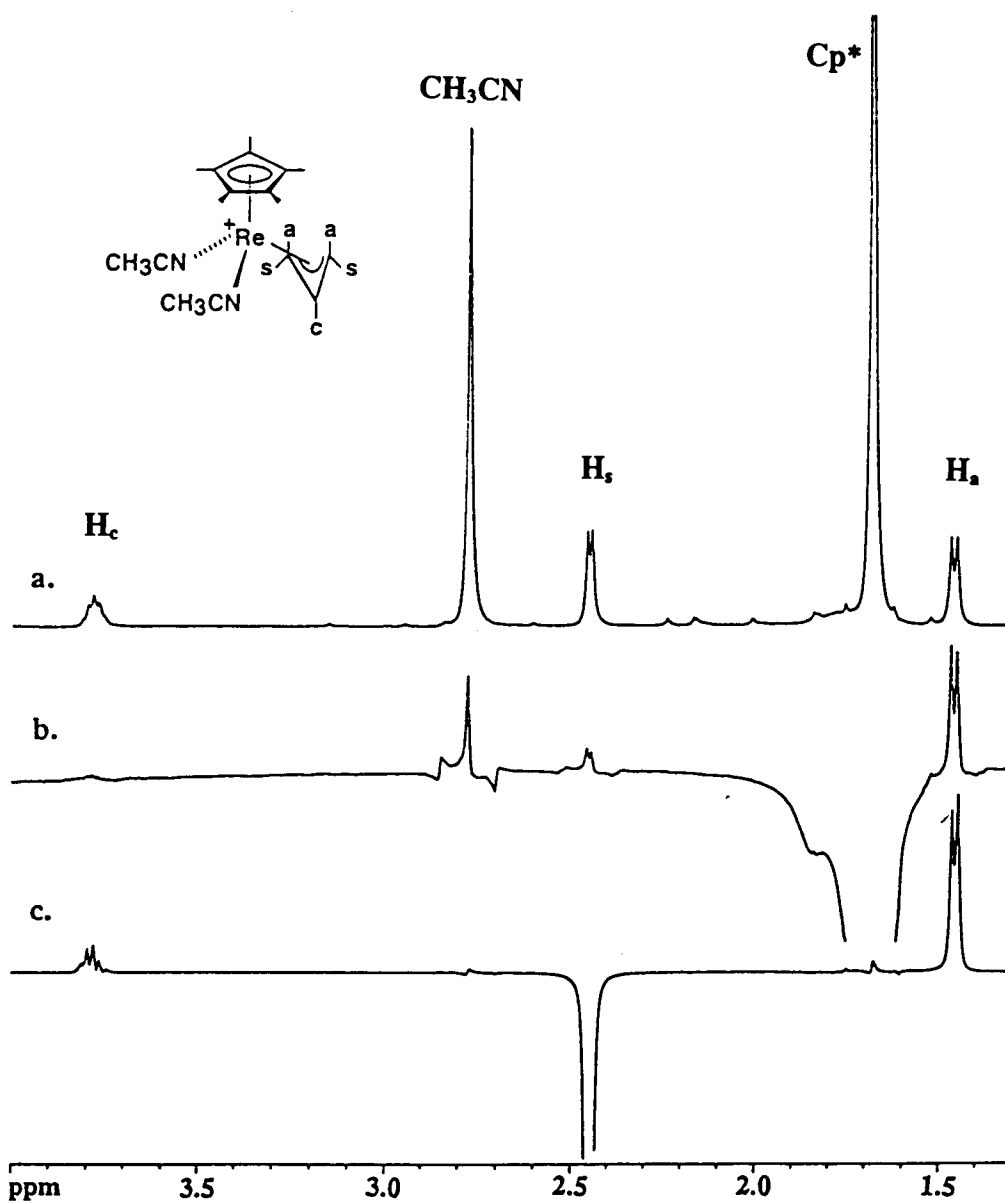
Figure 2.3. a. $^1$H NMR spectrum of $[Cp*Re(\eta^3\text{-}C_3H_5)(CH_3CN)_2][BF_4]$ (2.3). b. NOE difference spectrum with irradiation of Cp* at $\delta$ 1.71. c. NOE difference spectrum with irradiation of $H_s$ at $\delta$ 2.47.

undergoing no rearrangement within the time-scale of the $^1$H NMR experiment. In order to confirm that the *endo* isomer is thermodynamically preferred, complex **2.2** was heated in mixed solvents CDCl$_3$-toluene (1.5/1 by volume) to reflux (at 110 °C) for 12 h. The $^1$H NMR confirmed the absence of the *exo* isomer.

### 2.4.2. $^1$H NMR NOE Experiments of Complex 2.4

The interconversion of stereoisomeric $\eta^3$-allyl metal complexes is well documented.[29,84] There are two proposed mechanisms involved in the *endo-exo* interconversion process: **a.** pseudorotation of the $\eta^3$-allyl group about the allyl-metal bond axis, in which case there is no *syn-anti* conversion; **b.** $\eta^3$-$\eta^1$-$\eta^3$ transformation, which involves *syn-anti* proton exchange.[84c] A convincing method for assigning the allyl isomerization mechanism was developed by Faller through the use of NMR spin saturation transfer experiments.[84d] Investigation of the molybdenum system showed that for CpMo($\eta^3$-C$_3$H$_4$Me)(CO)$_2$, isomer interconversion occurred by pseudorotation since saturation of the *anti* proton in one conformer was transferred only to the *anti* proton of the other isomer.[84d] In another asymmetric molybdenum complex CpMo($\eta^3$-C$_3$H$_5$)(NO)I, $\eta^3$-$\eta^1$-$\eta^3$ interconversion occurred, since spin saturation was transferred from the *anti* protons of one isomer to both the *syn* and *anti* protons of the other isomer.[84e]

For the methallyl complex **2.4**, there are four possible isomers, these are: *endo-syn*, *endo-anti*, *exo-syn* and *exo-anti* as mentioned before. But the $^1$H NMR spectrum of **2.4** showed only two isomers. Casey's group has reported that three isomers of [CpRe($\eta^3$-C$_3$H$_4$Me)(CO)$_2$][PF$_6$] were obtained from a reaction of CpRe(*cis*-$\eta^2$-C$_4$H$_8$)(CO)$_2$ with [Ph$_3$C][PF$_6$], those are: *exo-syn*, *endo-syn* and *exo-anti* isomers.[84f] The isomerization studies of the molybdenum methallyl complex CpMo($\eta^3$-C$_3$H$_4$CH$_3$)(NO){(1S)-10-camphorsulfonate} indicated that in the solid state, the methyl group was *syn* and the crotyl was in an *endo* orientation, in another word, an *endo-syn* isomer was obtained. But, in solution, $\eta^3$-$\eta^1$-$\eta^3$ interconversion allows the *exo* conformer to be present.[84g] None of

their results indicated the presence of all four isomers of the methallyl complexes. And this is in agreement with our result.

In order to determine the conformation of the allyl ligand in complex **2.4**, $^1$H NMR NOE experiments were conducted. Saturation of the central proton signal at δ 4.62 induced a strong enhancement of the methyl group at δ 2.00, indicating the close proximity of these two groups; this can occur only when the methyl group is in a *syn* but not an *anti* position in the allyl ligand. No enhancement for the Cp* signal was observed as would be expected to occur for the *exo* isomer. Saturation of the multiplet *anti* proton (the *anti* proton from the same carbon terminus of the methyl group) at δ 2.69 caused a strong enhancement of the Cp* resonance at δ 2.18, this indicated a close proximity of the Cp* with the *anti* proton, and this corresponds to the case when the allyl adopts the *endo* structure. All the evidence supported an *endo-syn* structure of complex **2.4**.

The exchange of the *endo-exo* isomers in complex **2.1** has been reported in previous work.[29] Those studies indicated that **2.1** exists as a mixture of both the *endo* and the *exo* isomers in a ratio of *endo/exo* = 6.4/1 (at room temperature in $CD_2Cl_2$). The interconversion of the *endo-exo* isomers occurs without scrambling of the *syn* and the *anti* protons, consistent with a pseudorotation mechanism but not a $\eta^3$-$\eta^1$-$\eta^3$ mechanism.

For complex **2.4**, saturation of the central proton signal at δ 4.62 for the *endo-syn* isomer caused a saturation of a resonance at δ 4.20 which was assigned to the central proton of the *exo-syn* isomer. This indicated a fast *exo-endo* exchange, and magnetization transfer from $H_c$ of the *endo-syn* to the $H_c$ of the *exo-syn* isomers.

Saturation of the *syn* proton resonance at δ 3.69 of the *endo-syn* isomer induced a saturation of $H_s$ at δ 2.80, which is the *syn* proton resonance of the *exo-syn* isomer, but not the *anti* proton at δ 0.88, indicating no scrambling of the *syn* and the *anti* protons.

Saturation at δ 2.69 of the $H_a$ resonance in the *endo-syn* isomer (from the same carbon terminus with the methyl group) caused a saturation of the $H_a$ resonance at δ 3.35 for the *exo-syn* proton, and again indicated the magnetization transfer between these two protons because of the exchanging of the *endo-exo* isomers.

The results from the $^1$H NMR NOE experiments showed that the two isomers of complex **2.4** are the *endo-syn* and the *exo-syn*. The magnetization transfer of $H_c$-$H_c$, $H_s$-$H_s$ and $H_a$-$H_a$ between the two isomers indicated the exchanging of the *endo-syn* to the *exo-syn* isomer. Since no scrambling of the *syn* to *anti* protons was observed, the exchange must occur via a pseudorotation mechanism instead of the $\eta^3$-$\eta^1$-$\eta^3$ mechanism, in which the *syn* and the *anti* protons of the allyl ligand would be exchanged. This is in agreement with the result obtained for complex **2.1**.[29]

## 2.5. X–ray Crystal Structures of 2.2 and 2.3

The structure determination of complexes **2.2** and **2.3** were kindly carried out by Dr. F. W. B. Einstein and Dr. R. J. Batchelor, which confirmed the compositions indicated by the above spectroscopic data and demonstrated that these are *endo* stereoisomers in both cases. The structures of the cations are illustrated in Figures 2.4 and 2.5, and selected bond lengths and interbond angles are listed in Tables 2.2 and 2.3.

The structure of the bis-acetonitrile complex **2.3** was determined with good precision, and consists of discrete molecular ions $[Cp*Re(\eta^3\text{-}C_3H_5)(NCMe)_2]^+[BF_4]^-$ with no solvent of crystallization. There is an approximate mirror plane equating the two MeCN ligands and the two termini of the $\eta^3$-allyl ligand. The Re-C(7) bond length to the central carbon of the allyl group is shorter than the Re-C (terminal) distances, as has been observed previously.[1d,e] The dimensions for the coordinated MeCN groups are not exceptional.[85]

Unfortunately, the structure for the mono-acetonitrile complex **2.2** (which crystallized as the 0.5 toluene solvate) was not obtained to such good precision owing to crystal deterioration during the data collection and large thermal parameters, possibly a result of crystal twinning or other disorder. Therefore, no details of the influence of the unsymmetrical ligand environment on the metrical details of the allyl group emerge. Neither, unfortunately, can the influence be determined that systematically replacing the two CO groups in **2.1** by one and two MeCN groups in **2.2** and **2.3** has on the dimensions
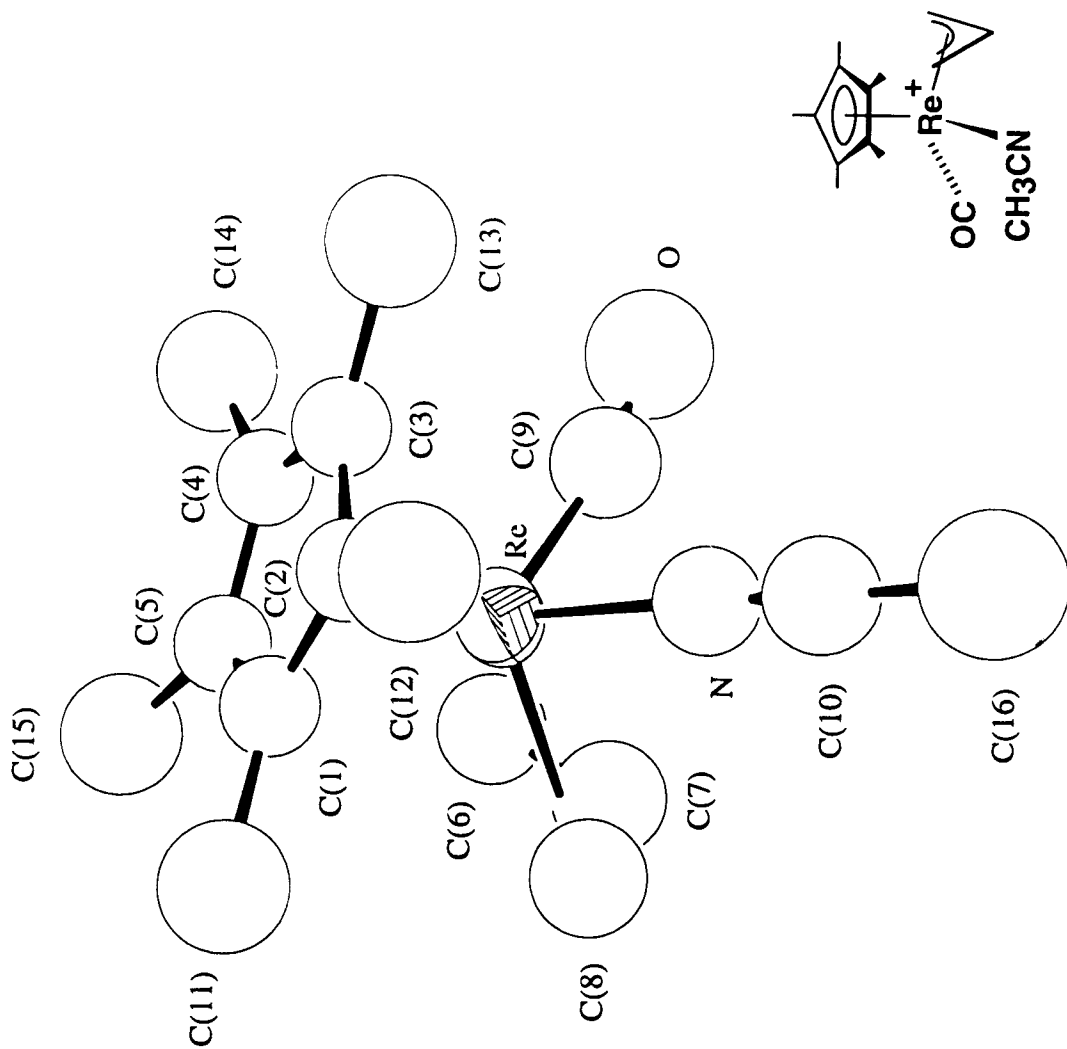
Figure 2.4. The structure of the [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(CH$_3$CN)]$^+$ cation in **2.2**.
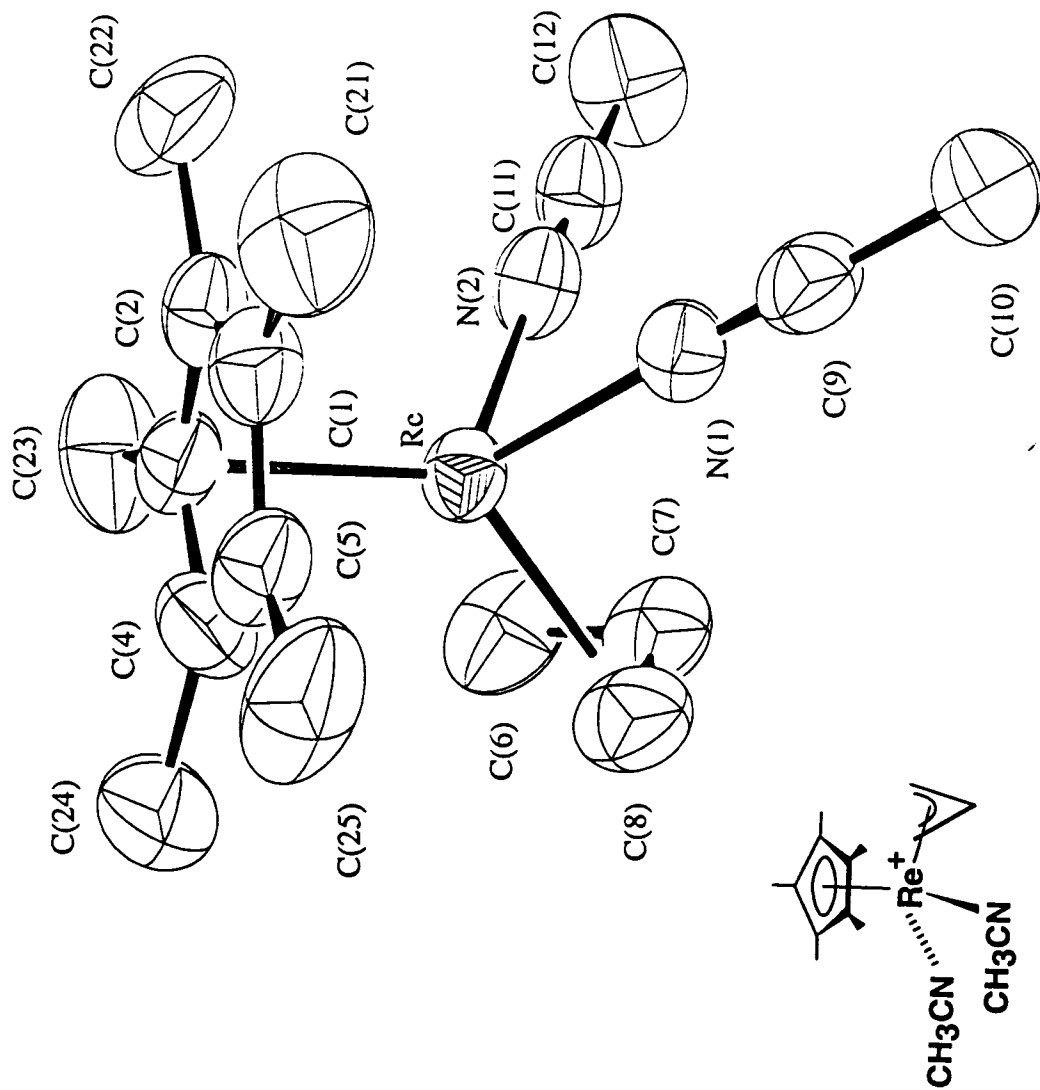
Figure 2.5. The structure of the $[Cp*Re(\eta^3-C_3H_5)(CH_3CN)_2]^+$ cation in **2.3**.

Table 2.2. Selected Intramolecular Distances (Å) and Angles (°) for the Complex Cation of [Cp*Re($\eta^3$-C$_3$H$_5$)(CH$_3$CN)(CO)][BF$_4$].1/2 toluene (**2.2**).

| Distance (Å) | | Distance (Å) | |
|---|---|---|---|
| Re - C(1) | 2.26(1) | C(10) - C(16) | 1.55(3) |
| Re - C(2) | 2.21(1) | Re - C(9) | 1.90(2) |
| Re - C(3) | 2.21(1) | O - C(9) | 1.21(2) |
| Re - C(4) | 2.26(1) | Re - C(6) | 2.24(2) |
| Re - C(5) | 2.29(1) | Re - C(7) | 2.21(2) |
| Re - Cp* [a] | 1.90 | Re - C(8) | 2.27(2) |
| Re - N | 2.06(2) | Re - allyl [b] | 1.99 |
| N - C(10) | 1.09(2) | | |
| **Angle (°)** | | **Angle (°)** | |
| N - Re - C(8) | 79.4(6) | N - Re - allyl | 100 |
| N - Re - C(9) | 84.5(7) | C(8) - C(7) - C(6) | 124(2) |
| Cp* - Re - allyl | 130 | O - C(9) - Re | 169(2) |
| Cp* - Re - C(9) | 120 | C(10) - N - Re | 177(2) |
| Cp* - Re - N | 115 | C(16) - C(10) - N | 179(3) |
| C(9) - Re - allyl | 97 | | |

a. Cp* denotes the center of mass of the ten half-occupied ring carbon atom sites of the disordered Cp* ring.

b. Allyl denotes the center of mass of the carbon atoms of the allyl group.

Table 2.3. Selected Intramolecular Distances (Å) and Angles (°) for the Complex Cation of $[Cp*Re(\eta^3-C_3H_5)(NCCH_3)_2][BF_4]$ **(2.3)**.

| Distance (Å) | | Distance (Å) | |
|---|---|---|---|
| Re - C(1) | 2.313(9) | Re - C(8) | 2.201(12) |
| Re - C(2) | 2.285(10) | Re - allyl [b] | 1.906 |
| Re - C(3) | 2.196(11) | Re - N(1) | 2.089(7) |
| Re - C(4) | 2.199(12) | N(1) - C(9) | 1.125(11) |
| Re - C(5) | 2.249(10) | C(9) - C(10) | 1.470(11) |
| Re - Cp* [a] | 1.898 | Re - N(2) | 2.086(10) |
| Re - C(6) | 2.177(12) | N(2) - C(11) | 1.134(14) |
| Re - C(7) | 2.124(11) | C(11) - C(12) | 1.470(17) |

| Angle (°) | | Angle (°) | |
|---|---|---|---|
| N(2) - Re - N(1) | 80.6(3) | C(8) - C(7) - C(6) | 112.1(12) |
| N(1) - Re - Cp* | 118.1 | C(10) - C(9) - N(1) | 179.1(9) |
| N(2) - Re - Cp* | 117.7 | C(12) - C(11) - N(2) | 179.1(13) |
| N(1) - Re - allyl | 97.2 | C(9) - N(1) - Re | 178.4(8) |
| N(2) - Re - allyl | 97.2 | C(11) - N(2) - Re | 176.3(8) |
| Cp* - Re - allyl | 132.6 | | |

a. Cp* denotes the center of mass of the five carbon atoms of the Cp* ring.
b. Allyl denotes the center of mass of the carbon atoms of the allyl group.

of the allyl ligand or its bonds to rhenium.

## 2.6. Conclusions

Rhenium allyl and methallyl bis carbonyl complexes **2.1** and **2.4** were synthesized by using a method similar to that reported in the literature,[41,42] which gave a higher yield for **2.1** compared with the method used for the preparation of **2.1** previously reported in our group. Complex **2.1** was obtained as a mixture of both the *endo* and *exo* isomers no matter which method was employed. Complex **2.4** should have four isomers: *endo-syn*, *endo-anti*, *exo-syn* and *exo-anti* referred to the relative position of the methyl group towards the Cp* ring. But the $^1$H NMR NOE experiments indicated that only two isomers of **2.4** were present in solution; these are the *endo-syn* (major, 83.5%) and the *exo-syn* (minor, 16.5%) isomers.

One of the CO ligands in both **2.1** and **2.4** can be oxidatively removed by PhIO in the presence of acetonitrile. The CO was replaced by CH$_3$CN to give the mono acetonitrile complexes **2.2** and **2.5**, but no bis-acetonitrile complex was produced. The $^1$H NMR NOE experiment and the X-ray crystal structure of **2.2** indicated that the allyl group adopted the *endo* structure in both solution and the solid state. The $^1$H NMR NOE experiment of **2.5** indicated an *endo-syn* structure for this compound.

The bis-acetonitrile complexes **2.3** and **2.6** were obtained when Me$_3$NO was used to react with **2.1** and **2.4**, respectively, in acetonitrile solvent. For **2.3**, both the $^1$H NMR NOE experiment and the X-ray crystal structure indicated that it is an *endo* isomer; the $^1$H NMR of **2.6** showed an *endo-syn* isomer, like that of **2.5**.

Replacement of one or two CO ligands in complexes **2.1** and **2.4** with acetonitrile ligands changed the distribution of the *endo*, *exo* isomers. The coordination of a better $\sigma$ donor ligand than CO, such as CH$_3$CN, made the allyl ligand in the piano-stool structure rhenium complexes **2.2**, **2.3**, **2.5** and **2.6** prefer to adopt the *endo* conformation, and this is the only conformation observed in these compounds.

The acetonitrile ligands in the mono-acetonitrile complexes are not as labile as was expected, but the FABMS of **2.3** and **2.6** indicated that loss of both acetonitrile ligands was a preferred process, and the parent ions of these complexes are very weak. The investigation of the reactivity of these carbonyl and acetonitrile allyl rhenium complexes is discussed in Chapters III and IV.

## 2.7. Experimental Section

### 2.7.1. General Procedure

All reactions were carried out under dry nitrogen in Schlenk apparatus. Solvents were purified by standard methods and were freshly distilled under dry nitrogen. Cp*H,[86] Cp*Re(CO)$_3$ [87] and PhIO [88] were synthesized according to the literature methods. All other reagents were obtained from Aldrich. Melting points were determined with a Fisher-Johns melting point apparatus. Irradiation was carried out by using a water-jacketed 200 W Hanovia Model 654A-0360 high pressure mercury vapour lamp. FTIR spectra were recorded on a Bomem Michelson-120 instrument in CH$_2$Cl$_2$, CH$_3$CN or THF solutions. $^1$H NMR and NOE spectra were recorded by Mrs. M. M. Tracey of the SFU NMR Service using a Bruker WM-400 instrument operating at 400.13 MHz. FABMS spectra were obtained by Mr. G. Owen on a Hewlett-Packard Model 5985 GC-MS instrument, equipped with a Phrasor Inc. fast atom bombardment accessory. The source gas was xenon, and samples were dispersed in *m*-nitrobenzyl alcohol. Masses are given for the $^{187}$Re isotope. Correct isotopic distribution patterns were observed for all parent peaks. Microanalyses were performed by Mr. M. K. Yang of the SFU Microanalytical Laboratory.

The crystal structure analyses of **2.2** and **2.3** reported in this Chapter were determined by Professor F. W. B. Einstein and Dr. R. J. Batchelor at Simon Fraser University.

## 2.7.2. Preparation of [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] (2.1)

A solution of Cp*Re(CO)$_3$ (216 mg, 0.53 mmol) in freshly distilled ether (40 mL) was placed in a Schlenk tube equipped with an inner condenser. Allyl alcohol (0.1 mL, 1.47 mmol) and HBF$_4$.O(C$_2$H$_5$)$_2$ (0.1 mL, 85%, 0.68 mmol) were added to this solution, then photolyzed under UV-light at the temperature of refluxing ether for 8 h. The solution was transferred to another Schlenk to recover the remaining Cp*Re(CO)$_3$. The resulting white precipitate was filtered, washed with ether (3 mL × 3), and recrystallized from CH$_2$Cl$_2$/ether to yield a white solid (140 mg, 0.277 mmol, 52%). Both the IR and the $^1$H NMR spectra of **2.1** showed that it was obtained as the mixture of the *endo* and the *exo* isomers, like that prepared by using the method reported in the previous work.[29]

## 2.7.3. Preparation of [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(NCCH$_3$)][BF$_4$] (2.2)

To a solution of **2.1** (78.9 mg, 0.156 mmol) in freshly distilled acetonitrile (8 mL) was added 93.3 mg (0.424 mmol) of PhIO. The reaction was stirred for 2 h at 0 °C and monitored by IR spectroscopy. The solution was filtered through Celite, then the solvent was removed under vacuum, and the residue was washed with ether. The solid was recrystallization from CH$_2$Cl$_2$/hexane, then washed with ether (0.3 mL × 5) to give the product as a yellowish solid (65.1 mg, 0.126 mmol, 81%), m. p.: 132-133 °C. IR (cm$^{-1}$, CH$_2$Cl$_2$): $\nu_{CO}$ = 1975. FABMS (m/z): 432 (M$^+$), 389 (M$^+$ - MeCN - 2H), 359 (M$^+$ - MeCN - CO - 4H). $^1$H NMR ($\delta$, CDCl$_3$): 4.85 (m, H$_c$), 3.21 (m, H$_s$), 3.16 (m, H$_{s'}$), 2.80 (s, CH$_3$CN), 2.04 (d, J$_{ac}$ = 11.6 Hz, H$_a$), 1.98 (s, Cp*), 1.33 (d, J$_{a'c}$ = 9.3 Hz, H$_{a'}$). Anal. Calcd for C$_{16}$H$_{23}$BF$_4$NORe: C, 37.01; H, 4.47; N, 2.70. Found: C, 37.04; H, 4.50; N, 2.68%.

## 2.7.4. Preparation of [Cp*Re($\eta^3$-C$_3$H$_5$)(NCCH$_3$)$_2$][BF$_4$] (2.3)

A solution of **2.1** (75 mg, 0.148 mmol) in freshly distilled acetonitrile (5 mL) was placed in a Schlenk tube and a solution of Me$_3$NO in acetonitrile (4.5 mL, 5.71 mg/mL) was added during 0.5 h. The reaction was stirred at room temperature for 2 h, and was monitored by IR; all the CO bands of **2.1** disappeared during this time. The solvent was

removed under vacuum and the residue was washed with ether. It was then dissolved in THF and recrystallized by careful addition of hexane. The product was obtained as a pale yellow solid (74.5 mg, 0.14 mmol, 94%), m. p.: 142-143 °C. FABMS (m/z): 445 ($M^+$), 404 ($M^+$ - MeCN), 361 ($M^+$ - 2MeCN - 2H). $^1$H NMR ($\delta$, CDCl$_3$): 3.81 (m, H$_c$), 2.80 (s, CH$_3$CN), 2.47 (d, J$_{sc}$ = 5.0 Hz, H$_s$), 1.71 (s, Cp*), 1.47 (d, J$_{ac}$ = 6.3 Hz, H$_a$). Anal. Calcd for C$_{17}$H$_{26}$BF$_4$N$_2$Re: C, 38.36; H, 4.92; N, 5.27. Found: C, 38.36; H, 4.94; N, 5.38%.

## 2.7.5. Preparation of [Cp*Re($\eta^3$-C$_3$H$_4$Me)(CO)$_2$][BF$_4$] (2.4)

A solution of Cp*Re(CO)$_3$ (562.7 mg, 1.38 mmol) in freshly distilled ether (150 mL) was placed in a Schlenk tube equipped with an inner condenser. Crotyl alcohol (0.12 mL, 1.41 mmol) and HBF$_4$.O(C$_2$H$_5$)$_2$ (0.2 mL, 85%) were added to this solution, then photolyzed under UV-light at the temperature of refluxing ether for 5 h. By using the same purification method as for **2.1**, the pure product was obtained as a white solid (mixture of the *endo-syn* and *exo-syn*, 169.4 mg, 0.33 mmol, 24%), m. p.: decomposed at 275 °C. IR (cm$^{-1}$, CH$_2$Cl$_2$): v$_{CO}$ = 2047, 1991. FABMS (m/z): 433 ($M^+$ and base), 405 ($M^+$ - CO), 375 ($M^+$ - 2CO - 2H). $^1$H NMR ($\delta$, CDCl$_3$), *endo-syn* isomer: 4.62 (m, H$_c$), 3.69 (d, J$_{s'c}$ = 6.5 Hz, H$_s$), 2.69 (m, H$_a$), 2.00 (d, J = 7.4 Hz, CH$_3$), 2.18 (s, Cp*), 1.70 (d, J$_{a'c}$ = 9.3 Hz, H$_{a'}$). *Exo-syn* isomer: 4.20 (m, H$_c$), 3.35 (m, H$_a$), 2.80 (d, J$_{s'c}$ = 6.5 Hz, H$_s$), 2.20 (s, Cp*), 1.98 (d, J = 7.4 Hz, CH$_3$), 0.88 (d, J$_{a'c}$ = 9.3 Hz, H$_{a'}$). Anal. Calcd for C$_{16}$H$_{22}$BF$_4$O$_2$Re: C, 37.00; H, 4.27. Found: C, 37.33; H, 4.37.

## 2.7.6. Preparation of [Cp*Re($\eta^3$-C$_3$H$_4$Me)(CO)(NCCH$_3$)][BF$_4$] (2.5)

To a solution of **2.4** (26.8 mg, 0.052 mmol) in freshly distilled acetonitrile (5 mL) was added PhIO (22.2 mg, 0.1 mmol). The reaction was stirred at 0 °C for 1 h and monitored by IR spectroscopy. The solution was filtered through Celite, then the solvent was pumped off and the residue was washed with ether. By using the same purification procedure as used for **2.2**, **2.5** was obtained as the pale yellow solid (*endo-syn*, 25.2 mg, 0.047 mmol, 91%), m. p.: 129-130 °C. IR (cm$^{-1}$, CH$_3$CN): v$_{CO}$ = 1962. FABMS (m/z):

446 (M$^+$), 405 (M$^+$ - CH$_3$CN, base), 375 (M$^+$ - CH$_3$CN - CO - 2H). $^1$H NMR ($\delta$, CDCl$_3$): 4.78 (m, H$_c$), 3.07 (d, J$_{s'c}$ = 6.9 Hz, H$_{s'}$), 2.78 (s, CH$_3$CN), 2.53 (m, H$_a$), 1.89 (s, Cp*), 1.86 (d, J = 6.7 Hz, CH$_3$), 1.32 (d, J$_{a'c}$ = 6.9 Hz, H$_{a'}$). Anal. Calcd for C$_{17}$H$_{25}$BF$_4$NORe: C, 38.35; H, 4.73; N, 2.63. Found: C, 38.20; H, 4.84; N, 2.67%.

### 2.7.7. Preparation of [Cp*Re($\eta^3$-C$_3$H$_4$Me)(NCCH$_3$)$_2$][BF$_4$] (2.6)

A solution of **2.4** (15.8 mg, 0.03 mmol) in freshly distilled acetonitrile (2 mL) was placed in a Schlenk tube, and a solution of Me$_3$NO in acetonitrile (14 mg, 0.19 mmol) was added. The reaction was stirred at room temperature for 5 h, and monitored by IR; all CO bands of **2.4** disappeared during this time. The solvent was removed under vacuum and the residue was recrystallized from CH$_2$Cl$_2$/ether to give the pure product as a yellowish solid (*endo-syn*, 12.4 mg, 0.023 mmol, 76%), m. p.: 123-124 °C. FABMS (m/z): 459 (M$^+$), 418 (M$^+$ - CH$_3$CN), 375 (M$^+$ - 2CH$_3$CN - 2H). $^1$H NMR ($\delta$, CDCl$_3$): 3.86 (m, H$_c$), 2.86 (s, CH$_3$CN), 2.35 (d, J$_{s'c}$ = 6.0 Hz, H$_{s'}$), 2.00 (m, H$_a$), 1.67 (s, Cp*), 1.33 (d, J$_{a'c}$ = 6.6 Hz, H$_{a'}$), 1.12 (d, J = 6.0 Hz, CH$_3$). Anal. Calcd for C$_{18}$H$_{28}$BF$_4$N$_2$Re: C, 39.63; H, 5.18; N, 5.14. Found: C, 39.38; H, 4.94; N, 4.87%.

### 2.7.8. Crystal Preparation for Complex (2.2)

Crystals of **2.2** were grown as small colorless plates from a solution in THF/toluene (1/5 by volume) kept in the refrigerator for two weeks. These were shown to be the 0.5 toluene solvate by the subsequent structure determination.

### 2.7.9. Crystal Preparation for Complex (2.3)

Crystals were grown from THF/toluene (1/5 by volume, kept in the refrigerator for three weeks) as yellow needles.

# Reactivity of [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] (2.1) Towards Various Nucleophiles

## 3.1. Introduction

Among carbon-carbon bond formation reactions promoted by transition metal compounds, allylic alkylation by nucleophilic addition at the $\eta^3$-allyl in cationic transition metal complexes has played an important role. The nucleophilic addition at the $\eta^3$-allyl occurs either at the central carbon, or at one of the terminal carbon atoms depending upon the metal and co-ligands. Although the terminal carbons are the preferred site of attack in most cases (Equations 3.1, 3.2),[89,90] the central carbon atom can also be attacked to give metallacyclobutanes (Equation 3.3, M = Mo, W).[91a, b]



(Eq. 3.1)



(Eq. 3.2)



(Eq. 3.3)
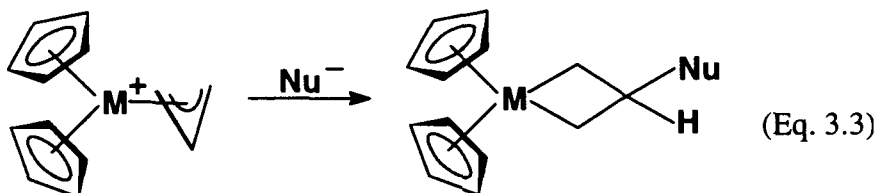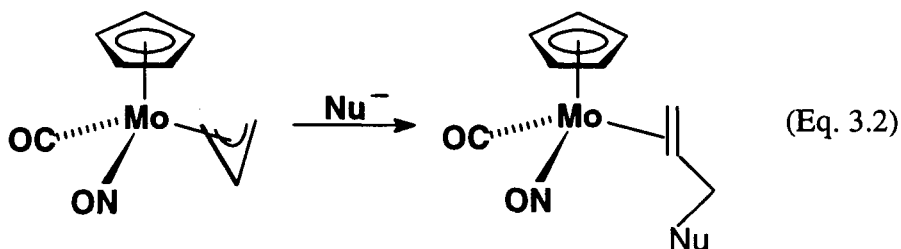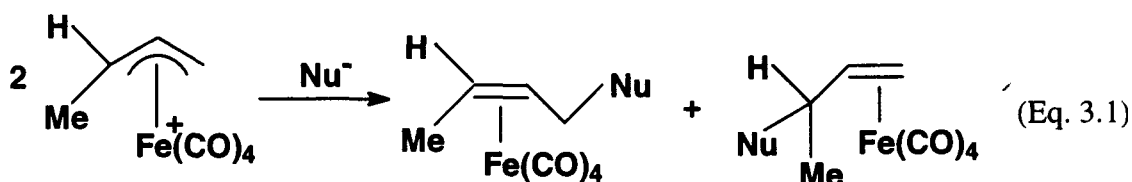
The nucleophilic addition reactions of the $\eta^3$-allyl in palladium complexes have been extensively applied in organic synthesis. Both regio- and stereoselectivities were achieved by using $\eta^3$-allyl palladium complexes as catalysts.[92] In addition to palladium, the nucleophilic addition at the coordinated $\eta^3$-allyl in cationic or neutral complexes of other transition metals, such as Ni,[93] Ti,[94] Mo,[95] and Fe [96] have also been studied in an attempt to seek new catalyst systems.[97-99]

Previously, in our group, the nucleophilic reactions of rhenium allyl complex $[Cp*Re(\eta^3\text{-}C_3H_5)(CO)_2][BF_4]$ (2.1) with MeO$^-$ and H$^-$ at room temperature were studied. The results showed that both of these nucleophiles attacked the terminal carbon of the $\eta^3$-allyl to give the substituted propene complexes. These are the only nucleophilic reactions reported for the pentamethylcyclopentadienyl $\eta^3$-allyl rhenium complex.[1e] The nucleophilic reactions of the $\eta^3$-allyl in $[Cp*Re(\eta^3\text{-}C_3H_5)(CO)_2][BF_4]$ have been extended to other nucleophiles in this work and are reported in this Chapter. The low temperature reactions showed a competition reaction between the $\eta^3$-allyl and the CO ligand in $[Cp*Re(\eta^3\text{-}C_3H_5)(CO)_2][BF_4]$ (2.1), but not between the central and the terminal carbons of the allyl.

## 3.2. Reactions of $[Cp*Re(\eta^3\text{-}C_3H_5)(CO)_2][BF_4]$ (2.1) with Various Nucleophiles

### 3.2.1. Reaction of $[Cp*Re(\eta^3\text{-}C_3H_5)(CO)_2][BF_4]$ (2.1) with NaBH$_4$

In an earlier paper, it was indicated briefly that at room temperature, complex 2.1 reacts with NaBH$_4$ in THF to give the $\eta^2$-propene complex $Cp*Re(\eta^2\text{-}C_3H_6)(CO)_2$ (3.1)[1e]. In this work, we have reexamined this reaction at -78 °C in THF and trace amount of H$_2$O. The purpose of conducting the reaction at low temperature was to seek an efficient method to synthesize $Cp*Re(\eta^3\text{-}C_3H_5)(CO)(H)$. We were expecting that the H could possibly attack the metal to replace one CO to produce the corresponding hydride complex. Alternatively, the CO ligand could be attacked, as in the case of $[Cp*Re(NO)(CO)(PPh_3)]^+$, in which the CO was attacked by H$^-$ to give first the formyl,

which was further reduced by H⁻ to the methyl complex Cp*Re(NO)(CH₃)(PPh₃).[100] In our case, when complex **2.1** was reacted with NaBH₄ at -78 °C, H⁻ attacked only the $\eta^3$-allyl to form complex **3.1**; no other product was observed.

### 3.2.2. Reaction of [Cp*Re($\eta^3$-C₃H₅)(CO)₂][BF₄] (2.1) with NaOCH₃

The reaction of **2.1** with NaOCH₃ at room temperature was reported in previous work in our group, and the substituted propene complex Cp*Re($\eta^2$-C₃H₅OCH₃)(CO)₂ (**3.3**) was the only product.[1e] In order to study the reactivity of complex **2.1** with nucleophiles under different reaction conditions, **2.1** was reacted with NaOCH₃ in methanol at - 78 °C, and two products were obtained (Scheme 3.1). As well as the $\eta^2$-methoxypropene complex Cp*Re($\eta^2$-C₃H₅OCH₃)(CO)₂ (**3.3**), a methoxycarbonyl complex Cp*Re($\eta^3$-C₃H₅)(CO)(COOCH₃) (**3.2**) was also produced, which resulted from the nucleophilic addition of CH₃O⁻ to the CO ligand. By the time the products were purified and warmed to room temperature to measure the ¹H NMR spectrum, **3.2** and **3.3** were obtained in approximately 1:1 ratio (according to the integration of the Cp* resonance in the ¹H NMR spectrum). The IR spectrum of the methanol solution, after three hours reaction, exhibited ν(CO) at 1956 and 1885 cm⁻¹ at room temperature, which were assigned to **3.3**, and ν(CO) at 1942 cm⁻¹ assigned to **3.2**. After removing the methanol, the IR spectrum of the hexane extract showed absorptions for **3.3** at 1964 and 1892 cm⁻¹, and ones at 1944 and 1634 cm⁻¹ for the terminal CO and methoxycarbonyl groups of **3.2** respectively. The ¹H NMR spectrum in CDCl₃ gave all the expected resonances for **3.3** and the presence of the $\eta^3$-allyl ligand in **3.2** was clearly evident: a multiplet at δ 4.20 (H_c), two doublets of doublets at δ 3.02 and δ 2.94 (inequivalent H_s protons), and two doublets at δ 1.10 and δ 0.69 (inequivalent H_a protons).

Interestingly, the reaction of **2.1** with NaBH₄ was highly regioselective. There was no evidence of other products such as the known hydrido(allyl) complex Cp*Re(CO)(H)($\eta^3$-C₃H₅) (from CO substitution) or possibilities such as a formyl or a metallacyclobutane complex.[101,102] By contrast, NaOMe resulted in products from elaboration of either the
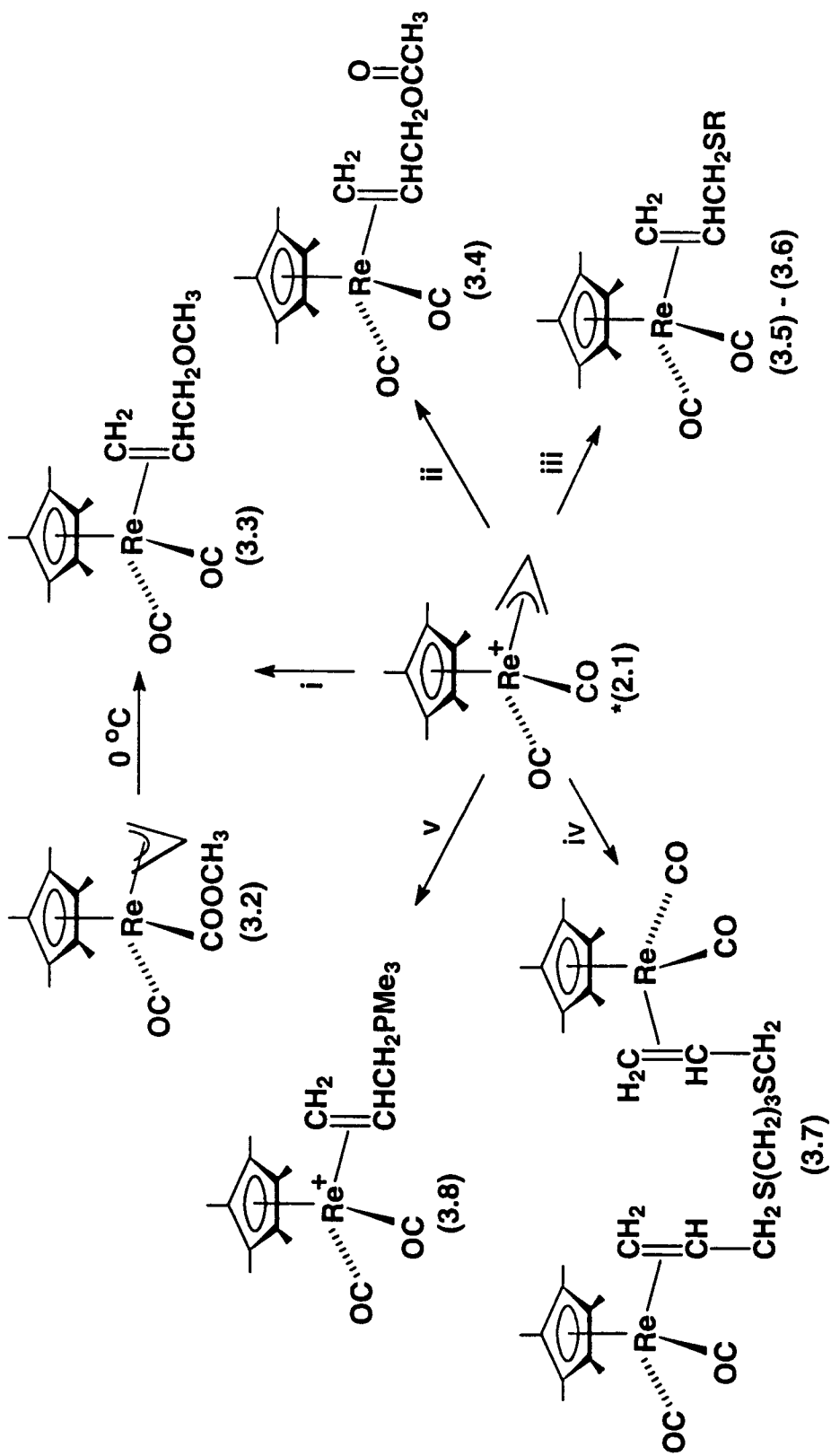
Scheme 3.1. Reactions of **2.1** (* Mixture of *endo* and *exo*) with oxygen, sulfur and phosphorus nucleophiles. i. NaOCH$_3$/CH$_3$OH; ii. CH$_3$COONa/CH$_2$Cl$_2$; iii. NaSR/CH$_2$Cl$_2$ {R = C$_2$H$_5$ (**3.5**), C$_6$H$_5$ (**3.6**)}; iv. NaS(CH$_2$)$_3$SNa/CH$_2$Cl$_2$; v. PMe$_3$/CH$_2$Cl$_2$.

49

allyl or a carbonyl ligand. However, when the product mixture in CDCl₃ was maintained at room temperature for 3 days, the $^1$H NMR then exhibited only the resonances for **3.3**, suggesting that **3.2** slowly isomerized to **3.3** in solution.

The variable temperature $^1$H NMR study of this reaction in CD₃OD was carried out from -70 °C to 21 °C. The percentage of complexes **3.2** and **3.3** (according to the integration of the Cp* signals) at different temperatures are listed in Table 3.1.

Table 3.1. Percentage of Complexes **3.2** and **3.3** at Different Temperatures.[a]

| Temperature (K) | Time (hour) | 3.2 (%) | 3.3 (%) |
|---|---|---|---|
| 203 | 0.00 | 89.35 | 10.65 |
| 213 | 0.43 | 88.54 | 11.46 |
| 223 | 0.97 | 87.57 | 12.43 |
| 243 | 1.78 | 86.91 | 13.10 |
| 263 | 2.43 | 83.52 | 16.48 |
| 283 | 2.92 | 80.26 | 19.74 |
| 283 | 4.10 | 59.47 | 40.53 |
| 294 | 28.10 | 0.00 | 100.00 |

a. The percentage of the complexes **3.2** and **3.3** were determined according to the integration of the Cp* resonances for the two complexes.

The $^1$H NMR spectrum of complex **2.1** in CD₃OD showed a mixture of both the *endo* and the *exo* isomers, with a ratio of *endo/exo* = 8.0/2.2 from the integration of the allyl protons (the two Cp* signals for the *endo* and the *exo* isomers are not separated very

well in $CD_3OD$). The $^1H$ NMR data at -70 °C indicated that the reaction of **2.1** with $MeO^-$ gave two products **3.2** and **3.3** (Figure 3.1). Complex **3.2** existed as the *endo* isomer, no *exo* isomer was detected from the $^1H$ NMR spectrum. The experimental result at 203 K suggests differing rate of attack at the allyl and CO ligands of **2.1**. The ratio of **3.2** to **3.3** is about 9/1. If *exo-endo* isomerization of **2.1** is slow at this temperature, this may indicate that *endo*-**2.1** preferentially undergoes attack at CO giving **3.2**, and *exo*-**2.1** preferentially undergos attack at the allyl to give **3.3**. However, if *exo-endo* isomerization of **2.1** is fast, the result simply reflects the faster attack at the carbonyl in the isomerizing **2.1**. The $^1H$ NMR experiment indicated that the conversion of **3.2** to **3.3** is an irreversible process (Schemes 3.1 and 3.2). Although nucleophilic additions at $\eta^3$-allyl in cationic transition metal complexes have been extensively studied, and it is common for carbonyl complexes to undergo nucleophilic addition by alkoxide ion to give an alkoxycarbonyl complex,[103] no
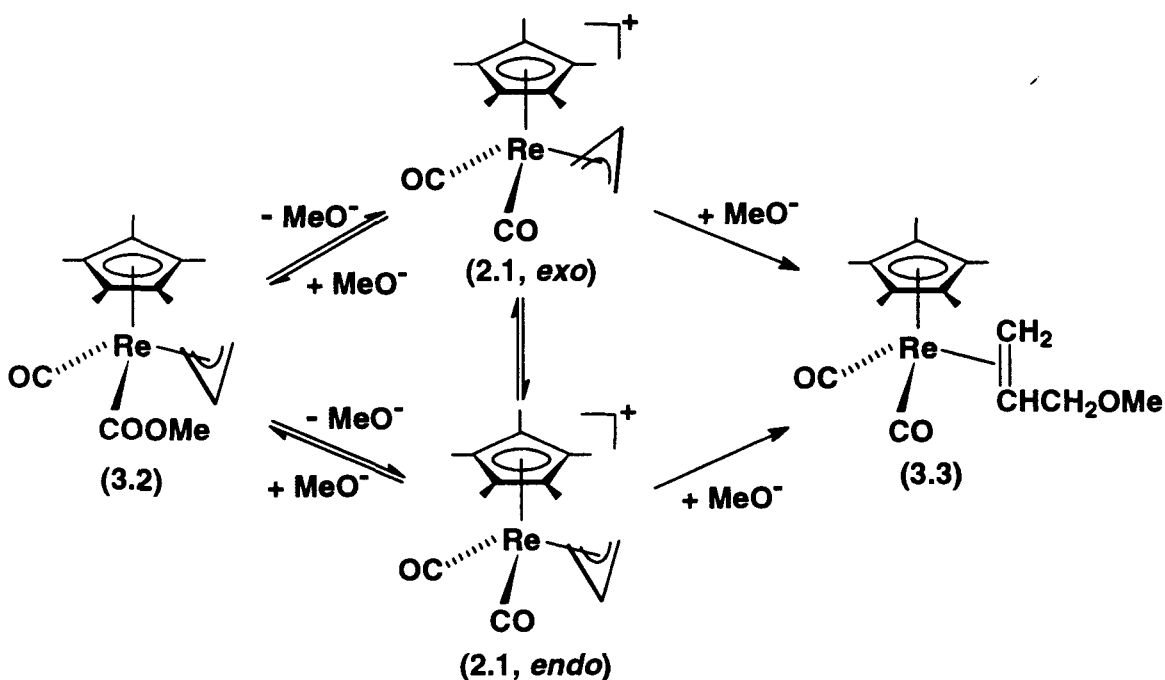


Scheme 3.2. Reversible addition of $MeO^-$ to $[Cp^*Re(\eta^3-C_3H_5)(CO)_2][BF_4]$ (**2.1**).
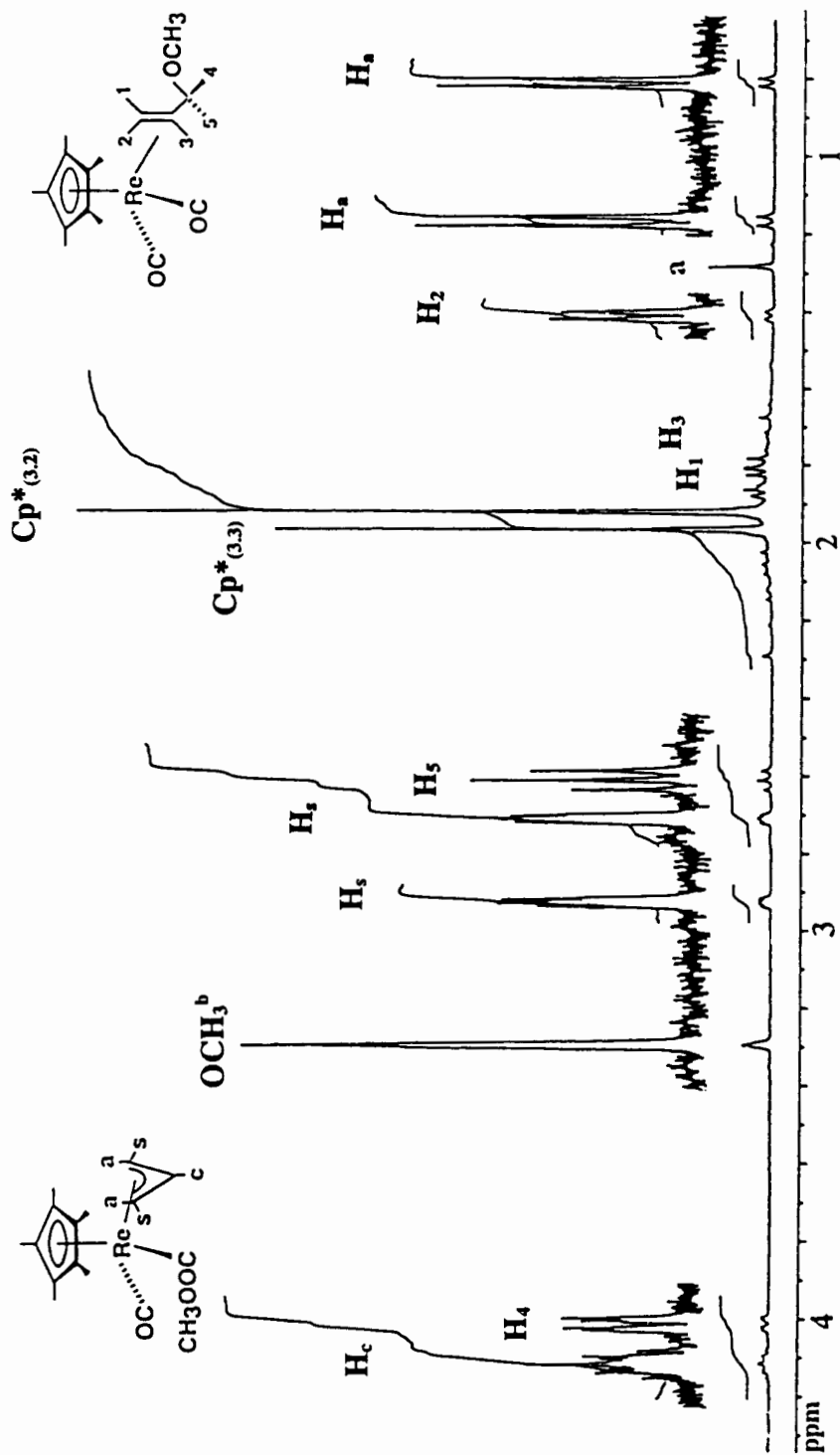
Figure 3.1. $^1$H NMR spectrum of a mixture of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(COOCH$_3$) (3.2) and Cp*Re($\eta^2$-CH$_2$=CHCH$_2$OCH$_3$)(CO)$_2$ (3.3) in CD$_3$OD at 283 K.

a. impurity; b. The OCH$_3$ resonances for 3.2 and 3.3 are overlapped.

52

competitive nucleophilic reaction between the CO and the $\eta^3$-allyl has been reported in the literature.

The $^1$H NMR experimental data indicated that the conversion of **3.2** to **3.3** occurred efficiently at 283 K, as complex **3.3** increased its percentage from 19.74 to 40.53 when the sample was held at this temperature for 1.18 h. The sample was cooled to 243 K again, and the $^1$H NMR spectrum showed that the ratio of **3.2** to **3.3** did not change. This suggested that the interconversion of **3.2** to **3.3** is irreversible. The reversible addition of OR$^-$ to coordinated CO is well documented.[104] A proposed mechanism for the conversion of **3.2** to **3.3** is described in Scheme 3.2. It involves the dissociation of MeO$^-$ from the methoxycarbonyl, and then it reattacks the $\eta^3$-allyl to give the methoxypropene complex **3.3**.
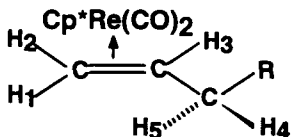
### 3.2.3. Reaction of [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] (2.1) with CH$_3$COONa

The reaction of **2.1** with CH$_3$COONa was carried out at room temperature for 5 h. The IR spectrum showed $\nu$(CO) absorptions for only Cp*Re($\eta^2$-C$_3$H$_5$OOCCH$_3$)(CO)$_2$ (**3.4**) (Scheme 3.1, Tables 3.2 and 3.3) at 1956, 1877 cm$^{-1}$ in CH$_2$Cl$_2$.

The EIMS of **3.4** gave a strong parent peak at m/z 478 with 52% intensity, indicating the stability of this complex. A fragment at m/z 378 corresponding to [M$^+$ - CH$_2$CHCH$_2$OOCCH$_3$] is 80% in intensity, which may be an indication of a possibility to release the substituted propene ligand in this kind of rhenium complexes in a chemical process.
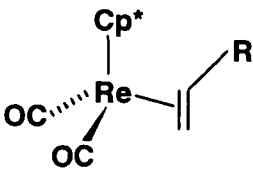
The $^1$H NMR spectrum of **3.4** in C$_6$D$_6$ showed a Cp* resonance at $\delta$ 1.32, and the CH$_3$ from CH$_3$COO at $\delta$ 1.85. The proton resonances for the substituted propene are listed in Table 3.2. The two protons at $\delta$ 5.18 and $\delta$ 3.71 in -CH$_2$- are diastereotopic, and each showed a doublet of doublets resulting from mutual coupling, and also with H$_3$. H$_1$ was overlapped with H$_3$ to give a multiplet at $\delta$ 2.21-2.24, and H$_2$ was at higher field to give a doublet at $\delta$ 1.32. These substituted propene protons gave the same coupling pattern as in the case of complex **3.3**. These data are listed in Tables 3.2 and 3.3.

Table 3.2. Chemical Shifts of the Substituted Propenes in **3.4-3.14**.[a]



| Complex | $^1$H NMR chemical shifts ($\delta$) [b] |
|---------|------------------------------------------|
| **3.4** | 5.18 (dd, H$_4$), 3.71 (dd, H$_5$), 2.21-2.24 (m, H$_1$ and H$_3$), 1.32 (d, H$_2$). |
| **3.5** | 3.71 (dd, H$_4$), 2.52 (m, H$_5$), 2.16-2.18 (m, H$_1$ and H$_3$), 1.37 (d, H$_2$). |
| **3.6** | 4.10 (dd, H$_4$), 2.89 (dd, H$_5$), 2.18-2.20 (m, H$_1$, H$_3$), 1.26 (d, H$_2$). |
| **3.7** | 3.73 (dd, H$_4$), 2.51 (dd, H$_5$), 2.22-2.25 (m, H$_3$, H$_1$), 1.42 (d, H$_2$). |
| **3.8** | 3.18 (m, H$_4$), 1.86 (m, H$_3$), 1.64 (m, H$_1$ and H$_5$, overlapped), 1.37 (m, H$_2$). |
| **3.10** | 3.75 (dd, H$_4$), 2.70 (dd, H$_5$), 2.04 (dd, H$_1$), 1.87 (m, H$_3$), 1.22 (dd, H$_2$). |
| **3.11** | 4.64 (dd, H$_4$), 4.53 (dd, H$_5$), 2.40 (m, H$_1$), 2.29 (m, H$_3$), 1.49 (d, H$_2$). |
| **3.12** | 2.50 (m, H$_4$), 2.17 (dd, H$_1$), 2.02 (m, H$_3$), 1.43 (dd, H$_2$), 1.27 (m, H$_5$). |
| **3.14** | 3.85 (dd, H$_4$), 2.57 (dd, H$_5$), 2.29 (dd, H$_1$), 2.12 (m, H$_3$), 1.34 (dd, H$_2$). |

a. The coupling constants were reported in the experimental section. b. The $^1$H NMR spectrum of **3.8** was recorded in $CD_2Cl_2$, all others in $C_6D_6$.

Table 3.3. Spectroscopic Data for Complexes **3.3-3.14**.

| Complex | R group | IR (cm$^{-1}$)[a] | MS (m/z)[b] M$^+$ | Base |
|---------|---------|-------------------|-------------------|------|
| **3.3** | **OCH$_3$** | 1964, 1892 | 450 | 348 |
| **3.4** | **OOCCH$_3$** | 1968, 1896, 1739 | 478 | 348 |
| **3.5** | **SC$_2$H$_5$** | 1964, 1892 | 480 | 439 |
| **3.6** | **SC$_6$H$_5$** | 1964, 1892 | 528 | 487 |
| **3.7**[c] | **S(CH$_2$)$_3$S** | 1962, 1892 | | 419ʹ |
| **3.8** | **PMe$_3$** | 1964, 1885[d] | 495[e] | 419 |
| **3.10** | **N$_3$** | 2101, 1969, 1898[f] | | 346 |
| **3.11** | **NH$_2$** | 1964, 1892 | 435[g] | 391 |
| **3.12** | **CHMe$_2$** | 1960, 1888 | 462 | 348 |
| **3.14** | **C$_6$H$_5$** | 1962, 1890 | 496 | 440 |

(Structure shown above table: Cp* and two OC groups bonded to Re, with Re bonded to a double bond bearing R)

a. Except where mentioned, all the IR spectra were measured in hexane; b. Except where mentioned, all the MS spectra were EIMS; c. See Scheme 3.1 for the structure; d. In CH$_2$Cl$_2$; e. FABMS; f. 2101 assigned to $v(N_3)$; g. CIMS;

The $^{13}$C{$^1$H} NMR spectrum of **3.4** was also obtained. Three substituted propene carbons gave resonances at 73.40, 37.33 and 26.62 ppm, which is in the same region compared with the literature data for these complexes.[105a]

## 3.2.4. Reaction of [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] (2.1) with CH$_3$CH$_2$SNa

In an attempt to coordinate a sulfur containing ligand to the rhenium $\eta^3$-allyl complex, the cationic dicarbonyl complex **2.1** was reacted with PhIO in the presence of NaSEt in CH$_2$Cl$_2$. The expected product is Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(SEt), if PhIO oxidatively removes one CO, as in the case of the reaction of PhIO with **2.1** in CH$_3$CN. Although PhIO or Me$_3$NO have been extensively used to remove coordinated CO from cationic carbonyl complexes, this is usually used in solvents which act as the ligand, such as CH$_3$CN. In that case, as soon as the carbonyl is removed, the solvent can coordinate to the metal to form the product.[100,105b] Gladysz's group had reported an example of using Me$_3$NO in CH$_2$Cl$_2$ to remove CO in [CpRe(CO)(NO)(PPh$_3$)][BF$_4$] to successfully coordinate PPh$_3$.[100] We tried to simulate the chemistry they achieved to extend the application of PhIO in the presence of a ligand other than solvent. Surprisingly, the strong nucleophilic ability of C$_2$H$_5$S$^-$ dominated the reaction, and it attacked the $\eta^3$-allyl, before the CO was removed by PhIO, to result in complex Cp*Re($\eta^2$-C$_3$H$_5$SEt)(CO)$_2$ (**3.5**) (Scheme 3.1). In order to confirm this result, complex **2.1** was treated with pure NaSC$_2$H$_5$ in CH$_2$Cl$_2$, and gave the same product, which was characterized by spectroscopic methods and microanalysis.

The IR spectrum of **3.5** showed $\nu$(CO) absorptions at 1964, 1892 cm$^{-1}$ in hexane, which is in the same region as for complexes **3.3** and **3.4** (Table 3.3). The EIMS of **3.5** showed the parent peak at m/z 480, which is very weak (11%); the base peak was observed at m/z 439, which corresponds to the loss of C$_3$H$_5$ from M$^+$. This is unusual compared with the allyl and substituted propene complexes reported in this thesis. Since the $\eta^3$-allyl or C=C double bond was directly coordinated to the metal center, in the MS experiments, the C$_3$H$_5$ unit stays with the metal center to form the base peak. It is not

common that the $C_3H_5$ unit is lost before the CO ligand, but no $[M^+ - CO]$ fragmentation was obtained for **3.5**. We propose that coordination transformation, involving a shift of Re from C=C to the lone pair electrons of the sulfur atom may have occurred in the MS process (Scheme 3.3); this might explain why loss of $C_3H_5$ was preferred to loss of CO
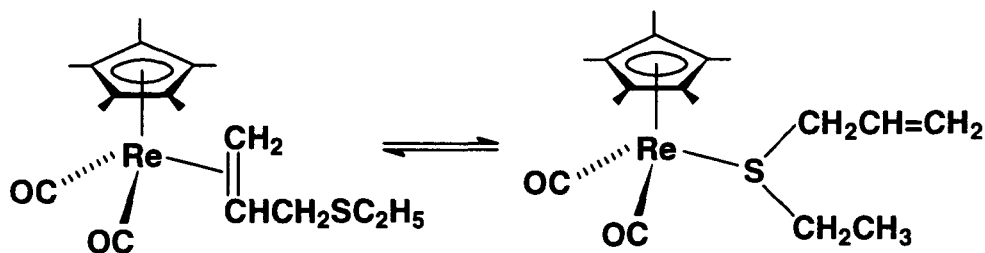


Scheme 3.3. Proposed coordination transformation in $Cp^*Re(\eta^2\text{-}C_3H_5SC_2H_5)(CO)_2$.

from $M^+$.

The $^1H$ NMR spectrum of **3.5** was recorded in $C_6D_6$. The $-SCH_2CH_3$ showed a triplet at $\delta$ 1.20 for $CH_3$, and a multiplet at $\delta$ 2.52 for the $CH_2$. Two diastereotopic protons for $-CH_2-$ gave a doublet of doublets at $\delta$ 3.71 and 2.52. These assignments were confirmed by the $^1H$ NMR decoupling and $^1H\text{-}^1H$ correlation experiments (Table 3.2).

The $^{13}C\{^1H\}$ NMR spectrum of **3.5** presented two signals at 42.33 and 41.09 ppm assigned to the two carbons from the $-CH_2-$ connected to the sulfur atom. The carbon atoms of the $Cp^*$ ring appeared at $\delta$ 97.29, consistent with all members of this series compounds, and the methyl carbon from the $Cp^*$ gave resonance at $\delta$ 9.80, and the signal at $\delta$ 26.41 was assigned to the carbon from the methyl of $SCH_2CH_3$. There were two weak signals at 226.00 and 207.00 ppm assigned to the CO carbons.

### 3.2.5. Reaction of $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)_2][BF_4]$ (2.1) with $NaSC_6H_5$

Complex **2.1** was treated with $Me_3NO$ in the presence of $NaSC_6H_5$ in $CH_2Cl_2$ in an attempt to coordinate $C_6H_5S$ to rhenium. But, the dominate product was complex

Cp*Re($\eta^2$-C$_3$H$_5$SC$_6$H$_5$)(CO)$_2$ (**3.6**), not complex Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(SC$_6$H$_5$). Although trace amount of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(OCOSC$_6$H$_5$) (**3.15**) was produced because of the presence of Me$_3$NO (see section 3.3.6). The nucleophilic addition of C$_6$H$_5$S$^-$ to the $\eta^3$-allyl in **2.1** dominated the reaction. The same product was obtained when **2.1** was reacted with pure NaSC$_6$H$_5$ in CH$_2$Cl$_2$. The IR spectrum of **3.6** in hexane showed two $\nu$(CO) bands at 1964 and 1892 cm$^{-1}$, which is similar to the $\nu$(CO) bands in compounds **3.3**, **3.4** and **3.5** (Tables 3.2 and 3.3).

The EIMS of **3.6** presented a weak parent peak at m/z 528 (5%), and again the fragment [M$^+$ - C$_3$H$_5$] at m/z 487 is the base peak. The fragment [M$^+$ - CO] was observed at m/z 500 (19%). This is consistent with the result obtained for **3.5**, which is consistent with the mechanism proposed in Scheme 3.3.

The $^1$H NMR spectrum of **3.6** showed resonances for the protons in SC$_6$H$_5$ at $\delta$ 7.48 (doublet), $\delta$ 7.08 (triplet), and $\delta$ 6.90 (multiplet), indicating the successful addition of SC$_6$H$_5$ to the allyl ligand. The two diastereotopic protons from –CH$_2$– produced two doublets of doublets at $\delta$ 4.10 and $\delta$ 2.89, the Cp* resonance is at $\delta$ 1.54, and the other protons from the substituted propene gave relatively the same coupling pattern and chemical shifts compared with complexes mentioned above: H$_3$ and H$_1$ overlapped at $\delta$ 2.18-2.20, while the H$_2$ for one of the =CH$_2$ protons is at $\delta$ 1.26, which is the most high field proton for **3.6**.

The $^{13}$C{$^1$H} NMR spectrum of **3.6** showed two carbon signals for the coordinated CO at $\delta$ 244.11 and 238.00. The carbon signals for SC$_6$H$_5$ appeared at $\delta$ 130.84-125.99 overlapped with C$_6$D$_6$ carbon signals, and three resonances at $\delta$ 44.93, 39.49 and 26.80 were assigned to the substituted propene carbon atoms. The carbon resonances for the ring and the methyl carbons of the Cp* were at $\delta$ 97.39 and $\delta$ 9.73 respectively.

Although the $^1$H NMR spectrum of **3.6** did not show the presence of any other product, such as complex Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(COSC$_6$H$_5$), (which would be produced from C$_6$H$_5$S$^-$ attacking the CO instead of the allyl), the $^1$H NMR sample used subsequently for the crystallization did produce several crystals, which the structure determination

indicated to be $Cp*Re(\eta^3-C_3H_5)(CO)(OCOSC_6H_5)$ (**3.15**), presumably obtained from the reaction of $[Cp*Re(\eta^3-C_3H_5)(CO)_2][BF_4]$ (**2.1**) with $Me_3NO$ in the presence of $C_6H_5SNa$. See section 3.3.6 for the discussion of the X-ray structure of $Cp*Re(\eta^3-C_3H_5)(CO)(OCOSC_6H_5)$ (**3.15**), and the proposed method of formation.

### 3.2.6. Reaction of $[Cp*Re(\eta^3-C_3H_5)(CO)_2][BF_4]$ (2.1) with $NaS(CH_2)_3SNa$

The reaction of **2.1** with a disulfur nucleophile $NaS(CH_2)_3SNa$ in $CH_2Cl_2$ at room temperature gave complex $Cp*Re(CO)_2(\eta^2-C_3H_5)S(CH_2)_3S(\eta^2-C_3H_5)(CO)_2ReCp*$ (**3.7**) (Scheme 3.1). Complex **3.7** was obtained because the two sulfur atoms attacked the different allyl groups in two molecules of rhenium complex **2.1**. The IR spectrum of **3.7** in hexane gave only two $\nu(CO)$ absorptions at 1962 and 1892 $cm^{-1}$, which indicated a symmetric structure for **3.7**. Unfortunately, there is no parent peak for **3.7** in the EIMS spectrum, but the fragment of $[Cp*Re(CO)_2(C_3H_5SCH_2CH_2CH_2S)]$ at m/z 525 was observed, which was produced from $[M^+ - Cp*Re(CO)_2(C_3H_5)]$. Loss of the $C_3H_5$ unit from $[Cp*Re(CO)_2(C_3H_5SCH_2CH_2CH_2S)]$ produced a fragment at m/z 456, which is consistent with the results obtained for **3.5** and **3.6**.

The $^1H$ NMR spectrum of **3.7** (Figure 3.2) showed resonances at $\delta$ 3.73 and $\delta$ 2.51 for the two diastereotopic protons from the substituted propene, and a multiplet at $\delta$ 2.76 for the four protons from two $-CH_2-$ groups in $-SCH_2CH_2CH_2S-$; the equivalence of these four protons again suggested a symmetric structure for **3.7**. Especially, a typical quintet of the central $-CH_2-$, with a coupling constant of 7.1 Hz at $\delta$ 1.97 (integrating for two protons), unambiguously supported the structure of a symmetrical dinuclear complex for **3.7**.

The $^{13}C\{^1H\}$ spectrum of **3.7** in $C_6D_6$ showed resonances for Cp* ring and methyl carbons at $\delta$ 97.35 and 9.84 respectively. The other five signals for the propene and thioether group carbons are: $\delta$ 42.81 for the $-CH_2S-$, $\delta$ 41.24 for the $=CH-$, $\delta$ 31.64 for the $-SCH_2CH_2CH_2S-$, $\delta$ 30.42 for the central carbon $-SCH_2CH_2CH_2S-$, and the one at $\delta$ 27.18 for $=CH_2$. The assignments of the $^1H$ and $^{13}C$ spectra of **3.7** were confirmed by the
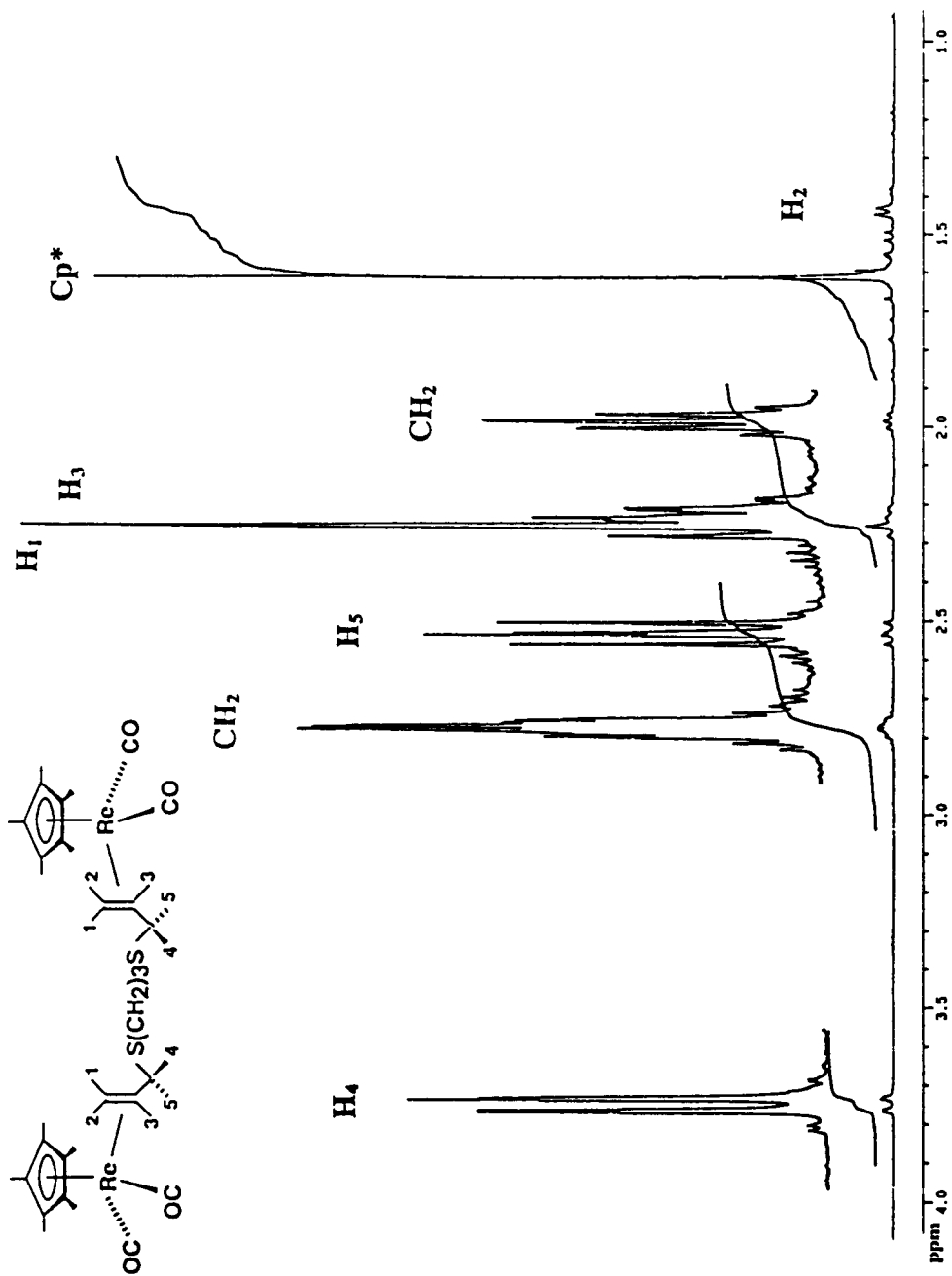
Figure 3.2. $^1$H NMR spectrum of complex Cp*Re(CO)$_2$($\eta^2$-C$_3$H$_5$)S(CH$_2$)$_3$S(CH$_2$)$_3$S($\eta^2$-C$_3$H$_5$)(CO)$_2$ReCp* (3.7) in C$_6$D$_6$ (resonances of the H$_1$ and H$_3$ are overlapped).

60
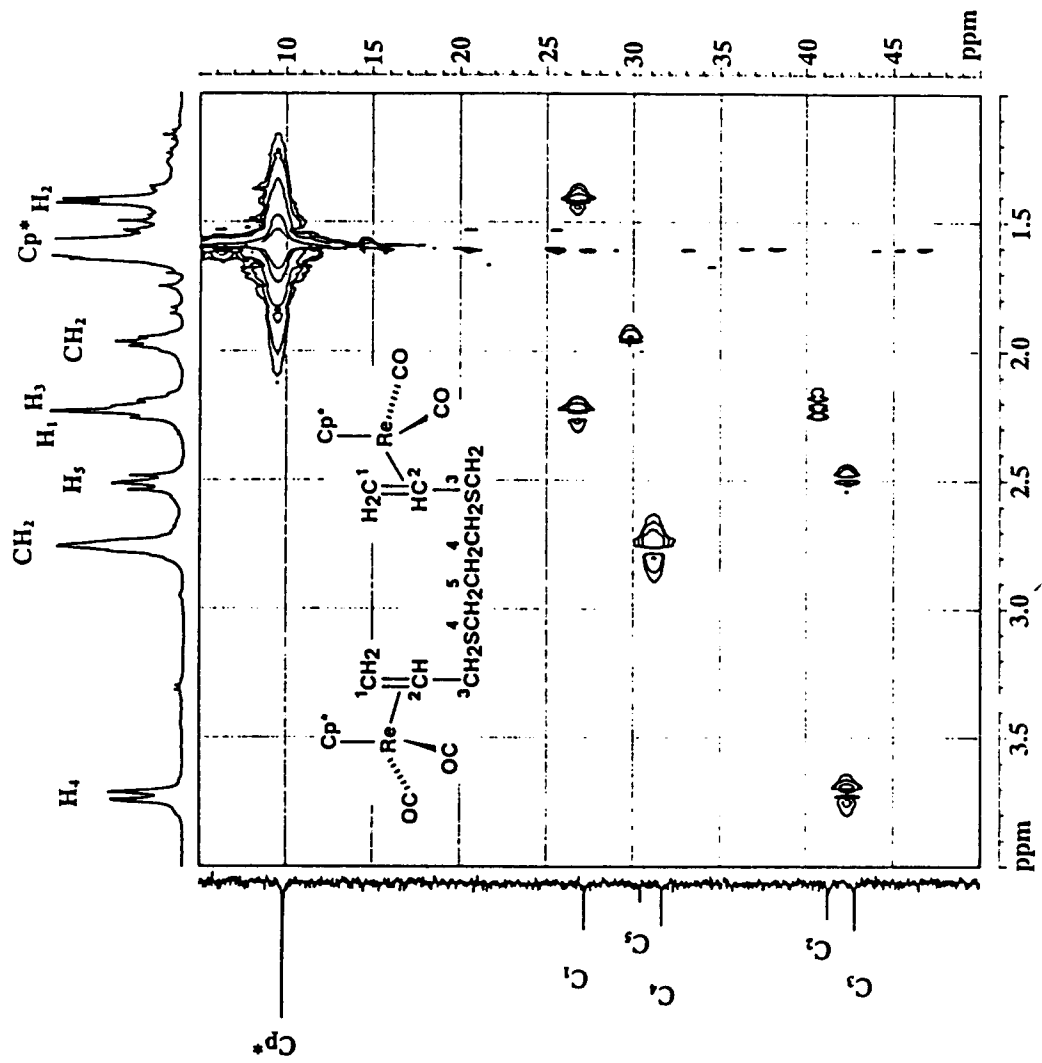
Figure 3.3. $^1$H-$^{13}$C correlation spectrum of Cp*Re(CO)$_2$($\eta^2$-C$_3$H$_5$)S(CH$_2$)$_3$S($\eta^2$-C$_3$H$_5$)(CO)$_2$ReCp* (3.7) in C$_6$D$_6$.

61

### 3.2.7. Reaction of [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] (2.1) with PMe$_3$

PMe$_3$ is well known as a strong $\sigma$-donor to coordinate to most of the transition metals to produce trimethylphosphine complexes. It is less known as a nucleophile to attack the ligand in a cationic complex. The initial goal in reacting **2.1** with PMe$_3$ was to try to coordinate the phosphine ligand to rhenium in the $\eta^3$-allyl complex. Related rhenium aryldiazenido phosphine complexes [Cp*Re(N$_2$C$_6$H$_4$OCH$_3$)(PR$_3$)(CO)][BF$_4$] had already been synthesized, but by using different methodology.[106] However, when complex **2.1** reacted with PMe$_3$ at room temperature in CH$_2$Cl$_2$ or acetone, PMe$_3$ acted as a nucleophile and attacked the $\eta^3$-allyl to give the allyltrimethylphosphonium complex [Cp*Re($\eta^2$-CH$_2$=CHCH$_2$PMe$_3$)(CO)$_2$][BF$_4$] **(3.8)**. The IR spectrum of **3.8** exhibited $\nu$(CO) absorptions at 1964 and 1885 cm$^{-1}$ in CH$_2$Cl$_2$. These values are at much lower frequencies in comparison with complex **2.1**, for which $\nu$(CO) absorption is at 2053 and 1999 cm$^{-1}$. This is due to the relocation of the positive charge in **3.8**, which is now formally located on the phosphorus instead of the metal.

The $^1$H NMR spectrum of **3.8** showed a strong doublet at $\delta$ 1.88 for the methyl protons of PMe$_3$ with $J_{PH}$ = 13.9 Hz. This coupling constant is larger than typically observed for coordinated PMe$_3$ (*ca.* 9 Hz) and is close to reported values (*ca* 14.5 Hz) for the Me$_3$PCH$_2$– group in related ruthenium complexes.[82a-c] The remaining resonances were assigned by a combination of phosphorus decoupling, $^1$H NOE, $^1$H-$^1$H correlation and $^1$H-$^{13}$C correlation results. The $^{31}$P{$^1$H} NMR spectrum gave a singlet at $\delta$ 29.73 ppm, in the range for -CH$_2$PMe$_3$ [82a-c,106] and downfield from the region typical of coordinated PMe$_3$.[107] The $^{13}$C{$^1$H} NMR spectrum showed resonances at $\delta$ 208.87 and $\delta$ 207.08 for the two inequivalent CO groups, and a doublet at $\delta$ 34.98 with $J_{PC}$ = 42.3 Hz assigned to the $C$H$_2$PMe$_3$ carbon unambiguously shows that PMe$_3$ has attacked the allyl terminal carbon resulting in this allyltrimethylphosphonium complex **3.8**. There have been reported cases of PPh$_3$ undergoing nucleophilic attack at an $\eta^3$-allyl to give triphenylphosphonium

complexes,[108,109] so the present result is not surprising, though we are not aware of previous examples involving PMe₃.

Complex **3.8** did not react with PhIO or Me₃NO in CH₃CN solution in attempts to substitute CO by MeCN as occurs for **2.1**.[110] This also can be explained as a result of the positive charge being displaced from the metal center to the -CH₂PMe₃ function group, so that there is more back bonding to the CO and reduced propensity to react with the nucleophile.

### 3.2.8. Reaction of [Cp*Re($\eta^3$-C₃H₄CH₃)(CO)₂][BF₄] (2.4) with PMe₃

By using the same method as used for the reaction of **2.1** with PMe₃, complex **2.4** reacted with PMe₃ in CH₂Cl₂ to form two products, **3.9a** and **3.9b**, which were produced by the PMe₃ attacking different carbon termini of the methallyl (Scheme 3.4).

The IR spectrum of the mixture of **3.9a** (67%) and **3.9b** (33%) in CH₂Cl₂ showed only two $\nu$(CO) absorptions at 1964 and 1881 cm⁻¹ indicating that the absorptions of **3.9a** and **3.9b** were unresolved. The FABMS of this mixture showed a parent ion at m/z 509, and the base peak at m/z 433, which is produced from [M⁺ - PMe₃].

The ¹H NMR spectrum indicated that **3.9a** is the major isomer, and **3.9b** is the minor one. The typical diastereotopic –C*H*₂PMe₃ proton resonances occurred at δ 3.04 and δ 2.15, with the same coupling pattern as in complex **3.8**, supporting the structure of **3.9a**. The resonances for the minor isomer **3.9b** in the ¹H NMR spectrum overlapped with the major isomer, but two Cp* signals for the two different isomers are apparent, which gave a singlet at δ 1.99 for **3.9a**, and δ 2.02 for **3.9b**. PMe₃ gave a doublet at δ 1.80 with a separation of 12.0 Hz, which is similar to the case of complex **3.8**. The ³¹P{¹H} NMR spectrum showed two signals: δ 34.30 for **3.9a**, and δ 29.27 for **3.9b**. The ¹H NMR resonances of **3.9a** and **3.9b** did not separate very well in CDCl₃ or CD₂Cl₂. Thus, further distinction between the *cis* and the *trans* isomers of CH(Me)=CHCH₂PMe₃ in **3.9a** was unsuccessful.

The nucleophilic addition on the substituted allyl has been reported for $[CpRe(CO)_2(\eta^3\text{-}C_3H_4CH_3)][BF_4]$ by Casey's group.[84f] In their case, when $LiCu(CH_3)_2$ was used as the nucleophile, addition occurred at the less substituted allyl carbon to give both the *cis* and the *trans* isomers, with a ratio of *cis/trans* = 65/35. The same regioselectivity of malonate to the less substituted allyl carbon of the methallyl was obtained, although addition to the substituted carbon also occurred. This is consistent with the result obtained for **2.4** when $PMe_3$ was used as a nucleophile.
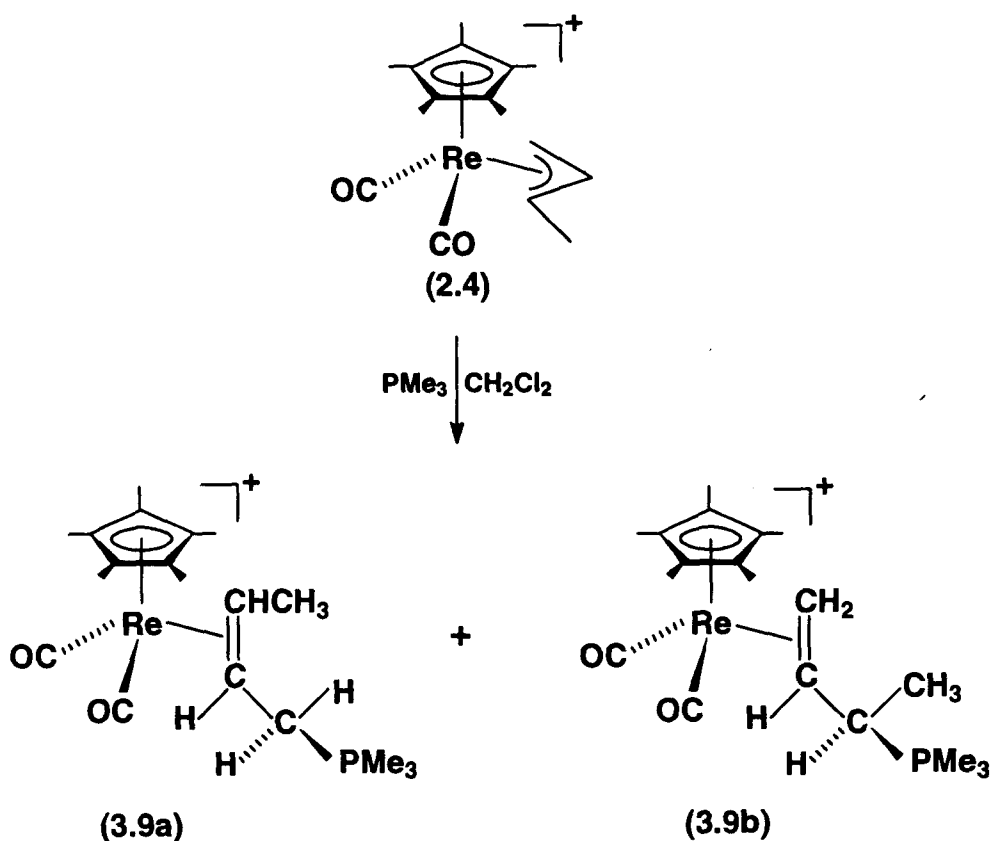


Scheme 3.4. Reaction of $[Cp^*Re(\eta^3\text{-}C_3H_4CH_3)(CO)_2][BF_4]$ (**2.4**) with $PMe_3$.

### 3.2.9. Reaction of $[Cp^*Re(\eta^3\text{-}C_3H_5)(CO)_2][BF_4]$ (2.1) with $NaN_3$

$N_3^-$ is a common nucleophile in addition reactions of cationic transition metal complexes.[111a] Reaction of **2.1** with $NaN_3$ at room temperature in $CH_2Cl_2$ resulted in

complex $Cp*Re(\eta^2-C_3H_5N_3)(CO)_2$ (**3.10**) (Scheme 3.5). The IR spectrum of **3.10** showed the $v(CO)$ absorptions at 1969, 1898 cm$^{-1}$, and a $v(NN)$ absorption at 2101 cm$^{-1}$ in hexane (Figure 3.4). This is an indication of the successful addition of $N_3^-$ to the allyl in **2.1**.[11b] Both the EIMS and CIMS of **3.10** did not give the parent peak for **3.10**. Instead, a fragment at m/z 433, corresponding to $[M^+ - N_2]$, is the highest mass fragment in the mass spectrum of **3.10**. The base peak of **3.10** occurred at m/z 346, which was produced by loss of CO, $C_3H_5N_3$ and 4H from the parent ion $[M^+ - CO - C_3H_5N_3 - 4H]$.

The $^1H$ NMR spectrum of **3.10** showed a doublet of doublets for the substituted propene at $\delta$ 3.75 and $\delta$ 2.70 for the $-CH_2-$ diastereotopic protons, and a doublet of doublets at $\delta$ 2.04 for $H_1$, and a multiplet at $\delta$ 1.87 for $H_3$. This is the first example in which the resonances of $H_1$ and $H_3$ did not overlap in the substituted propene complexes obtained in this work.

The $^{13}C\{^1H\}$ NMR spectrum of **3.10** gave resonances for the two CO carbon signals at $\delta$ 206.47 and $\delta$ 205.68, and three resonances at $\delta$ 60.99, 36.62 and 25.48 for the $-CH_2-$, $-CH=$ and $=CH_2$ carbons respectively. The ring and methyl carbon signals of the Cp* occurred at $\delta$ 97.60 and 9.66 respectively.

Complex **3.10** was treated with LiBEt$_3$H in ether at -78 °C in an attempt to reduce the $\eta^2-C_3H_5N_3$ ligand to $\eta^2-C_3H_5NH_2$ to get $Cp*Re(\eta^2-C_3H_5NH_2)(CO)_2$ (**3.11**). However, the disappearance of the $v(CO)$ absorption in the IR spectrum, and loss of the Cp* signal in the $^1H$ NMR spectrum indicated that **3.10** decomposed in the presence of LiBEt$_3$H.

### 3.2.10. Reaction of $[Cp*Re(\eta^3-C_3H_5)(CO)_2][BF_4]$ (2.1) with NaNH$_2$

Complex **2.1** reacted with NaNH$_2$ at room temperature to give two products: $Cp*Re(\eta^3-C_3H_5)(CO)(CONH_2)$ (**3.11a**) and $Cp*Re(\eta^2-C_3H_5NH_2)(CO)_2$ (**3.11**) (Scheme 3.5). The IR spectrum of the reaction solution showed four $v(CO)$ absorptions at 1950, 1927, 1873 and 1715 cm$^{-1}$. When the crude product was extracted with hexane, the hexane solution gave three $v(CO)$ absorptions at 1964 and 1892 cm$^{-1}$ for **3.11**, and 1941 cm$^{-1}$ for the terminal CO of **3.11a**. But, after the product was worked up at room
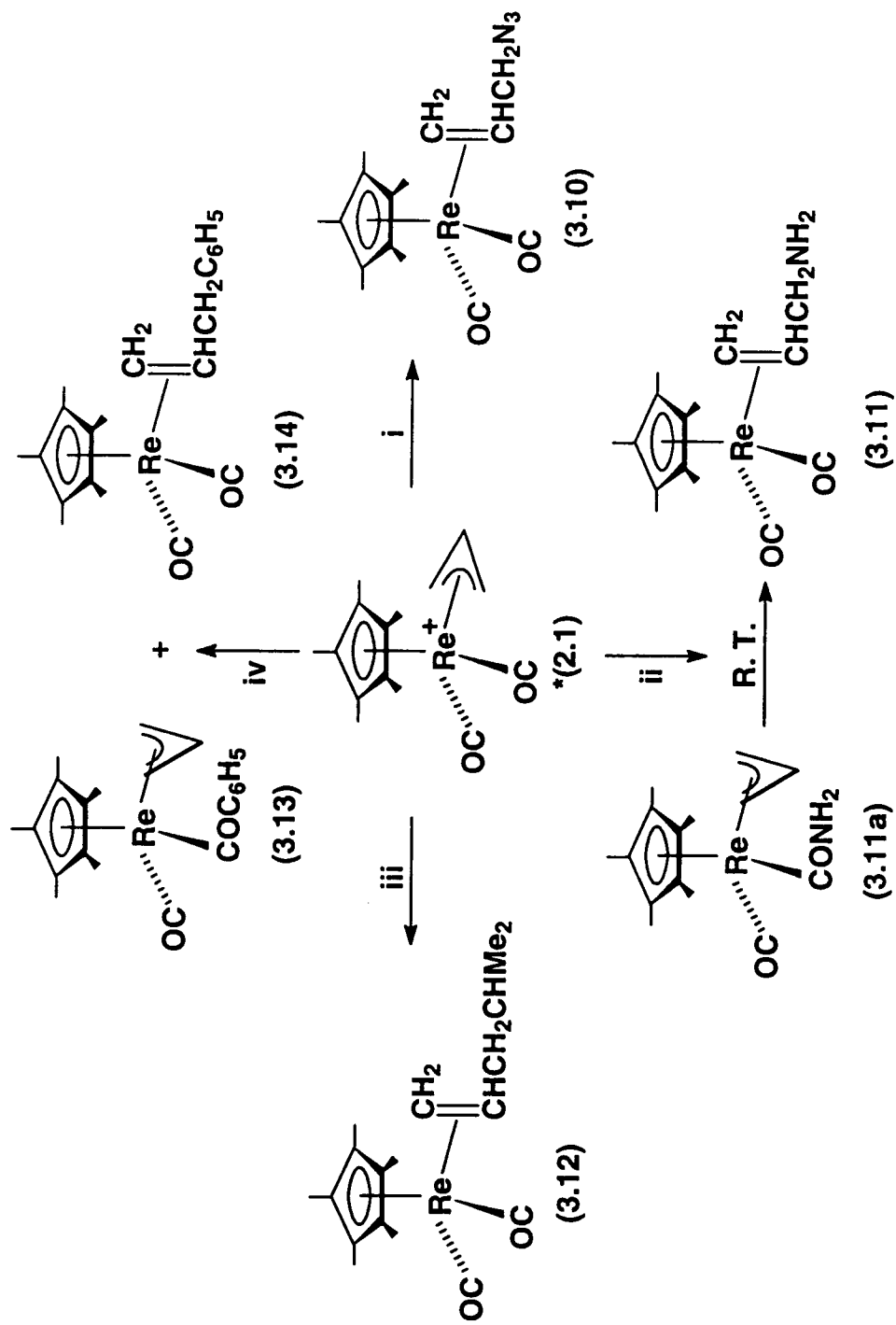
Scheme 3.5. Reactions of **2.1** (* Mixture of *endo* and *exo*) with nitrogen and carbon nucleophiles. i. NaN$_3$/CH$_2$Cl$_2$; ii. NaNH$_2$/CH$_2$Cl$_2$; iii. Me$_2$CHMgCl/CH$_2$Cl$_2$; iv. C$_6$H$_5$Li/CH$_2$Cl$_2$.
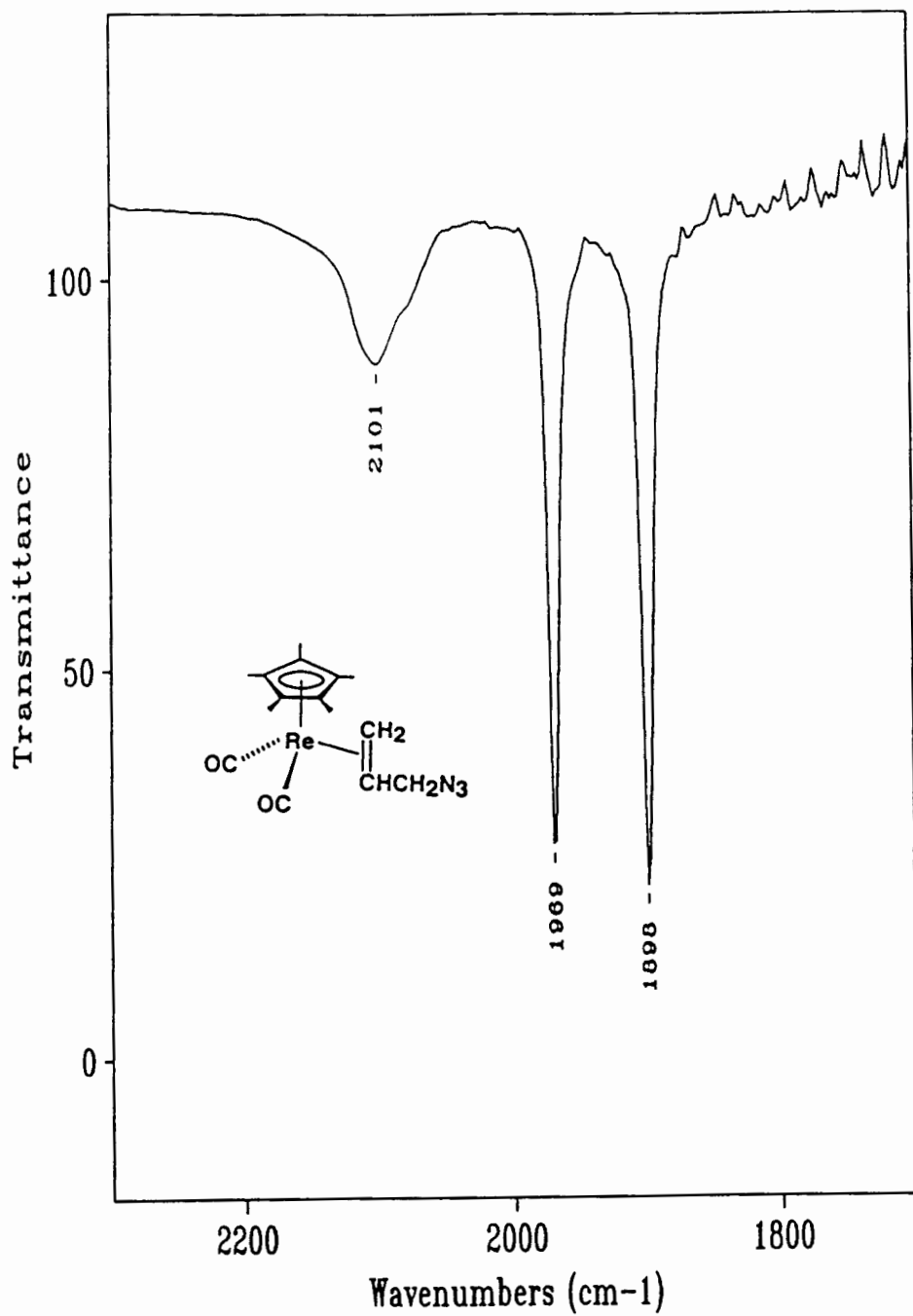
Figure 3.4. IR spectrum of $Cp^*Re(\eta^2\text{-}CH_2=CHCH_2N_3)(CO)_2$ (**3.10**) in hexane ($cm^{-1}$).

temperature for the $^1$H NMR, only **3.11** was observed in both the IR and the $^1$H NMR spectra. The **3.11a** converted to **3.11**.

The parent ion peak of **3.11** was not observed in the EIMS spectrum. Instead, the fragment at m/z 419, corresponding to loss of $NH_2$ from the $M^+$, is the base peak. The other fragment consistent with loss of $C_3H_5NH_2$ from the $M^+$ at m/z 378 is also very strong. The CIMS gave $M^+$ at m/z 435, and the base peak in this case is m/z 391, which is in agreement with loss of $NH_2$ and CO from the parent ion.

The $^1$H NMR spectrum of **3.11** showed two $NH_2$ proton triplets at $\delta$ 3.45 and $\delta$ 3.27 respectively. The five protons from the substituted propene were assigned as: doublet of doublets at $\delta$ 4.64, $\delta$ 4.53 for $H_4$ and $H_5$, multiplet at $\delta$ 2.29 for $H_3$, multiplet at $\delta$ 2.40 for $H_1$, and doublet at $\delta$ 1.49 for $H_2$. These assignments were confirmed by $^1$H-$^1$H correlation experiments. The presence of two separate NH resonances indicates that the $NH_2$ protons are inequivalent. This could be a result of no inversion at the nitrogen.

The $^{13}$C{$^1$H} NMR spectrum of **3.11** showed two carbon signals for Re-CO at $\delta$ 206.77 and 203.85. The carbon signals for the Cp* ring and methyl group are at $\delta$ 97.30 and 9.82, and the resonances for the coordinated substituted propene carbons were assigned as: $\delta$ 78.91 for $-CH_2NH_2$, $\delta$ 40.59 for $=CH-$, and $\delta$ 27.76 for $=CH_2$. Both the $^1$H and $^{13}$C NMR resonances of **3.11** indicated that the coordination of $CH_2=CHCH_2NH_2$ to the rhenium center is through the C=C bond instead of the nitrogen atom.

### 3.2.11. Reaction of [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] (2.1) with (CH$_3$)$_2$CHMgCl

Nucleophilic addition to the $\eta^3$-allyl in cationic complexes by carbon nucleophiles is an important method to form C-C bonds. When complex **2.1** was treated with Me$_2$CHMgCl in CH$_2$Cl$_2$ at -78 °C for 2 h, complex Cp*Re($\eta^2$-C$_3$H$_5$CHMe$_2$)(CO)$_2$ (**3.12**) was produced (Scheme 3.5). The IR spectrum of **3.12** showed two v(CO) bands at 1960 and 1888 cm$^{-1}$. The EIMS of **3.12** showed a strong parent peak at m/z 462. A fragment [$M^+$ - C$_3$H$_5$CHMe$_2$] at m/z 378 is the second highest peak in the mass spectrum. The base peak at m/z 348 is consistent with fragment [$M^+$ - C$_3$H$_5$CHMe$_2$ - CO - 2H].

The $^1$H NMR spectrum of **3.12** showed complicated coupling patterns for the two diastereotopic protons for $-CH_2-$. The resonance at $\delta$ 2.50 is assigned to $H_4$ and interestingly the eight lines generated from the doublet of doublets of doublets for this proton, with the coupling constants of $J_{45}$ = 13.6 Hz, $J_{34}$ = 6.13 and $J_{4\text{-}CH}$ = 3.37, did not overlap. The other proton $H_5$ also gave the same coupling pattern with eight lines, but appeared at higher field ($\delta$ 1.27). The two isopropyl methyls are diastereotopic and gave two doublets at $\delta$ 1.08 and $\delta$ 1.04 respectively. The proton from C*H*Me$_2$ showed a multiplet at $\delta$ 1.77. Introduction of the CHMe$_2$ group to the $\eta^3$-allyl caused all the proton chemical shifts to move to the higher field. This indicated the strong electron donating ability of the CHMe$_2$ group. As a result, the Cp* signal of **3.12** appeared at $\delta$ 1.43, which is the highest field of all resonances for this series of complexes in section 3.2. These assignments were confirmed by $^1$H-$^1$H NMR correlation experiments.

The $^{13}$C{$^1$H} NMR spectrum of **3.12** showed carbon signals at $\delta$ 207.47 and 207.09 for the two Re-*C*O. The Cp* gave two resonances at $\delta$ 96.87 for the ring carbons, and $\delta$ 9.89 for the methyl groups. The two methyl carbons from CH(*C*H$_3$)$_2$ showed very close resonances at $\delta$ 22.67 and 22.52, the CH carbon resonance appeared at $\delta$ 28.27, and the resonances at $\delta$ 49.04, 42.68 and 33.43 were assigned for the $-CH_2-$, $=CH-$ and $=CH_2$. The $^{13}$C NMR was not as sensitive as the $^1$H NMR to the electron density changing in the complex, as there was no obvious chemical shift difference of these signals compared with the other complexes mentioned above.

### 3.2.12. Reaction of [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] (2.1) with C$_6$H$_5$Li

Complex **2.1** reacted with C$_6$H$_5$Li in CH$_2$Cl$_2$ at -78 °C for 4 h, and both the CO and the allyl were attacked by C$_6$H$_5^-$ to produce complexes Cp*Re($\eta^3$-C$_3$H$_5$)(CO) (COC$_6$H$_5$) (**3.13**) and Cp*Re($\eta^2$-CH$_2$=CHCH$_2$C$_6$H$_5$)(CO)$_2$ (**3.14**). The ratio of **3.13/3.14** is 1/1.33 according to the integration of the $^1$H NMR resonances. The IR spectrum of the mixture of **3.13** and **3.14** in hexane showed three $\nu$(CO) bands in the region of 1600-2200 cm$^{-1}$, which were assigned as: 1962 and 1890 cm$^{-1}$ for **3.14**, and 1919 cm$^{-1}$ for **3.13**.

A mixture of **3.13** and **3.14** in $C_6D_6$ was refluxed 12 h in order to observe the conversion of **3.13** to **3.14**. The IR of this solution after being refluxed in $C_6D_6$ was measured at room temperature, and neither the position nor the intensity of the $\nu(CO)$ bands changed. This suggested that if there was a conversion of **3.13** to **3.14** at the temperature that the mixture was refluxed, it changed back to the ratio as it had at room temperature, or no conversion of **3.13** to **3.14** occurred. We tried to separate **3.13** and **3.14** by chromatography on a neutral alumina column, but it was unsuccessful. Elution with ether gave a mixture of **3.13** and **3.14**. Elution with hexane, however, gave only **3.14**.

The EIMS was obtained from the mixture of **3.13** and **3.14**. The parent peak at m/z 496 is very strong in intensity (65%) in comparison with the base peak. The base peak at m/z 440 is consistent with loss two CO from the $M^+$. The fragment at m/z 378 is in agreement with the loss of $C_3H_5C_6H_5$ from the parent ion, and the other fragment at m/z 348 was generated from $[M^+ - C_3H_5C_6H_5 - CO - 2H]$. The fragmentations in the EIMS were mainly produced from **3.14**. Only the fragment at m/z 391 consistent with $[M^+ - COC_6H_5]$ is expected for **3.13**, and it is very weak.

The $^1H$ NMR spectrum of the mixture of **3.13** and **3.14** (Figure 3.5) showed all the resonances for both products. For $\eta^3$-allyl in **3.13** which has inequivalent protons, the proton resonances were assigned as: a multiplet at $\delta$ 4.26 for $H_c$; the doublet of doublets at $\delta$ 2.83 and $\delta$ 2.74 for the two $H_s$; and the two doublets at $\delta$ 0.83 and 0.66 for the two $H_a$. The Cp* signal gave a singlet at $\delta$ 1.66, while the proton signals for the phenyl group in Re–$C(O)C_6H_5$ were overlapped with the signals from the phenyl protons in $C_3H_5C_6H_5$. The substituted propene resonances for **3.14** showed two diastereotopic proton signals at $\delta$ 3.85 and 2.57, which are doublets of doublets. $H_3$ gave a multiplet at $\delta$ 2.12, and $H_1$ and $H_2$ showed two doublets at $\delta$ 2.29 and $\delta$ 1.34. These assignments were confirmed by the $^1H$-$^{13}C$ correlation experiment.

The $^{13}C\{^1H\}$ spectrum showed resonances for the carbon signal of **3.14** at: $\delta$ 46.5 for $-CH_2-$, $\delta$ 43.2 for $=CH-$, and $\delta$ 26.7 for $=CH_2$. The carbon signals for **3.13** were assigned as: $\delta$ 81.1 for the central carbon, $\delta$ 48.9 and $\delta$ 31.6 for the two terminal carbons
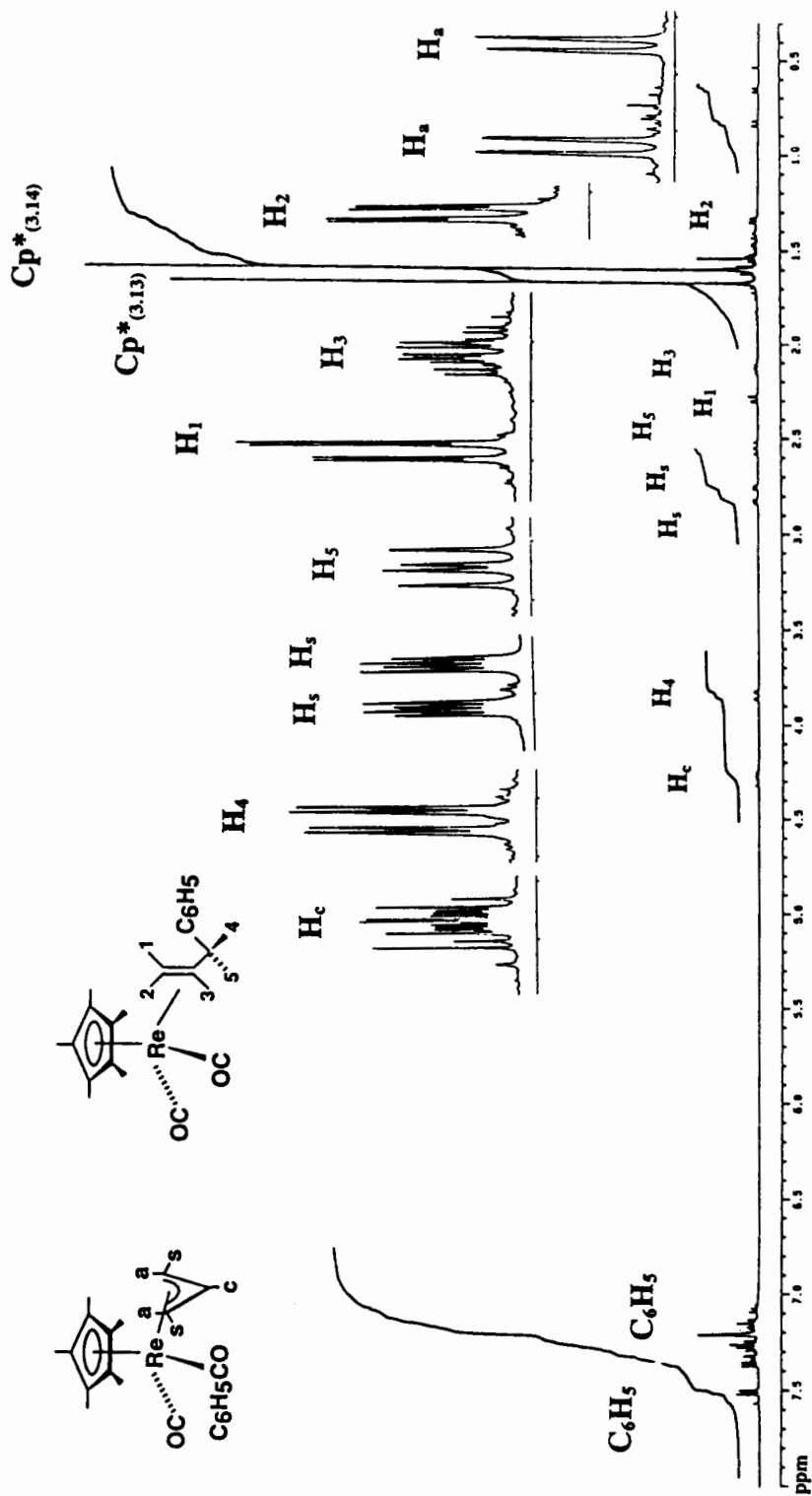
Figure 3.5. $^1$H NMR spectrum of a mixture of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(COC$_6$H$_5$) (3.13) and Cp*Re($\eta^2$-CH$_2$=CHCH$_2$C$_6$H$_5$)(CO)$_2$ (3.14) in C$_6$D$_6$.

of the $\eta^3$-allyl.[112a] The methyl carbon signals of the Cp* group for both complexes are at $\delta$ 9.80. Although complex Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(COOCH$_3$) (**3.2**) and complex Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(CONH$_2$) (**3.11a**) were obtained when the nucleophilic addition occurred at the CO ligand in **2.1**, each converted to the dicarbonyl isomer. Here, complex Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(COC$_6$H$_5$) (**3.13**) is the first one of this type to be found to be stable at room temperature, and it did not convert to Cp*Re($\eta^2$-C$_3$H$_5$C$_6$H$_5$)(CO)$_2$ (**3.14**) after refluxing in C$_6$D$_6$ for 12 h.

## 3.3. Discussion

### 3.3.1. The IR Spectra of Complexes 3.2-3.14

The $\nu$(CO) absorptions of complexes **3.2-3.14** in the IR spectra are listed in Table 3.3. For the substituted propene compounds, although the substituents are different, the IR absorptions for the coordinated CO ligands are almost at the same frequency (1960-1890 cm$^{-1}$). This indicated that the electron density of the metal center was not affected when the substituents on the propene changed.

For complexes **3.11a** and **3.13**, the CO absorption of the Re-C(O)R (R = NH$_2$, C$_6$H$_5$) were not detected in the IR spectrum.

### 3.3.2. The Mass Spectra of Complexes 3.2-3.14

The MS spectra of **3.2-3.14** showed parent ion peaks for most of these complexes, except for those of **3.7** and **3.10**. This reflects the stability of these complexes in the mass experiments. The fragments of [M$^+$ - C$_3$H$_5$R] for all these complexes are also very strong, which may suggest a possibility of release the ligand C$_3$H$_5$R (R = nucleophiles) from these series of complexes. For **3.7**, the C-S bond is weaker compared with the C-C bond, and it is easily broken. This fact was also noticed in complexes **3.5** and **3.6**.

### 3.3.3. The $^1$H NMR Spectra of Complexes 3.2-3.14

The $^1$H NMR spectra of the substituted propene in complexes **3.2-3.14** can be summarized as follows: **i.** the resonances of the two diastereotopic protons from $-CH_2-$ occurred at lower field compared with the other protons, regardless if the complex is neutral or cationic. The one at higher field shows a resolved doublet of doublets, but the resonance at the lower field gives an overlapped doublet of doublets, in some cases, it becomes a triplet. **ii.** The central proton $H_3$ of the substituted propene, which frequently overlapped with one of the terminal protons, named $H_1$ (trans to $H_3$) in this work, forms a multiplet because of the coupling with five inequavelent protons. **iii.** One $=CH_2$ proton, $H_2$, always gives a doublet at the highest field in the substituted propene rhenium complexes reported in this Chapter.

The Cp* resonances were a singlet at $\delta$ 1.45-1.65 for all these compounds. This result, again, indicates that the electron density of the metal center was not significantly affected when the substituents on the coordinated propene were changed. Otherwise, we expect the chemical shift of the Cp* ligand to vary as the substituents of the propene are changed.

### 3.3.4. The $^{13}$C{$^1$H} NMR Spectra of Complexes 3.3-3.14

There are not many references in the literature to the $^{13}$C{$^1$H} NMR data for substituted propene complexes, although many of these compounds have been synthesized and characterized.[1d,112] The $^{13}$C NMR resonances of complexes **3.3-3.14** vary with the substituted group. But the carbon signals of the $-CH_2-$ group always occurs at the lower field, and the $=CH-$ and the $=CH_2$ give resonances at relatively higher field. The carbon resonances of the Cp* ring and methyl group appeared around $\delta$ 97.00 and $\delta$ 9.50 respectively. These resonances were not affected when the substituents of the propene changed. The assignments made in this work were confirmed by the $^1$H-$^{13}$C correlation experiment, and also by comparison with the literature data.[98]

The carbon resonances of the Re–CO were usually the expected two singlets in the $^{13}C\{^1H\}$ NMR spectrum and were separated by 0.4-19 ppm. In some cases (in complexes **3.4**, **3.7** and **3.9**) only one carbon signal was observed, even though two are required by symmetry. It is possible that the two resonances were too close to be resolved.

### 3.3.5. Stereochemical Consideration of the Substituted Propene Complexes Cp*Re($\eta^2$-C$_3$H$_5$Nu)(CO)$_2$ (Nu = Nucleophile)

The stereochemical selectivity of nucleophilic additions to the $\eta^3$-allyl ligand has been extensively studied.[113] For complex [CpMo($\eta^3$-C$_3$H$_5$)(NO)(CO)][BF$_4$], nucleophilic addition occurred *trans* to the NO ligand in an *endo* isomer, but *cis* to the NO in an *exo* isomer (Scheme 3.6), and finally lead to the same product.
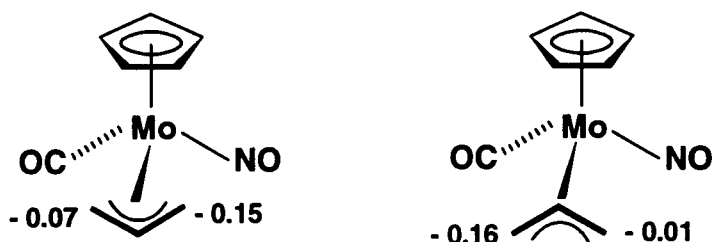


Figure 3.6. Calculated charge for the carbon termini in $\eta^3$-C$_3$H$_5$.

The molecular orbital analysis of this complex was reported by the same group. The calculated results indicated: for an *exo* isomer, the carbon terminus *cis* to the NO ligand is most positive; but in an *endo* isomer, this is reversed (Figure 3.6).[113]

In our case, the nucleophilic additions at the two $\eta^3$-allyl carbon termini in any one isomer of **2.1** are evenly preferred (Scheme 3.7). Although four ways for attack of Nu⁻ can be visualized as in Scheme 3.7, assuming the rotamers **a** and **b** can interconvert, and similarly **c** and **d**, the result is simply the formation of enantiomers. They are not

74

distinguishable in the $^1$H NMR spectrum. This is why only one isomer of each substituted propene complex (**3.3-3.14**) was observed in the $^1$H NMR spectra. But in cases of
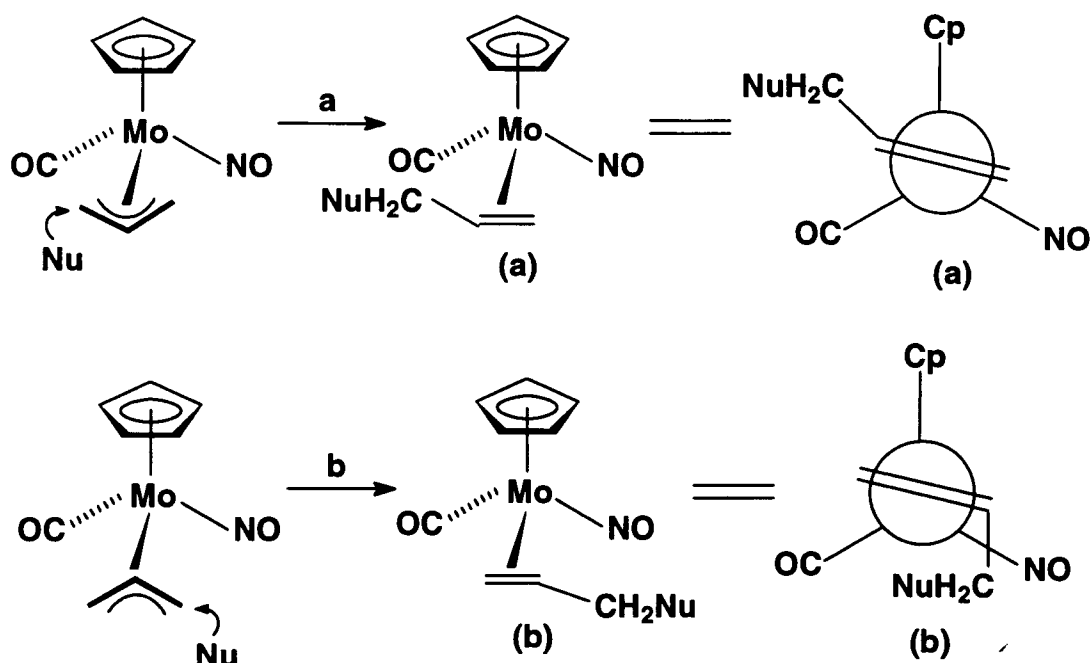


Scheme 3.6. Nucleophilic addition at the $\eta^3$-allyl in $[CpMo(\eta^3\text{-}C_3H_5)(NO)(CO)]^+$.

$[Cp*Re(\eta^2\text{-}C_3H_6)(NO)(PPh_3)]^+$ [122] and $[Cp*Re(\eta^2\text{-}C_3H_6)(NO)(CO)]^+$ (**6.1**, see section 6.2.4), two sets of propene $^1$H NMR resonances were observed because the existence of the two diastereomers resulted from the unsymmetric ligand environment.

### 3.3.6. X-ray Structure of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(OCOSC$_6$H$_5$) (3.15)

The product from the reaction of complex **2.1** with NaSC$_6$H$_5$ in CH$_2$Cl$_2$ or acetone with or without the presence of Me$_3$NO was characterized as **3.6** from the spectroscopic data. But in the $^1$H NMR spectrum, there were also some weak unassigned resonances indicative of a second product (for the product obtained from the reaction of **2.1** with NaSC$_6$H$_5$ and Me$_3$NO only). This impure **3.6** was dissolved in a solvent mixture of ether/hexane in 1/5 ratio, and kept in the refrigerator to crystallize. Two weeks later,
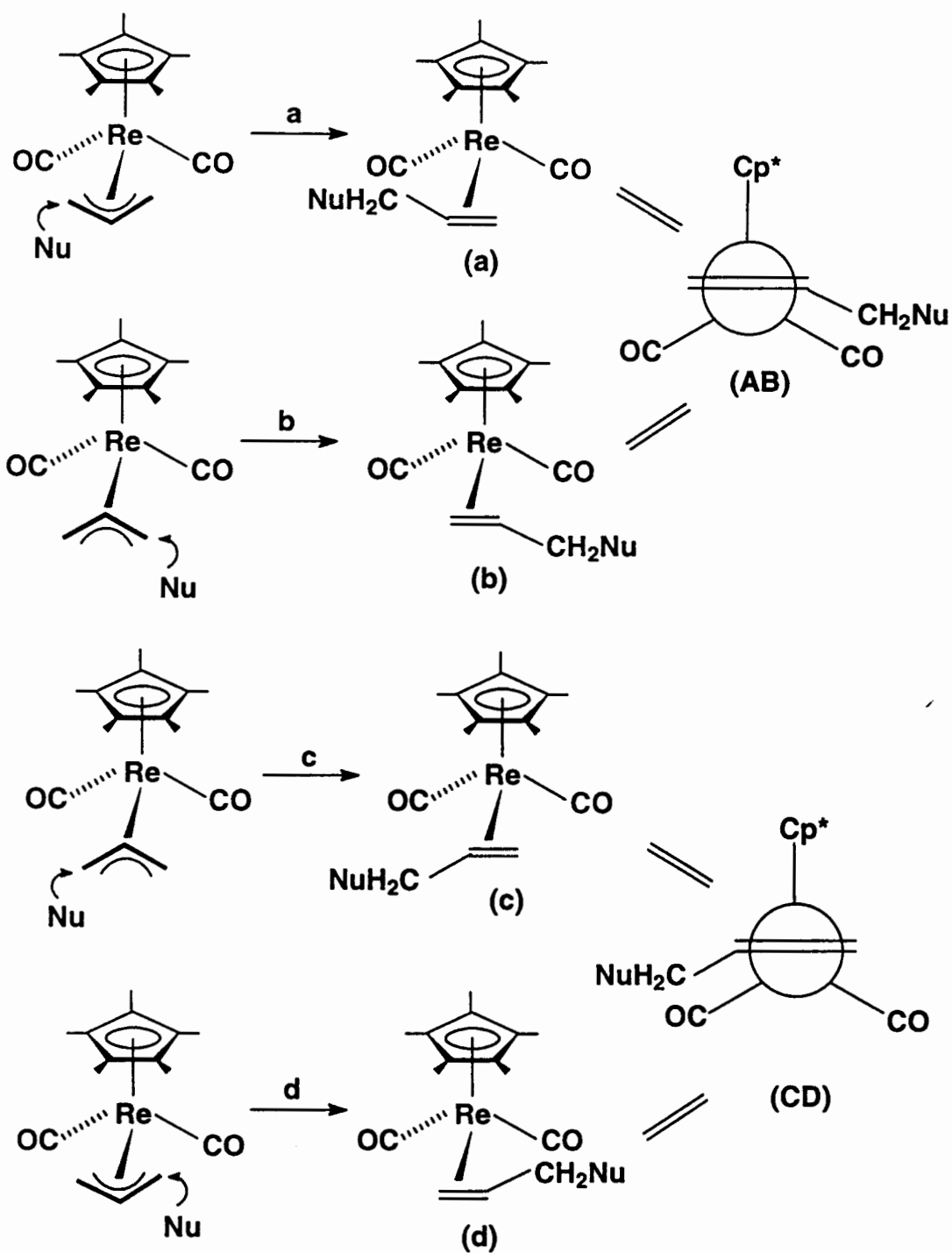
Scheme 3.7. Isomers produced from nucleophilic addition of Nu⁻ on the $\eta^3$-allyl in **2.1**.

several yellowish crystals formed. These crystals were kept in the refrigerator until the sample was used for X-ray analysis (about two months later). Surprisingly, the X-ray structure determination, which was kindly carried out by Dr. F. W. B. Einstein and Dr. R. J. Batchelor, indicated that the structure of this crystal is **3.15** instead of **3.6**. The structure of complex **3.15** is illustrated in Figure 3.7, and selected bond lengths and interbond angles are listed in Table 3.4. The $\eta^3$-allyl adopts the *endo* structure in complex **3.15**.

We presume that the formation of complex $Cp*Re(\eta^3\text{-}C_3H_5)(CO)(OCOSC_6H_5)$ (**3.15**) resulted from the reaction of **2.1** with $Me_3NO$ in the presence of $C_6H_5SNa$. If, even though not the major reaction, $Me_3NO$ did react with a carbonyl of **2.1**, it would release $CO_2$. This $CO_2$ can react with $C_6H_5S^-$ to give $C_6H_5SCOO^-$. The addition of this trace amount of $C_6H_5SCOO^-$ to the intermediate produced from the reaction of **2.1** with $Me_3NO$ will give complex **3.15**. Only a few crystals of **3.15** were obtained, and were consumed for the X-ray structure determination. No spectroscopic data were obtained for **3.15**. The mother liquid, after the crystal was removed, was evaporated to dryness and redissolved in $C_6D_6$ to measure the $^1H$ NMR; the spectrum verified that the complex in solution is **3.6**.

$C_6H_5S^-$ was used as the nucleophile to attack the $\eta^3$-allyl ligand in the Mo complex $[(CH_3CO\text{-}Cp)Mo(\eta^3\text{-}C_3H_5)(NO)(CO)][PF_6]$.[96] The reaction resulted in a substituted propene complex $(CH_3CO\text{-}Cp)Mo(\eta^2\text{-}C_3H_5SC_6H_5)(NO)(CO)$, but no CO group was attacked. This is consistent with the result obtained in the reaction of **2.1** with $C_6H_5SNa$ in $CH_2Cl_2$ without the presence of $Me_3NO$.

## 3.4. Conclusions

The nucleophilic addition to complex **2.1** of oxygen, sulfur, phosphorus, nitrogen and carbon nucleophiles has been investigated. Complexes **3.1-3.15** generated from these reactions were characterized. The experimental results indicated that this nucleophilic addition can occur either at the $\eta^3$-allyl, or at the CO depending upon both the nucleophile and the temperature at which the reaction was carried out. At low temperature (-78-0 °C),
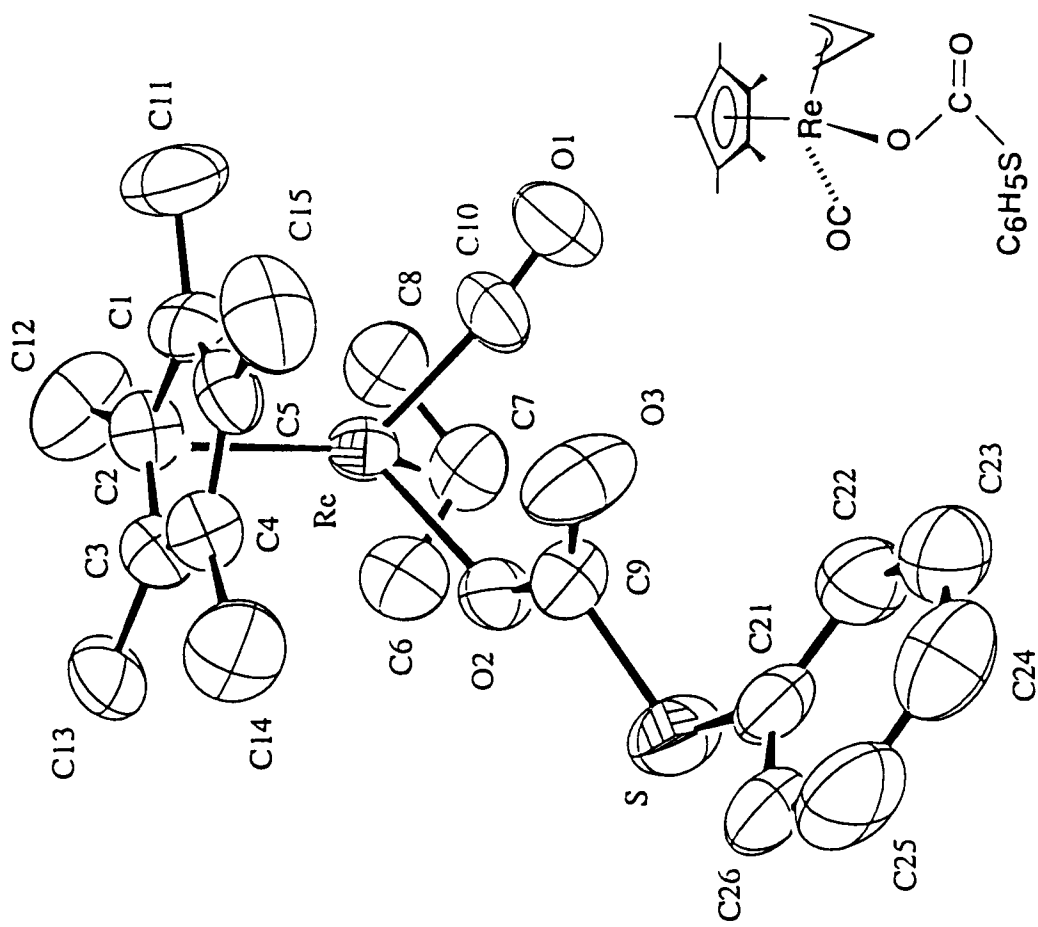
Figure 3.7. The structure of complex Cp*Re($\eta^3$-C₃H₅)(CO)(OCOSC₆H₅) (3.15).

Table 3.4. Selected Intramolecular Distances (Å) and Angles (°) for the Complex of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(OCOSC$_6$H$_5$) (**3.15**).

| Distance (Å) | | Distance (Å) | |
|---|---|---|---|
| Re - C(1) | 2.182(15) | Re - allyl [b] | 1.96 |
| Re - C(2) | 2.242(15) | Re - O(2) | 2.142(9) |
| Re - C(3) | 2.311(14) | Re - C(10) | 1.934(17) |
| Re - C(4) | 2.312(13) | O(1) - C(10) | 1.118(15) |
| Re - C(5) | 2.241(15) | O(2) - C(9) | 1.262(16) |
| Re - Cp* [a] | 1.91 | O(3) - C(9) | 1.185(18) |
| Re - C(6) | 2.215(17) | S - C(9) | 1.800(15) |
| Re - C(7) | 2.201(16) | S - C(21) | 1.797(16) |
| Re - C(8) | 2.193(14) | | |

| Angle (°) | | Angle (°) | |
|---|---|---|---|
| O(2) - Re - C(10) | 88.7(6) | O(2) - Re - Cp* | 114.1 |
| O(2) - Re - Allyl | 97.7 | C(10) - Re - Cp* | 121.5 |
| C(10) - Re - Allyl | 94.2 | Cp* - Re - Allyl | 130.9 |
| C(9) - S - C(21) | 102.9(7) | Re - O(2) - C(9) | 125.0(9) |
| C(6) - C(7) - C(8) | 111.8(16) | S - C(9) - O(2) | 109.4(10) |
| S - C(9) - O(3) | 121.5(11) | O(2) - C(9) - O(3) | 129.1(14) |
| Re - C(10) - O(1) | 171.8(17) | | |

a.  Cp* represents the center of mass of the five carbon atoms of the Cp* ring.
b.  Allyl represents the center of mass of the carbon atoms of the allyl group.

when the CO was attacked, complexes with the general formula $Cp*Re(\eta^3-C_3H_5)$ (CO)(COR) (R = MeO, $NH_2$ and $C_6H_5$) were produced. But when MeO and $NH_2$ were used at room temperature, these complexes converted to the substituted propene complexes. When R was $C_6H_5$, the product was stable and was observed along with the substituted propene complex in $C_6D_6$ solution.

In all cases, addition of the nucleophile to the allyl ligand in **2.1** was observed in the final product, giving the substituted propene complexes with the general formula $Cp*Re(CO)_2(\eta^2-C_3H_5R)$ (R = MeO, $CH_3COO$, $C_2H_5S$, $C_6H_5S$, $S(CH_2)_3S$, $PMe_3$, $NH_2$, $N_3$, $CHMe_2$ and $C_6H_5$). No product of attack at the central carbon was observed for any of the nucleophiles employed in this work.

The nucleophile attacked neither the metal center, nor the Cp* in all cases. This suggests that the positive charge in **2.1** located on the $\eta^3$-allyl, which led the nucleophilic addition to occur preferentially on the allyl instead of the other ligands. The chemistry reported in this Chapter provided an effective way to make C–X bonds (X = O, S, P, N and C) by utilizing the coordinated $\eta^3$-allyl in a cationic rhenium complex **2.1**.

## 3.5. Experimental Section

### 3.5.1. General Procedure

All reactions were carried out under dry nitrogen in Schlenk apparatus. Solvent purification, spectroscopic measurements, and the crystal structure analysis were carried out as described in Chapter II.

### 3.5.2. Preparation of NaSEt, $NaSC_6H_5$ and $NaS(CH_2)_3SNa$

#### i. NaSEt:

Sodium (0.3 mg, 0.01 mmol) was placed in a Schlenk tube, and $C_2H_5SH$ (0.5 mL, 6.75 mmol) was added dropwise to the Schlenk (-78 °C) until all the sodium disappeared.

A white powder formed and $H_2$ gas was released from the sodium surface during the addition of $C_2H_5SH$. Excess of $C_2H_5SH$ was removed, and the solid $NaSC_2H_5$ was washed with ether (1 mL × 5) to give the product, which was used for the preparation of **3.5**.

### ii. $NaSC_6H_5$:

Sodium (0.4 mg, 0.017 mmol) was placed in a Schlenk tube, and $C_6H_5SH$ (0.5 mL, 4.86 mmol) was added dropwise. The mixture was heated to 80 °C and stirred for 5 h. The sodium disappeared, and a white powder formed. Excess $C_6H_5SH$ was removed, and the solid was washed with benzene (1 mL × 5) to give the pure product used for the preparation of **3.6**.

### iii. $NaS(CH_2)_3SNa$:

Sodium (0.5 mg, 0.022 mmol) was placed in a Schlenk tube, and $HS(CH_2)_3SH$ (0.5 mL, 3.19 mmol) was added dropwise and stirred at 100 °C for 3 h. $H_2$ gas was released from the sodium surface. The sodium was consumed and a white powder formed. Excess $HS(CH_2)_3SH$ was removed by using syringe, and the residue was washed with ether to give the pure product for the preparation of **3.7**.

### 3.5.3. Preparation of Cp\*Re($\eta^2$-$C_3H_6$)(CO)$_2$ (3.1)

[Cp\*Re($\eta^3$-$C_3H_5$)(CO)$_2$][BF$_4$] (**2.1**) (19.2 mg, 0.038 mmol) was dissolved in THF (4 mL), and NaBH$_4$ (10 mg, 0.26 mmol, in 1 mL THF and 5 drops of $H_2O$) was added to the solution, and stirred at room temperature for 1 h. The solvent was pumped off, and the residue was extracted with hexane. Two new $\nu$(CO) bands at 1962 and 1890 cm$^{-1}$ were observed in the IR spectrum. This hexane solution was transferred to a neutral alumina column, and eluted with hexane to give **3.1** as a white solid (10.1 mg, 0.024 mmol, 63%), m. p.: 71-72 °C. IR (cm$^{-1}$, hex): $\nu_{CO}$ = 1962, 1890. EIMS (m/z): 420 (M$^+$), 390 (M$^+$ - CO - 2H), 376 (M$^+$ - $C_3H_6$ - 2H), 360 (M$^+$ - 2CO - 4H), 348 (M$^+$ - $C_3H_6$ - CO - 2H, base). $^1$H

NMR ($\delta$, $C_6D_6$): 2.15 (1H, dd, =CH$_2$), 2.06 (3H, d, J = 5.0 Hz, CH$_3$), 1.97 (1H, m, =CH–), 1.61 (15H, s, Cp*), 1.36 (1H, dd, =CH$_2$).

### 3.5.4. Preparation of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(COOCH$_3$) (3.2) and Cp*Re($\eta^2$-CH$_2$CHCH$_2$OCH$_3$)(CO)$_2$ (3.3)

NaOCH$_3$ (10 mg, 0.19 mmol) was added to a solution of complex (2.1) (11.9 mg, 0.024 mmol) in MeOH (3 mL) at 0 °C and the solution was stirred for 3 h. New $\nu$(CO) absorptions were observed in the IR spectrum at 1956, 1942, and 1885 cm$^{-1}$. The solvent was pumped off and the solid residue was extracted with hexane (2 mL × 3), filtered through Celite and the solution was pumped to dryness at 0 °C. The white solid obtained was shown by $^1$H NMR and IR spectroscopy to be a mixture of isomers 3.2 and 3.3. In attempt to separate 3.2 and 3.3 by room temperature chromatography on neutral alumina, the fraction that eluted with hexane contained pure 3.3, and that which eluted with ether contained a mixture of 3.2 and 3.3. Upon repeated chromatographing, a fraction containing both 3.2 and 3.3 was obtained, with successively decreasing of 3.2 (relative to 3.3 from IR) indicated that 3.2 is isomerizing to 3.3, and the equilibrium is being shifted as 3.3 is removed. Pure 3.2 could not be obtained. Data for 3.3 were identical with those reported previously.[1e] Spectroscopic data for 3.2: IR (hexane, cm$^{-1}$): $\nu_{CO}$ = 1944, 1634. $^1$H NMR ($C_6D_6$, $\delta$): 4.20 (1H, m, H$_c$), 3.40 (3H, s, COOCH$_3$), 3.02 (1H, dd, $J_{sc}$ = 5.1 Hz, $J_{ss}$ = 3.7 Hz, H$_s$), 2.94 (1H, dd, $J_{sc}$ = 5.1 Hz, $J_{ss}$ = 3.7 Hz, H$_s$), 1.91 (15H, s, Cp*), 1.10 (1H, d, $J_{ac}$ = 9.0 Hz, H$_a$), 0.69 (1H, d, $J_{ac}$ = 9.0 Hz, H$_a$). Spectroscopic data for 3.3: IR (hexane, cm$^{-1}$): $\nu_{CO}$ = 1964, 1892. EIMS (m/z): 450 (M$^+$), 392 (M$^+$ - 2CO - 2H), 376 (M$^+$ - C$_3$H$_5$OCH$_3$ - 2H), 362 (M$^+$ - 2CO - CH$_3$OH), 348 (M$^+$ - C$_3$H$_5$OCH$_3$ - CO - 2H, base). $^1$H NMR ($C_6D_6$, $\delta$): 4.06 (1H, dd, –CH$_2$OMe), 3.36 (3H, s, –OCH$_3$), 2.63 (1H, t, $J$ = 10.8 Hz, –CH$_2$OMe), 1.99 (1H, dd, =CH$_2$), 1.95 (15H, s, Cp*), 1.81 (1H, m, =CH–), 1.41 (1H, dd, =CH$_2$).

### 3.5.5. Preparation of Cp*Re($\eta^2$-CH$_2$CHCH$_2$OOCCH$_3$)(CO)$_2$ (3.4)

Complex **2.1** (30 mg, 0.059 mmol) and CH$_3$COONa (20 mg, 0.24 mmol) were placed in a Schlenk tube. CH$_2$Cl$_2$ (2 mL) was added to dissolve **2.1**, and CH$_3$COONa was only partially dissolved. This mixture was stirred at room temperature for 5 h, and the IR showed that the v(CO) bands for **2.1** disappeared, and new v(CO) bands at 1956 and 1877 cm$^{-1}$ were observed. The solution was filtered through Celite and transferred to another Schlenk. The solvent was pumped off, and the residue was extracted with hexane (1 mL). This hexane solution was kept at -78 °C overnight to crystallize. Solvent was removed, and the white crystals were dried under vacuum to give the pure product for analysis (25.8 mg, 0.054 mmol, 92%), m. p.: 124-125 °C. IR (hex, cm$^{-1}$): $v_{CO}$ = 1968, 1896, and 1739. EIMS (m/z): 478 (M$^+$), 422 (M$^+$ - 2CO), 378 (M$^+$ - C$_3$H$_5$OOCCH$_3$), 360 (M$^+$ - 2CO - CH$_3$COOH - 2H), 348 (M$^+$ - C$_3$H$_5$OOCCH$_3$ - CO - 2H, base). $^1$H NMR (C$_6$D$_6$, $\delta$): 5.18 (1H, dd, $J_{45}$ = 11.5 Hz, $J_{34}$ = 3.5 Hz, H$_4$), 3.71 (1H, dd, $J_{45}$ = 11.5 Hz, $J_{35}$ = 9.5 Hz, H$_5$), 2.24 (1H, overlapped with H$_3$, H$_1$), 2.21 (1H, m, H$_3$), 1.85 (3H, s, OOCCH$_3$), 1.56 (15H, s, Cp*), 1.32 (1H, d, $J_{23}$ = 6.5 Hz, H$_2$). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, $\delta$): 206.00 (s, Re-CO), 170.00 (s, C$_3$H$_5$COOMe), 97.61 (s, $C_5$Me$_5$), 73.40 (s, -CH$_2$-), 37.33 (s, =CH-), 26.62 (s, =CH$_2$), 20.93 (-COCH$_3$), 9.73 (s, C$_5${CH$_3$}$_5$). Anal. Calcd for C$_{17}$H$_{23}$O$_4$Re: C, 42.75; H, 4.86. Found: C, 42.53; H, 4.93.

### 3.5.6. Preparation of Cp*Re($\eta^2$-CH$_2$CHCH$_2$SCH$_2$CH$_3$)(CO)$_2$ (3.5)

Complex **2.1** (50 mg, 0.1 mmol) and NaSCH$_2$CH$_3$ (16.8 mg, 0.2 mmol) were dissolved in acetone (4 mL) in a Schlenk tube, then stirred at room temperature for 0.5 h. By this time, the IR showed the disappearance of the v(CO) for **2.1**, and two new CO bands at 1950, 1875 cm$^{-1}$ appeared. The solvent was pumped off, and the residue was extracted with hexane (1 mL × 5). The hexane solution was concentrated to 1 mL, then kept at -78 °C overnight, and white crystals formed. The solvent was removed, and the solid was dried under vacuum for 12 h to give the analytically pure sample (44.1 mg, 0.092 mmol, 92%), m. p.: 67-68 °C. IR (hex, cm$^{-1}$): $v_{CO}$ = 1964, 1892. EIMS (m/z): 480

(M$^+$), 439 (M$^+$ - C$_3$H$_5$, base), 409 (M$^+$ - C$_3$H$_7$ - CO), 381 (M$^+$ - 2CO - C$_3$H$_7$), 353 (M$^+$ - C$_3$H$_5$ - C$_2$H$_6$ - 2CO). $^1$H NMR (C$_6$D$_6$, δ): 3.71 (1H, dd, $J_{45}$ = 12.4 Hz, $J_{34}$ = 2.1 Hz, H$_4$), 2.53 (2H, m, –SCH$_2$–), 2.52 (1H, overlapped with –SCH$_2$–, H$_5$), 2.18 (1H, m, H$_3$), 2.16 (1H, m, H$_1$), 1.58 (15H, s, Cp*), 1.37 (1H, m, H$_2$), 1.20 (3H, t, $J$ = 7.4 Hz, –CH$_3$). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, δ): 226.00, 207.00 (s, Re-CO), 97.29 (s, $C_5$Me$_5$), 42.33 (s, SCH$_2$), 41.09 (s, SCH$_2$), 27.04 (s, =CH–), 26.41 (s, CH$_3$), 15.02 (s, =CH$_2$), 9.80 (s, C$_5${$CH_3$}$_5$). Anal. Calcd for C$_{17}$H$_{25}$O$_2$SRe: C, 42.57; H, 5.25. Found: C, 42.80; H, 5.32.

### 3.5.7. Preparation of Cp*Re(η$^2$-CH$_2$CHCH$_2$SC$_6$H$_5$)(CO)$_2$ (3.6)

Complex **2.1** (50 mg, 0.1 mmol) and NaSC$_6$H$_5$ (40 mg, 0.3 mmol) were dissolved in acetone (4 mL) in a Schlenk tube, then stirred at room temperature for 2 h. By this time, the IR showed the disappearance of the ν(CO) for **2.1**, and two new CO bands at 1952, 1877 cm$^{-1}$ appeared. The solvent was pumped off, the residue was extracted with hexane (0.5 mL × 4). The hexane solution was concentrated to 1 mL, then kept at -78 °C overnight to give greenish crystals, but the crystals changed to a sticky oily state when they were warmed up to room temperature. Solvent was removed, and the green oily product was dried under vacuum overnight to give samples for the spectroscopic data (38.25 mg, 0.073, 72.5%). IR (hex, cm$^{-1}$): ν$_{CO}$ = 1964, 1892. EIMS (m/z): 528 (M$^+$), 500 (M$^+$ - CO), 487 (M$^+$ - C$_3$H$_5$, base), 470 (M$^+$ - 2CO - 2H), 431 (M$^+$ - 2CO - C$_3$H$_5$), 419 (M$^+$ - SC$_6$H$_5$), 389 (M$^+$ - C$_6$H$_5$S - CO - 2H). $^1$H NMR (C$_6$D$_6$, δ): 7.48, 7.08 (4H, dd, C$_6$H$_5$), 6.90 (1H, m, C$_6$H$_5$), 4.10 (1H, dd, $J_{45}$ = 12.3 Hz, $J_{34}$ = 3.2 Hz, H$_4$), 2.89 (1H, dd, $J_{45}$ = 12.3 Hz, $J_{35}$ = 10.0 Hz, H$_5$), 2.20 (1H, m, H$_3$), 2.18 (1H, m, H$_1$), 1.54 (15H, s, Cp*), 1.26 (1H, dd, $J_{23}$ = 7.2 Hz, $J_{21}$ = 1.5 Hz, H$_2$). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, δ): 244.11, 238.00 (s, Re-CO), 130.84-125.99 (s, C$_6$H$_5$), 97.39 (s, $C_5$Me$_5$), 44.93 (s, –CH$_2$–), 39.49 (s, =CH–), 26.80 (s, =CH$_2$), 9.73 (s, C$_5${$CH_3$}$_5$). Anal. Calcd for C$_{21}$H$_{25}$O$_2$SRe: C, 47.80; H, 4.78. Found: C, 65.03; H, 5.22. The found data is not in agreement with the theoretical result, it may contain the contribution of some solvent, because the sample is in a sticky oily state,

completely removing solvent from this sample is very difficult.

The $^1$H NMR sample of **3.6** (unclean) was dissolved in a mixed solvent of ether / hexane, and kept in refrigerator to crystallize. The X-ray structure determination indicated that the crystals obtained from this sample are complex **3.15**, not **3.6**. See section 3.3.6 for more detail.

### 3.5.8. Preparation of {Cp*Re(CO)$_2$($\eta^2$-CH$_2$CHCH$_2$SCH$_2$)}$_2$CH$_2$ (3.7)

Complex **2.1** (23 mg, 0.05 mmol) and NaS(CH$_2$)$_3$SNa (20 mg, 0.13 mmol) were dissolved in CH$_2$Cl$_2$ (3 mL) in a Schlenk tube, then stirred at room temperature for 5 h. By this time, the IR showed the disappearance of the $\nu$(CO) for **2.1**, and two new CO bands at 1950 and 1873 cm$^{-1}$ were observed. The solvent was pumped off, and the residue was extracted with hexane (0.5 mL × 3). This hexane solution was concentrated to 1 mL, then recrystallized at -78 °C overnight, and some pink solid formed. The solvent was removed, and the solid changed into a sticky oily state when it was warmed up to room temperature. This product was dried overnight to prepare the sample for spectroscopic analysis (18.52 mg, 0.02 mmol, 86.24%). IR (hex, cm$^{-1}$): $\nu_{CO}$ = 1962, 1892. EIMS (m/z): 525 (M$^+$ - Cp*Re(C$_3$H$_5$)(CO)$_2$), 497 (M$^+$ - Cp*Re(C$_3$H$_5$)(CO)$_2$ - CO), 485 (M$^+$ - Cp*Re(C$_3$H$_5$)(CO)$_2$ - C$_3$H$_4$), 456 (M$^+$ - Cp*Re(C$_3$H$_5$)(CO)$_2$ - CO - C$_3$H$_5$), 419 (M$^+$ - Cp*Re(C$_3$H$_5$)(CO)$_2$ - SC$_3$H$_6$S, base), 389 (M$^+$ - Cp*Re(C$_3$H$_5$)(CO)$_2$ - SC$_3$H$_6$S - CO - 2H), 359 (M$^+$ - SC$_3$H$_6$S - 2CO - Cp*Re(C$_3$H$_5$)(CO)$_2$ - 4H). $^1$H NMR (C$_6$D$_6$, $\delta$): 3.73 (1H, dd, $J_{45}$ = 13.0 Hz, $J_{34}$ = 3.0 Hz, H$_4$), 2.76 (4H, dt, $J$ = 3.6 Hz, $J$ = 1.3 Hz, -SCH$_2$- & -CH$_2$S-), 2.51 (1H, dd, $J_{45}$ = 13.0 Hz, $J_{35}$ = 10.0 Hz, H$_5$), 2.25 (1H, dd, overlapped with H$_3$, H$_1$), 2.22 (1H, m, H$_3$), 1.97 (2H, dp, $J$ = 7.0 Hz, $J$ = 1.1 Hz, -CH$_2$-), 1.60 (15H, s, Cp*), 1.42 (1H, d, $J_{23}$ = 6.2 Hz, H$_2$). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, $\delta$): 207.10 (s, Re-CO), 97.35 (s, $C_5$Me$_5$), 42.81 (s, CH$_2$S), 41.24 (s, =CH-), 31.64 (s, SCH$_2$), 30.42 (s, -CH$_2$-), 27.18 (s, =CH$_2$), 9.84 (s, C$_5${$CH_3$}$_5$). Anal. Calcd. for C$_{33}$H$_{46}$O$_4$S$_2$Re$_2$: C, 42.02; H, 4.92. The microanalysis of **3.7** gave data for: C, 48.03; H, 5.62. The found data is not in agreement with the theoretical

result, it may contain the contribution of some solvent, because the sample is in a sticky oily state, the solvent in this sample can not be completely removed.

### 3.5.9. Preparation of [Cp*Re(CO)$_2$($\eta^2$-CH$_2$CHCH$_2$PMe$_3$)][BF$_4$] (3.8)

Complex **2.1** (40 mg, 0.08 mmol) was dissolved in CH$_2$Cl$_2$ (4 mL), and excess PMe$_3$ (0.2 mL, 1.93 mmol) was added by syringe. The reaction mixture was stirred at room temperature for 1 h. The IR then showed two new CO bands at 1964 and 1885 cm$^{-1}$ due to complex **3.8**. The solvent and excess PMe$_3$ were pumped off. The residue was washed with 2 mL ether then recrystallized from CH$_2$Cl$_2$/hexane (1/6). The product obtained was a white solid (41 mg, 0.07 mmol, 88%), m. p.: 210-211 °C. IR (CH$_2$Cl$_2$, cm$^{-1}$): $\nu_{CO}$ = 1885, 1964. FABMS (m/z): 495 (M$^+$ of cation), 419 (M$^+$ - PMe$_3$, base), 391 (M$^+$ - PMe$_3$ - CO), 389 (M$^+$ - PMe$_3$ - CO - 2H), 361 (M$^+$ - PMe$_3$ - 2CO), 359 (M$^+$ - PMe$_3$ - 2CO - 2H). $^1$H NMR (CD$_2$Cl$_2$, δ): 3.18 (1H, m, H$_4$), 1.97 (15H, s, Cp*), 1.88 (9H, d, $J_{PH}$ = 13.9 Hz, PMe$_3$), 1.86 (1H, m, H$_3$), 1.64 (2H, m, H$_1$ and H$_5$, overlapped), 1.37 (1H, m, H$_2$). $^{13}$C\{$^1$H\} NMR (CD$_3$CN, δ): 208.87 (s, Re-CO), 207.08 (s, Re-CO), 99.73 (s, $C_5$Me$_5$), 34.98 (d, $J_{PC}$ = 42.3 Hz, -$C$H$_2$PMe$_3$), 27.49 (s, d in $^1$H-coupled spectrum, =CH-), 26.47 (s, t in $^1$H-coupled spectrum, =CH$_2$), 10.37 (s, C$_5$\{$C$H$_3$\}$_5$), 8.24 (d, $J_{PC}$ = 53.3 Hz, P\{$C$H$_3$\}$_3$). $^{31}$P\{$^1$H\} NMR (CD$_3$CN, δ): 29.73 (s, PMe$_3$). Anal. Calcd. for C$_{18}$H$_{29}$BF$_4$O$_2$PRe: C, 37.18; H, 5.03; Found: C, 37.30; H, 4.91.

### 3.5.10. Preparation of [Cp*Re(CO)$_2$\{$\eta^2$-CH$_2$CHCH(CH$_3$)PMe$_3$\}][BF$_4$] (3.9)

Complex **2.4** (20 mg, 0.039 mmol) was dissolved in CH$_2$Cl$_2$ (3 mL), and an excess PMe$_3$ (0.2 mL, 1.93 mmol) was added by syringe. The reaction mixture was stirred at room temperature for 1 h. The IR then showed two new CO bands at 1964 and 1881 cm$^{-1}$ due to complex **3.9**. The solvent and excess PMe$_3$ were pumped off. The residue was washed with 2 mL ether, then recrystallized from CH$_2$Cl$_2$/hexane (1/6). The product was obtained as a white solid which is a mixture of **3.9a** (67%) and **3.9b** (33%) (14.9 mg, 0.025 mmol, 65%), m. p.: 202-203 °C. IR (CH$_2$Cl$_2$, cm$^{-1}$): $\nu_{CO}$ = 1964, 1881. FABMS

(m/z): 509 ($M^+$ of cation), 433 ($M^+$ - PMe$_3$, base), 405 ($M^+$ - PMe$_3$ - CO), 375 ($M^+$ - PMe$_3$ - 2CO - 2H). Spectroscopic data for **3.9a**: $^1$H NMR (CD$_3$CN, $\delta$): 3.04 (1H, dd, $-$CH$_2$PMe$_3$), 2.15 (1H, m, $-$CH$_2$PMe$_3$), 1.99 (15H, s, Cp*), 1.96 (1H, m, =CH$-$), 1.80 (9H, d, $J_{PH}$ = 12.0 Hz, PMe$_3$), 1.58 (1H, m, =CH$_2$), 1.45 (3H, d, $J$ = 6.0 Hz, CH$_3$). $^{13}$C{$^1$H} NMR (CD$_3$CN, $\delta$): 207.65 (s, Re-CO), 99.91 (s, $C_5$Me$_5$), 38.56 (d, $J_{PC}$ = 42.40 Hz, -CH$_2$PMe$_3$), 26.73 (s, =CH-), 15.79 (s, =CHCH$_3$), 10.92 (s, =CHCH$_3$), 10.42 (s, C$_5${CH$_3$}$_5$), 7.25 (d, $J_{PC}$ = 55.12 Hz, P{CH$_3$}$_3$). $^{31}$P{$^1$H} NMR (CD$_3$CN, $\delta$): 34.30 (s, $-$CH$_2$PMe$_3$). Spectroscopic data for **3.9b**: $^1$H NMR (CD$_3$CN, $\delta$): 2.61 (1H, m, $-$CH(Me)PMe$_3$), 2.02 (15H, s, Cp*). $^{31}$P{$^1$H} NMR (CD$_3$CN, $\delta$): 29.27 (s, $-$CH(Me)PMe$_3$). Anal. Calcd. for C$_{19}$H$_{31}$BF$_4$O$_2$PRe: C, 38.32; H, 5.25; Found: C, 38.61; H, 5.40.

### 3.5.11. Preparation of Cp*Re(CO)$_2$($\eta^2$-CH$_2$CHCH$_2$N$_3$) (3.10)

Complex **2.1** (25 mg, 0.05 mmol) and NaN$_3$ (20 mg, 0.31 mmol) were dissolved in CH$_2$Cl$_2$ (3 mL) in a Schlenk tube, then stirred at room temperature overnight. By this time, the IR showed the disappearance of the v(CO) for **2.1**, and new CO bands at 1956 and 1876 cm$^{-1}$, and a v(NN) band at 2124 cm$^{-1}$ appeared. The solvent was pumped off, the residue was extracted with hexane (1 mL × 3), and the volume was reduced to 1 mL, recrystallized at -78 °C overnight to give white crystals. Solvent was removed and the solid was dried under vacuum overnight and used for analysis (20.28 mg, 0.044 mmol, 89%). IR (hex, cm$^{-1}$): v$_{CO}$ = 1969, 1898, v$_{NN}$ = 2101. EIMS (m/z): 433 ($M^+$ - N$_2$), 419 ($M^+$ - N$_3$), 405 ($M^+$ - 2CO), 375 ($M^+$ - 2CO - N$_2$ - 2H), 373 ($M^+$ - 2CO - N$_2$ - 4H), 348 ($M^+$ - CO - C$_3$H$_5$N$_3$ - 2H), 346 ($M^+$ - CO - C$_3$H$_5$N$_3$ - 4H, base). $^1$H NMR (C$_6$D$_6$, $\delta$): 3.75 (1H, dd, $J_{45}$ = 12.5 Hz, $J_{34}$ = 3.5 Hz, H$_4$), 2.70 (1H, dd, $J_{45}$ = 12.5 Hz, $J_{35}$ = 10.0 Hz, H$_5$), 2.04 (1H, dd, $J_{13}$ = 9.5 Hz, $J_{12}$ = 2.6 Hz, H$_1$), 1.87 (1H, m, H$_3$), 1.50 (15H, s, Cp*), 1.22 (1H, dd, $J_{23}$ = 7.5 Hz, $J_{21}$ = 2.6 Hz, H$_2$). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, $\delta$): 206.47, 205.68 (s, Re-CO), 97.60 (s, $C_5$Me$_5$), 60.99 (s, $-$CH$_2-$), 36.62 (s, =CH$-$), 25.48 (s, =CH$_2$), 9.66 (s, C$_5${CH$_3$}$_5$). Anal. Calcd. for C$_{15}$H$_{20}$N$_3$O$_2$Re: C, 39.12; H, 4.38; N, 9.12. The found data

from the microanalysis of **3.10** gave C, 42.44; H, 5.01; N, 7.22. The C% and H% values are higher than those of calculated, but the N% is lower. This may because of the decomposition of **3.10**, which lead to the releasing of $N_2$ from the $CH_2=CHCH_2N_3$ ligand.

### 3.5.12. Preparation of Cp*Re(CO)$_2$($\eta^2$-CH$_2$CHCH$_2$NH$_2$) (3.11)

Complex **2.1** (30 mg, 0.059 mmol) and $NaNH_2$ (10 mg, 0.26 mmol) were dissolved in $CH_2Cl_2$ (3 mL) in a Schlenk tube, then stirred at room temperature overnight. By this time, the IR showed the disappearance of the $\nu(CO)$ for **2.1**, and new CO bands at 1950, 1927 and 1873 cm$^{-1}$ were observed. The solvent was pumped off, the residue was extracted with hexane (1 mL × 3), and the volume was reduced to 1 mL (only two $\nu(CO)$ at 1964, 1892 for **3.11** were observed by this time) and recrystallized at -78 °C overnight to give **3.11** as white crystals. The solvent was removed and the solid was dried under vacuum overnight then used for analysis (21.5 mg, 0.05 mmol, 84%), m. p.: 121-122 °C. IR (hex, cm$^{-1}$): $\nu_{CO}$ = 1964, 1892. CIMS (m/z): 435 (M$^+$), 419 (M$^+$ - NH$_2$), 391 (M$^+$ - CO - NH$_2$, base). $^1$H NMR (C$_6$D$_6$, δ): 4.64 (1H, dd, $J_{45}$ = 10.0 Hz, $J_{34}$ = 3.9 Hz, H$_4$), 4.53 (1H, dd, $J_{45}$ = 10.0 Hz, $J_{35}$ = 3.9 Hz, H$_5$), 3.45, 3.27 (2H, t, $J$ = 10.0 Hz, NH$_2$), 2.40 (1H, m, H$_1$), 2.29 (1H, m, H$_3$), 1.60 (15H, s, Cp*), 1.49 (1H, d, $J_{13}$ = 8.1 Hz, H$_2$). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, δ): 206.77, 203.88 (s, Re-CO), 97.30 (s, $C_5$Me$_5$), 78.89 (s, –CH$_2$–), 40.59 (s, =CH–), 27.76 (s, =CH$_2$), 9.82 (s, C$_5${CH$_3$}$_5$). Anal. Calcd. for C$_{15}$H$_{22}$NO$_2$Re: C, 41.46; H, 5.10; N, 3.22; Found: C, 41.36; H, 4.98; N, 3.01.

### 3.5.13. Preparation of Cp*Re(CO)$_2$($\eta^2$-CH$_2$CHCH$_2$CHMe$_2$) (3.12)

Complex **2.1** (40 mg, 0.079 mmol) was dissolved in $CH_2Cl_2$ (3 mL) in a Schlenk tube, at -78 °C, 0.2 mL Me$_2$CHMgCl (1 M) ether solution was added by syringe. The reaction was continued at -78 °C for 2 h. Two new CO bands at 1946 and 1865 cm$^{-1}$ were observed in the IR spectrum. The solvent was pumped off, the residue was extracted with hexane (1 mL × 3), and the volume was reduced to 1 mL, and recrystallized at -78 °C overnight to give white crystals. The solvent was removed, the solid was dried under

vacuum overnight and used for analysis (31.85 mg, 0.069 mmol, 87%). IR (hexane, cm$^{-1}$): $\nu_{CO}$ = 1960, 1888. EIMS (m/z): 462 (M$^+$), 432 (M$^+$ - CO - 2H), 419 (M$^+$ - CH(CH$_3$)$_2$), 402 (M$^+$ - 2CO - 4H), 376 (M$^+$ - C$_3$H$_5$CH(CH$_3$)$_2$ - 2H), 348 (M$^+$ - CO - C$_3$H$_5$CH(CH$_3$)$_2$, base). $^1$H NMR (C$_6$D$_6$, δ): 2.50 (1H, m, H$_4$), 2.17 (1H, dd, $J_{13}$ = 10.5 Hz, $J_{12}$ = 1.9 Hz, H$_1$), 2.02 (1H, m, H$_3$), 1.77 (1H, m, –CH), 1.54 (15H, s, Cp*), 1.43 (1H, dd, $J_{12}$ = 1.9 Hz, $J_{23}$ = 8.1 Hz, H$_2$), 1.27 (1H, m, H$_5$), 1.08, 1.04 (6H, d, $J$ = 6.5 Hz, CH$_3$). $^{13}$C\{$^1$H\} NMR (C$_6$D$_6$, δ): 207.47, 207.09 (s, Re-CO), 96.87 (s, $C_5$Me$_5$), 49.04 (s, –CH$_2$–), 42.68 (s, =CH–), 33.43 (s, –$C$HMe$_2$), 28.27 (s, =CH$_2$), 22.67, 22.52 (s, CH$_3$), 9.89 (s, C$_5$\{$C$H$_3$\}$_5$). Anal. Calcd. for C$_{18}$H$_{27}$O$_2$Re: C, 46.83; H, 5.90; Found: C, 46.68; H, 6.00.

### 3.5.14. Preparation of Cp*Re(CO)($\eta^3$-C$_3$H$_5$)(COC$_6$H$_5$) (3.13) and Cp*Re(CO)$_2$($\eta^2$-CH$_2$CHCH$_2$C$_6$H$_5$) (3.14)

Complex **2.1** (25 mg, 0.049 mmol) was dissolved in CH$_2$Cl$_2$ (3 mL) in a Schlenk tube, at -78 °C, 0.3 mL C$_6$H$_5$Li (1 M) ether solution was added by syringe, then stirred at -78 °C for 4 h. The IR showed only three new CO bands at 1950, 1913 and 1871 cm$^{-1}$ by this time. The solvent was pumped off, the residue was extracted with hexane (2 mL × 3), and the volume was reduced to 1 mL, recrystallized at -78 °C to give the white crystals. The solvent was removed, the solid was dried under vacuum overnight and used for analysis (22.53 mg, 0.046 mmol, 93%). EIMS (m/z, mixture of **3.13** and **3.14**): 496 (M$^+$), 466 (M$^+$ - CO - 2H), 440 (M$^+$ - 2CO, base), 419 (M$^+$ - C$_6$H$_5$), 391 (M$^+$ - COC$_6$H$_5$), 378 (M$^+$ - C$_3$H$_5$C$_6$H$_5$), 348 (M$^+$ - CO - C$_3$H$_5$C$_6$H$_5$ - 2H). Spectroscopic data for **3.13**: IR (hex, cm$^{-1}$): $\nu_{CO}$ = 1919. $^1$H NMR (C$_6$D$_6$, δ): 7.5-7.05 (5H, m, C$_6$H$_5$), 4.26 (1H, m, H$_c$), 2.83, 2.74 (2H, dd, $J_{sc}$ = 5.6 Hz, $J_{ss}$ = 2.9 Hz, H$_s$), 1.66 (15H, s, Cp*), 0.83 (1H, d, $J_{ac}$ = 9.5 Hz, H$_a$), 0.66 (1H, d, $J_{ac}$ = 8.0 Hz, H$_a$). $^{13}$C\{$^1$H\} NMR (C$_6$D$_6$, δ): 129.0 (s, C$_6$H$_5$), 81.1 (s, –CH=), 48.9 (s, =CH$_2$), 31.6 (s, =CH$_2$), 9.80 (s, C$_5$\{$C$H$_3$\}$_5$). Spectroscopic data for **3.14**: IR (hex, cm$^{-1}$): $\nu_{CO}$ = 1962, 1890. $^1$H NMR (C$_6$D$_6$, δ): 7.5-7.05 (5H, m, C$_6$H$_5$), 3.85 (1H, dd, $J_{45}$ = 14.0 Hz, $J_{34}$ = 3.2 Hz, H$_4$), 2.57 (1H, dd, $J_{45}$ = 14.0 Hz, $J_{35}$ = 10.1 Hz, H$_5$), 2.29 (1H, dd, $J_{13}$ = 10.5 Hz, $J_{12}$ = 2.0 Hz, H$_1$), 2.12 (1H, m, H$_3$), 1.60 (15H, s, Cp*), 1.34 (1H,

dd, $J_{23}$ = 8.0 Hz, $J_{21}$ = 2.0 Hz, H$_2$). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, δ): 129.0 (s, C$_6$H$_5$), 46.5 (s, −CH$_2$−), 43.2 (s, =CH−), 26.7 (s, =CH$_2$), 9.80 (s, C$_5${$CH_3$}$_5$). The $^{13}$C data were obtained from the $^{13}$C-$^1$H correlation experiment, no $^{13}$C resonance of the Cp* ring carbon was obtained. Anal. Calcd. for C$_{21}$H$_{25}$O$_2$Re: C, 50.89; H, 5.09; Found: C, 50.78; H, 5.15.

### 3.5.15. Crystal Preparation of Cp*Re(CO)(η$^3$-C$_3$H$_5$)(OCOSC$_6$H$_5$) (3.15)

The $^1$H NMR sample of impure **3.6** (product obtained from the reactions of **2.1** with NaSC$_6$H$_5$ with or without the presence of Me$_3$NO in CH$_2$Cl$_2$) was dissolved in a solvent mixture (ether/hexane = 1/5), and kept in the refrigerator to crystallize. Two weeks later, several yellowish crystals formed. These crystals were kept in the refrigerator till the sample was used for X-ray analysis. Only a few crystals of **3.15** were obtained, and all were used for the X-ray structure determination.

# Chapter IV

## Reactivity of Mono- and Bis-Acetonitrile Complexes [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(NCMe)][BF$_4$] (2.2) and [Cp*Re($\eta^3$-C$_3$H$_5$)(NCMe)$_2$][BF$_4$] (2.3) Towards Hydride, Trimethylphosphine and Hydroxide

## 4.1. Introduction

The synthesis, characterization and X-ray crystal structure of the cationic rhenium $\eta^3$-allyl complex [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] (2.1) (Cp* = $\eta^5$-C$_5$Me$_5$) and its mono- and bis-acetonitrile derivatives [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(NCMe)][BF$_4$] (2.2) and [Cp*Re($\eta^3$-C$_3$H$_5$)(NCMe)$_2$][BF$_4$] (2.3) have been reported in Chapter II and previous papers.[29a,110] The acetonitrile derivatives 2.2 and 2.3 were synthesized in anticipation that the acetonitrile ligand would be more substitutionally labile than CO and would be readily substituted by neutral (L), or anionic (X) ligands leading to a series of new half-sandwich rhenium $\eta^3$-allyl complexes of the type [Cp*Re(CO)(L)($\eta^3$-C$_3$H$_5$)]$^+$, [Cp*ReL$_2$($\eta^3$-C$_3$H$_5$)]$^+$, and Cp*Re(CO)X($\eta^3$-C$_3$H$_5$).

In this Chapter, we describe the reactions of the acetonitrile compounds 2.2 and 2.3 with potential nucleophiles such as borohydride, trimethylphosphine and hydroxide. We find that acetonitrile in these rhenium complexes is not a good leaving group, and that ligand substitution does not usually occur preferentially. Instead, nucleophilic attack occurs at one or other of the possible ligand sites, and the result depends on the particular nucleophile employed.

There is currently considerable interest in nucleophilic additions to cationic cyclopentadienyl allyl complexes.[114] One of the most extensively explored is the molybdenum complex [CpMo(CO)(NO)(allyl)]$^+$.[115] Rather less is known about the reactions of manganese [108] or rhenium [84f] compounds. Besides the nucleophilic additions to the coordinated allyl in [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] (2.1) reported in Chapter III,

there has been only one preliminary study of additions to pentamethylcyclopentadienyl rhenium allyl complexes.[1e,116]

## 4.2. Reactivity of [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(NCMe)][BF$_4$] (2.2)

### 4.2.1. Reaction of [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(NCMe)][BF$_4$] (2.2) with NaBH$_4$

The reactions of complex **2.2** with NaBH$_4$ in THF or THF/H$_2$O solutions at low (0 °C) or room temperatures were investigated. The reason for these experiments was to determine which of the four possible complexes shown in Scheme 4.1 actually results; i.e., does NaBH$_4$ proceed by attacking or replacing the coordinated CH$_3$CN, CO or allyl? Especially, substitution of coordinated acetonitrile by H$^-$ to produce Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) would be desirable, since an improved synthesis of this complex is one of the targets of this Thesis. Unfortunately, none of the four products anticipated was actually obtained in the reaction under the conditions employed. When **2.2** was treated with NaBH$_4$ in dry THF for 2 h, the solution changed color from yellow to darker brown. At this time, a sample was removed from the Schlenk to measure the IR (without N$_2$ protection), but the IR spectrum of this solution did not give an obvious CO absorption. This was expected to occur around 1930 ± 30 cm$^{-1}$ for a neutral complex if, for example, H$^-$ attacked CH$_3$CN to give Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(N=CHCH$_3$) as the product. Hexane was used to extract the residue after the solvent was pumped off, but the $^1$H NMR spectrum did not even show a clear Cp* signal. When the reaction was repeated with addition of one drop of water, after 0.5 h, the IR showed a v(CO) absorption for the ethylamine complex **4.1** (Scheme 4.2). This indicated that the stepwise reaction did occur, but the intermediates before the final product **4.1** are air sensitive and decomposed when the sample was removed from an inert atmosphere to record the IR spectrum.

A proposed reaction mechanism is described in Scheme 4.3. Unfortunately, we did not observe the proposed intermediates during the reaction, but related intermediates were reported by Templeton for a tungsten MeCN complex.[117a] The $^1$H NMR spectrum of **4.1**
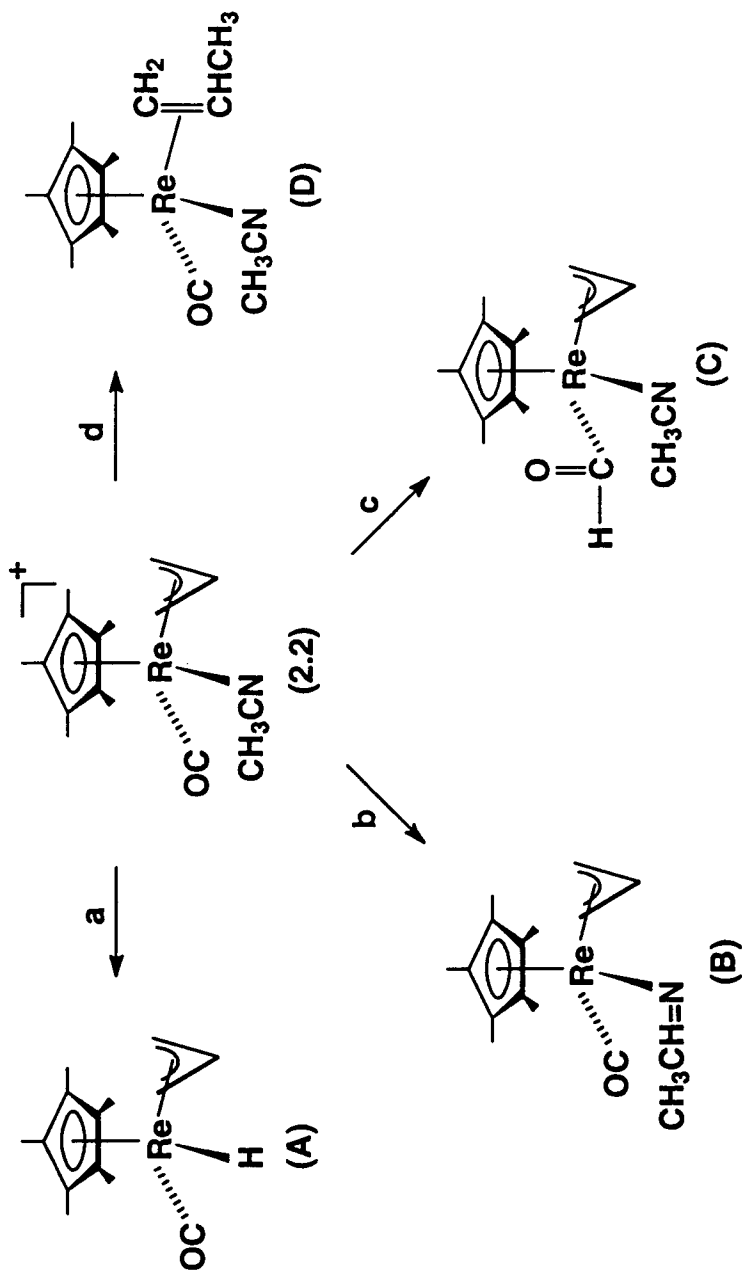
Scheme 4.1. Proposed products from the reaction of **2.2** with hydride.
a. Replacing $CH_3CN$; b. Attacking $CH_3CN$; c. Attacking CO; d. Attacking allyl.
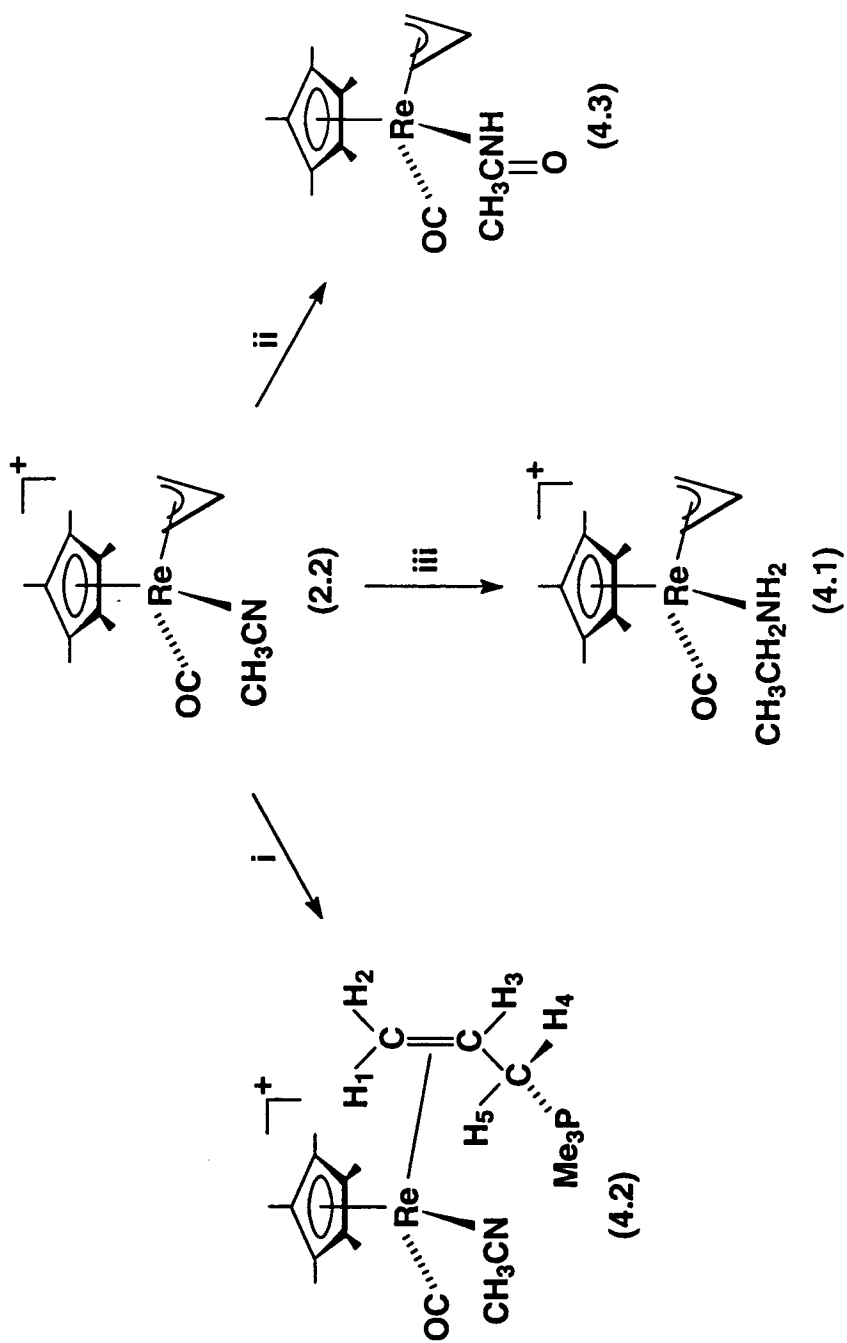
Scheme 4.2. Reactions of complex **2.2** with different nucleophiles.
i. PMe$_3$/CH$_2$Cl$_2$;  ii. NaOH/CH$_3$OH;  iii. NaBH$_4$/THF/H$_2$O.
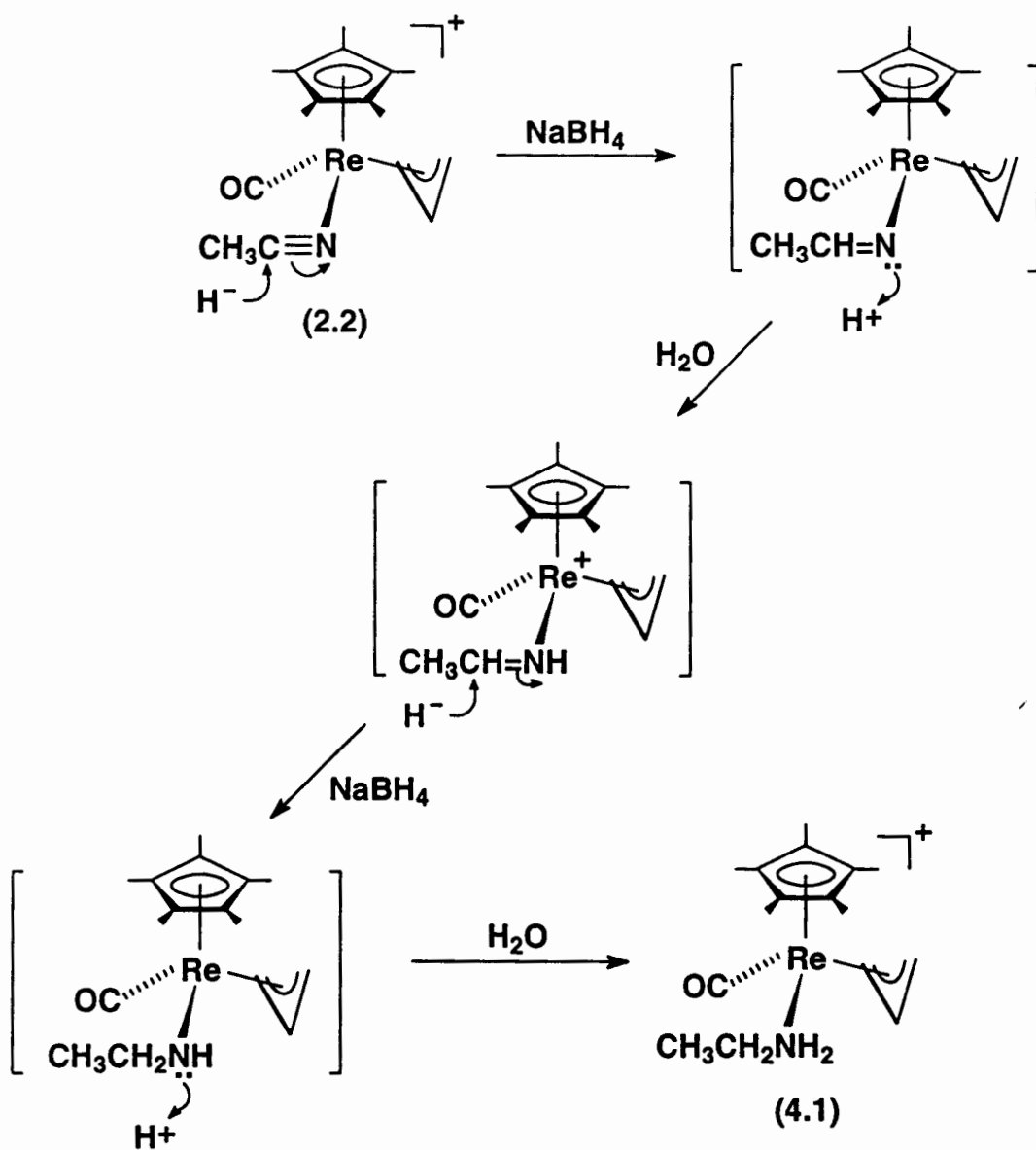
Scheme 4.3. Proposed mechanism for the formation of complex **4.1**.

showed that all five allyl protons are inequivalent and exhibited a similar coupling pattern to that of **2.2** (Tables 4.1 and 4.2). Consequently, the multiplet at δ 5.00 was assigned to H$_c$, the multiplets at δ 3.12 and δ 2.73 to H$_s$, and the doublets at δ 2.05 and δ 1.48 to H$_a$. Broad resonances at δ 3.95 and δ 3.76 were assigned to the diastereotopic NH$_2$ protons. No H–D exchange was observed for these protons over one week at room temperature after D$_2$O was added. The IR spectrum showed ν(CO) at 1937 cm$^{-1}$ (in THF). This compared with ν(CO) of 1975 cm$^{-1}$ (in CH$_2$Cl$_2$) for **2.2** [110] and is an indication that the ethylamine ligand increases back-bonding to the carbonyl by being a stronger σ donor compared with CH$_3$CN and by having no π-acceptor properties.

We tried to react **2.2** with H$_2$ in THF at 1 atm (72 h) by using activated Pd/C as a catalyst, but no reaction occurred.
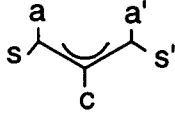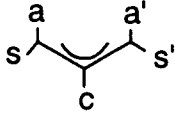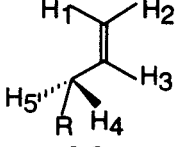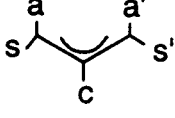
## 4.2.2. Reaction of [Cp*Re(η$^3$-C$_3$H$_5$)(CO)(NCCH$_3$)][BF$_4$] (2.2) with PMe$_3$

Since H$^-$ did not lead to a substitution of coordinated CH$_3$CN, some two electron donor ligands like PMe$_3$, PPh$_3$, and P(OMe)$_3$ were reacted with **2.2** in order to find out the possibility of utilizing complex **2.2** for developing rhenium allyl chemistry. Complex **2.2** did not react with PPh$_3$ or P(OMe)$_3$ in acetone, even after the solution was refluxed overnight. But it did react with PMe$_3$ which, however, did not substitute the CH$_3$CN ligand, but attacked the allyl ligand to form an allyltrimethylphosphonium complex **4.2** (Scheme 4.2). This is, of course, the CH$_3$CN derivative of [Cp*Re(CO)$_2$(η$^2$-CH$_2$CHCH$_2$PMe$_3$)][BF$_4$] (**3.8**), but it is not as stable as **3.8**. It slowly decomposed in solution at 0 °C, even under N$_2$. The IR spectrum of this complex showed ν(CO) at 1823 cm$^{-1}$ (CH$_2$Cl$_2$) (Table 4.1). This can be compared with **2.2** {ν(CO) = 1975 cm$^{-1}$ in CH$_2$Cl$_2$} [110] and, as discussed previously for **3.8**, this indicates more π-back donation to CO since the formal positive charge is now located on the phosphorus atom. The FABMS of **4.2** gave a parent peak at m/z = 508 for M$^+$ of the cation, and fragments at m/z = 467 and m/z = 432 are consistent with the loss of CH$_3$CN and PMe$_3$ separately from the parent ion.

Table 4.1. Spectroscopic Data of Complexes **2.2**, **4.1**, **4.2** and **4.3**.

| Complex | IR {ν(CO), cm$^{-1}$} | MS (m/z) M$^+$ | MS (m/z) Base | $^1$H NMR of δ Cp* (ppm)[h] |
|---------|------------------------|-----------------|-----------------|------------------------------|
| **2.2** | 1975 [a] | 432 | 389 | 1.98 [d] |
| **4.1** | 1937 [b] | 436 | 389 | 1.98 [e] |
| **4.2** | 1823 [a] | 508 | 432 | 1.97 [f] |
| **4.3** | 1952, 1595 [c] | 449 | 379 | 1.54 [g] |

Table 4.2. Chemical Shifts and Coupling Constants of Allyl in **2.2**, **4.1**, **4.2** and **4.3**.

| Complex | Chemical Shifts δ (ppm) and Coupling Constants J (Hz) |
|---------|--------------------------------------------------------|
| **2.2** | 4.85 (m, H$_c$), 3.21 (m, H$_s$), 3.16 (m, H$_{s'}$), 2.04 (d, J$_{ac}$ = 11.6, H$_a$), 1.33 (d, J$_{a'c}$ = 9.3, H$_{a'}$)[d] |
| **4.1** | 5.00 (m, H$_c$), 3.12 (m, H$_{s'}$), 2.73 (m, H$_s$), 2.05 (d, J$_{a'c}$ = 9.7, H$_{a'}$), 1.48 (d, J$_{ac}$ = 8.5, H$_a$)[e] |
| **4.2** | 3.01 (m, H$_4$), 1.93 (m, H$_3$), 1.82 (m, H$_5$), 1.71 (m, H$_1$), 1.43 (m, H$_2$)[f] |
| **4.3** | 4.39 (m, H$_c$), 2.48 (ddd, J$_{s'c}$ = 5.6, J$_{ss'}$ = 3.4, J$_{s'a'}$ = 0.6, H$_{s'}$), 1.92 (dd, J$_{sc}$ = 5.6, J$_{ss'}$ = 3.4, H$_s$), 1.60 (d, J$_{ac}$ = 5.5, H$_a$), 0.76 (d, J$_{a'c}$ = 4.2, H$_{a'}$)[g] |

a. in CH$_2$Cl$_2$; b. in THF; c. in hexane; d. in CDCl$_3$; e. in Acetone-d$_6$; f. in CD$_2$Cl$_2$; g. in C$_6$D$_6$; h. Cp* was a singlet peak in all cases.

The $^1$H NMR of **4.2** showed a multiplet at δ 3.01 which was assigned to one of the diastereotopic -CH$_2$PMe$_3$ protons (H$_4$) and, as expected, it changed to a doublet of doublets after $^{31}$P decoupling. The chemical shift and coupling pattern of H$_4$ are similar to that of **3.8**. The singlet resonance at δ 2.70 ppm integrating for three protons was assigned to the CH$_3$CN ligand. A doublet at δ 1.89 with $J_{PH}$ = 14.0 Hz was assigned to PMe$_3$ methyls, and multiplets at δ 1.93, 1.82, 1.71 and 1.43 to H$_3$, H$_5$, H$_1$ and H$_2$; these assignments were confirmed by $^{31}$P, $^1$H decoupling, $^1$H-$^1$H and $^1$H-$^{13}$C correlation experiments.

The $^{13}$C{$^1$H} NMR spectrum showed a resonance at δ 128.50 which is in a typical position for a nitrile carbon, supporting the presence of coordinated CH$_3$CN. A doublet at δ 25.85 with $J_{PC}$ = 44.2 Hz was assigned to the -CH$_2$PMe$_3$ carbon, and another doublet at δ 8.02 with $J_{PC}$ = 53.2 Hz to PMe$_3$ methyl carbons. These data are typical for the allyltrimethylphosphonium fragment by comparison with literature values [106] and our own results for **3.8**.

### 4.2.3. Reaction of [Cp*Re(η$^3$-C$_3$H$_5$)(CO)(NCMe)][BF$_4$] (2.2) with NaOH

Hydroxycarbonyl complexes have been postulated as intermediates in the reactions of metal carbonyls with water or base to give the corresponding metal-hydrides [117c-e]. We were trying to use the same method to synthesize a rhenium allyl hydrido complex. When **2.2** was treated with NaOH in MeOH at -78 °C, OH$^-$ did not attack the coordinated CO to give Cp*Re(η$^3$-C$_3$H$_5$)(COOH)(NCMe), which might have lead to a hydrido complex Cp*Re(η$^3$-C$_3$H$_5$)(H)(NCMe) by decarboxylation. The nucleophilic attack occurred on the carbon atom in MeCN, followed by a migration of a proton to the nitrogen atom to give the acetamido complex **4.3** (Schemes 4.2 and 4.4).[118] The IR spectrum of **4.3** (in hexane) gave absorptions at 1952 cm$^{-1}$ which was assigned to coordinated CO, and at 1595 cm$^{-1}$ assigned to the amide CO (Table 4.1). The $^1$H NMR in C$_6$D$_6$ (Figure 4.1) showed a broad signal at δ 3.34 integrating for one proton, which is in the range for δ (NH) by comparison with compound **4.1**. The five inequivalent protons of the η$^3$-allyl group were assigned on
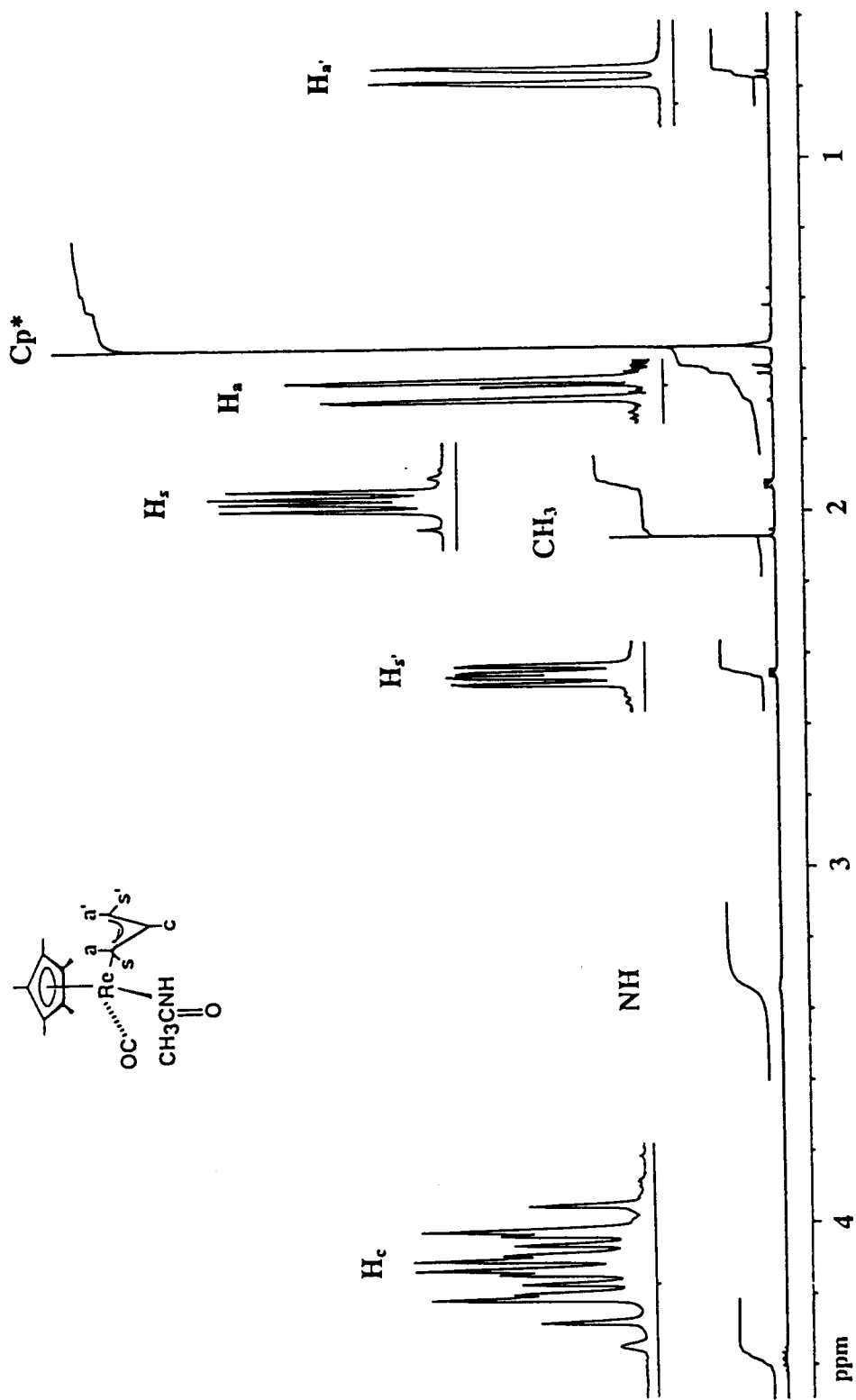
Figure 4.1. $^1$H NMR spectrum of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(NHCOCH$_3$) (4.3) in C$_6$D$_6$.

99

the basis of NOE experiments. Saturation at $\delta$ 0.76 ($H_{a'}$) induced enhancements at $\delta$ 1.54 (Cp*), $\delta$ 1.60 ($H_a$) and $\delta$ 2.48 ($H_{s'}$). Irradiation of Cp* at $\delta$ 1.54 gave an enhancement at $\delta$ 0.76 for $H_{a'}$, and indicated the $\eta^3$-allyl group to be in the *endo* conformation in complex **4.3**. The EIMS gave strong peaks for $M^+$ and $[M^+ - CO]$, but the peak for $[M^+ - NHCOCH_3]$ at m/z 391 was hardly detectable. An attempt to protonate the coordinated amide with $HBF_4$ at -78 °C resulted in loss of carbonyl IR absorption. No product extracted into hexane or ether according to NMR spectra, and the residue left from these extractions did not give a clear Cp* signal in the $^1H$ NMR spectrum.

Hydrolysis of coordinated acetonitrile has been commonly reported and the mechanism has been discussed (Scheme 4.4).[118] Recent examples for platinum [119] and tungsten [120] complexes have been reported.
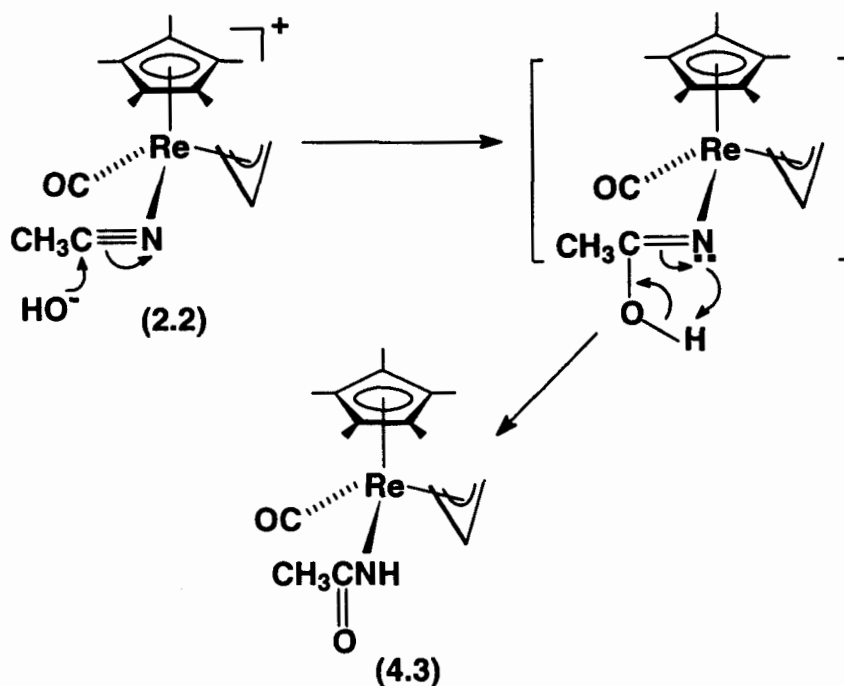


Scheme 4.4. Hydrolysis reaction of coordinated $CH_3CN$.

## 4.3. Reactivity of [Cp*Re(η³-C₃H₅)(NCMe)₂][BF₄] (2.3)

### 4.3.1. Reaction of [Cp*Re(η³-C₃H₅)(NCMe)₂][BF₄] (2.3) with NaBH₄

The reduction of one coordinated acetonitrile by NaBH₄ in the presence of a proton source to give ethylamine complexes has been reported,[117a,b] and as mentioned above it was also observed for the mono acetonitrile rhenium compound **2.2**. The reduction of two coordinated acetonitriles has not been reported in previous work. Based on the result from **2.2**, complex **2.3** was reacted with NaBH₄ under the same conditions, and the bis-ethylamine complex [Cp*Re(η³-C₃H₅)(NH₂CH₂CH₃)₂][BF₄] **(4.4)** (Scheme 4.5) was obtained, where both CH₃CN ligands have been reduced to the ethylamine. The FABMS spectrum of **4.4** showed a parent peak for the cation at m/z = 453, and a base peak at m/z = 406 which was resulted from the loss of one ethylamine ligand and 2H (presumably from Cp*) (Table 4.3).[83]

The ¹H NMR spectrum of **4.4** (Figure 4.2) gave two broad signals at δ 3.50 and δ 3.38 which are assigned to the two diastereotopic NH₂ protons. The two ethylamine ligands are, however, equivalent by symmetry. Therefore the η³-allyl protons gave, as expected, only three signals assigned as: δ 3.77 (H$_c$), δ 2.44 (H$_s$), and δ 1.52 (H$_a$). Saturation of the CH₂ multiplet at δ 2.50 resulted in a broad AB quartet for the NH protons. All the assignments were confirmed by ¹H NMR decoupling experiments.

### 4.3.2. Reaction of [Cp*Re(η³-C₃H₅)(NCMe)₂][BF₄] (2.3) with PMe₃

Although PMe₃ attacked the allyl group in the mono-acetonitrile complex **2.2**, it did not undergo nucleophilic attack on the allyl in complex **2.3**. It can be rationalized that the coordination of the second acetonitrile increased the electron density on the metal center, and therefore, the positive charge on the complex, whether located on the metal center or the allyl, was partially neutralized. This accounts for the electrophilic ability of the allyl ligand decreasing in the order **2.1** > **2.2** > **2.3**. PMe₃ reacted with **2.3** to give **4.5** in which one CH₃CN was substituted by PMe₃ (Scheme 4.5). Increasing the amount of
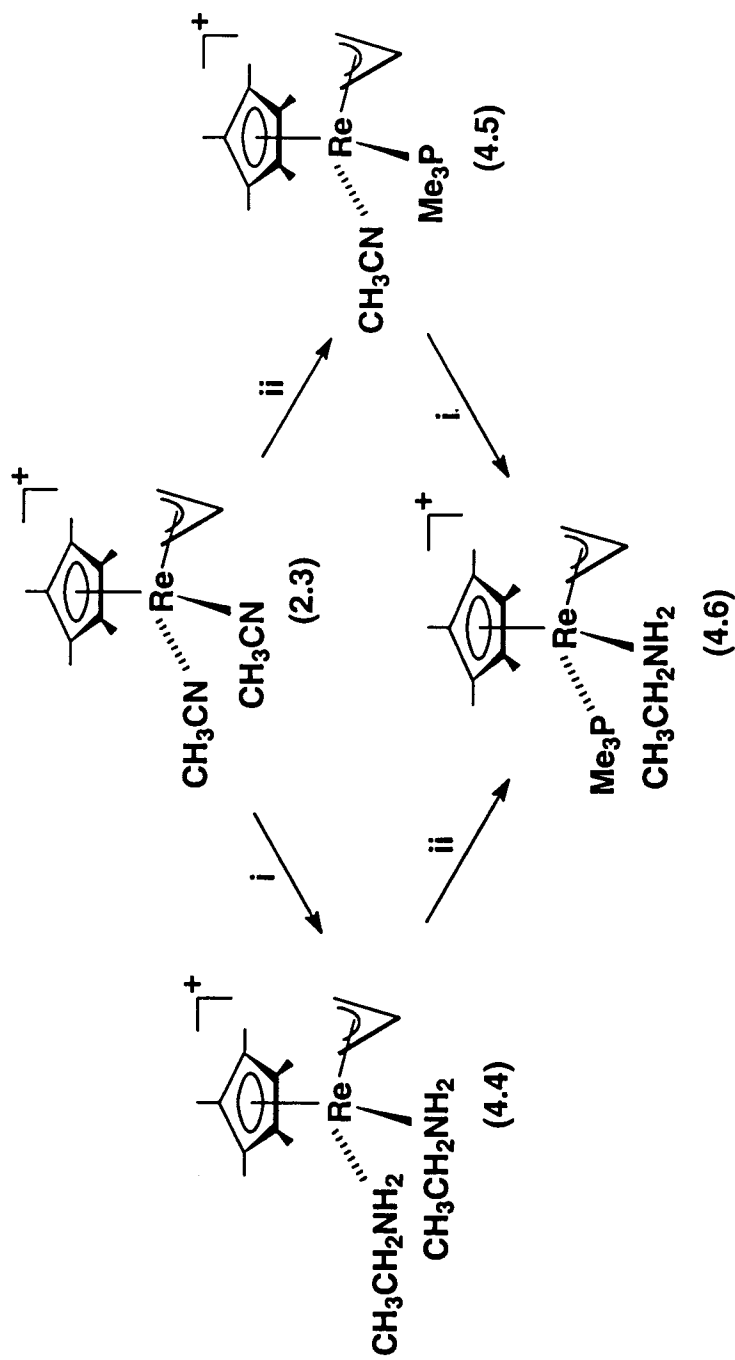
Scheme 4.5. Reactions of complex 2.3 with different nucleophiles.
i. NaBH$_4$/THF/H$_2$O; ii. PMe$_3$/CH$_2$Cl$_2$.
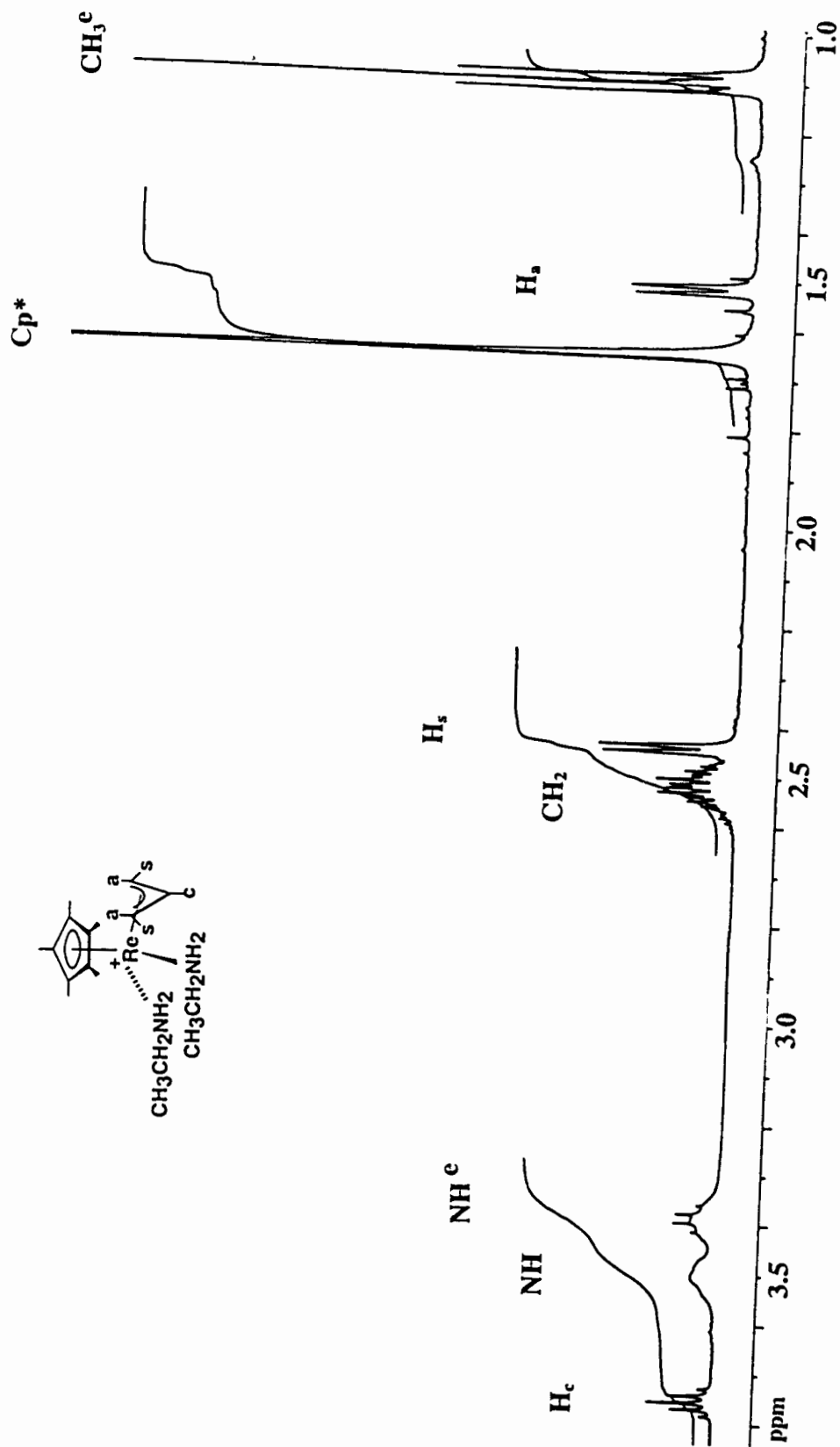
Figure 4.2. $^1$H NMR spectrum of $[Cp*Re(\eta^3\text{-}C_3H_5)(NH_2CH_2CH_3)_2][BF_4]$ (4.4) in acetone-$d_6$. e. Superimposed with ether signal.

103

PMe₃ and reaction time did not lead to the substitution of the second nitrile ligand to give the bis-PMe₃ complex. The FABMS for **4.5** gave a parent peak at m/z = 480 for the cation M⁺, and base peak at m/z = 439 which is consistent with the loss of $CH_3CN$ from M⁺ (Table 4.3). The ¹H NMR spectrum for **4.5** (Figure 4.3) gave a doublet at δ 2.84 ($J_{PH}$ = 2.2 Hz) assigned to the coordinated $CH_3CN$, and a doublet at δ 1.38 ($J_{PH}$ = 8.8 Hz) assigned to the PMe₃ ligand. The chiral rhenium center makes all five protons for the η³-allyl ligand inequivalent, giving resonances for $H_c$ at δ 3.68, $H_s$ at δ 2.26 and δ 2.14, and $H_a$ at δ 1.45 and δ 1.03.

Table 4.3. Spectroscopic Data of Complexes **2.3**, **4.4**, **4.5** and **4.6**.

| Complex | MS (m/z) | | ¹H NMR δ (ppm) and Coupling Constants J (Hz) | |
| --- | --- | --- | --- | --- |
| | M⁺ | Base | Cp*[a] | η³-allyl |
| **2.3**[b] | 445 | 361 | 1.71 | 3.81 (m, $H_c$), 2.47 (d, $J_{sc}$ = 5.0, $H_s$), 1.47 (d, $J_{ac}$ = 6.3, $H_a$) |
| **4.4**[c] | 453 | 406 | 1.67 | 3.77 (m, $H_c$), 2.44 (d, $J_{sc}$ = 4.9, $H_s$), 1.52 (d, $J_{ac}$ = 6.7, $H_a$) |
| **4.5**[b] | 480 | 439 | 1.73 | 3.68 (m, $H_c$), 2.26 (m, $H_{s'}$), 2.14 (m, $H_s$), 1.45 (m, $H_{a'}$), 1.03 (m, $H_a$) |
| **4.6**[b] | 484 | 439 | 1.69 | 3.67 (m, $H_c$), 1.92 (m, $H_{s'}$), 1.83 (m, $H_s$), 1.43 (m, $H_{a'}$), 1.13 (m, $H_a$) |

a. Cp* was a singlet peak in all cases; b. in $CDCl_3$; c. in acetone-d₆.
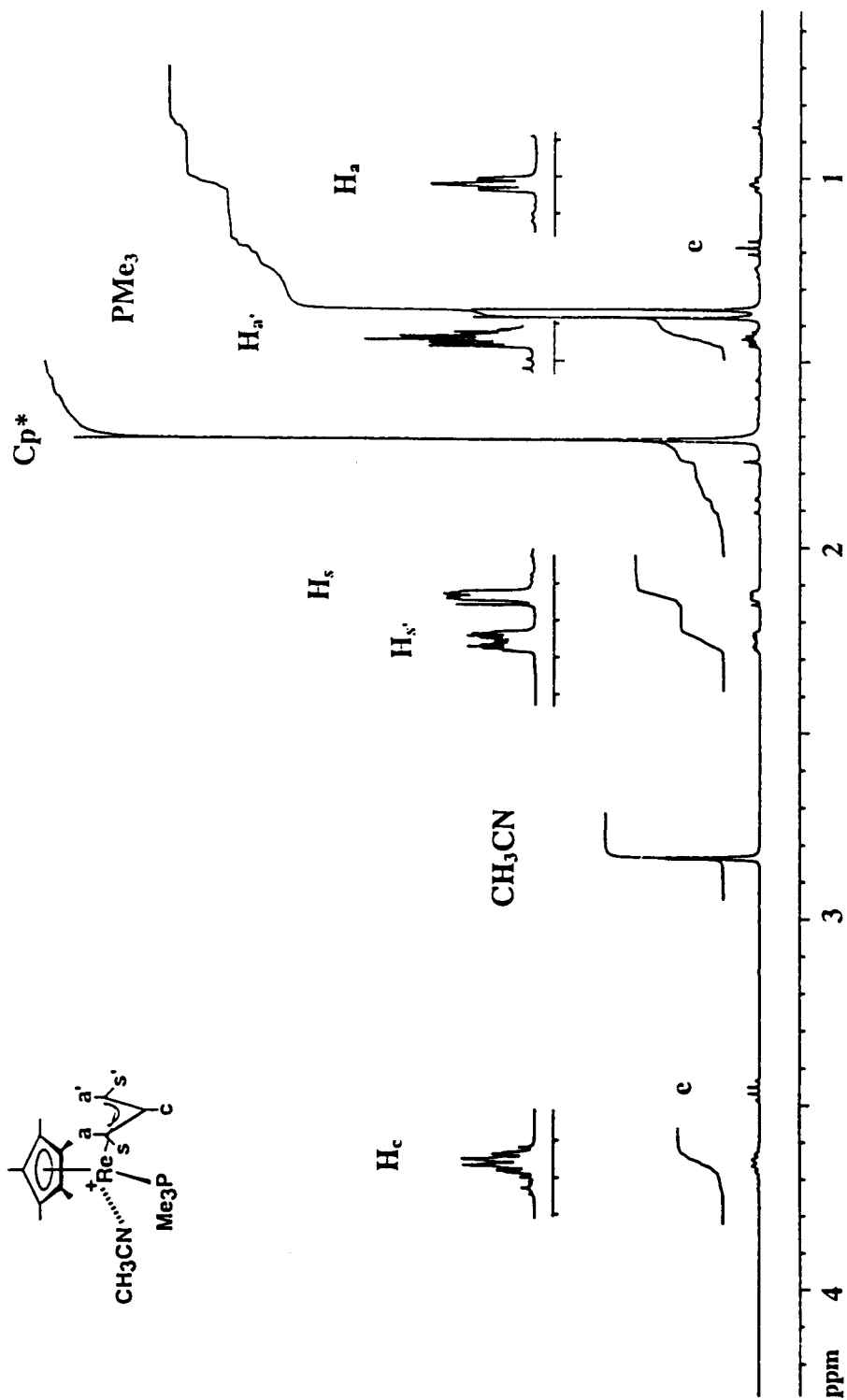
Figure 4.3. $^1$H NMR spectrum of $[Cp*Re(\eta^3-C_3H_5)(CH_3CN)(PMe_3)][BF_4]$ (4.5) in

CDCl$_3$. e. ether signal.

### 4.3.3. Reaction of [Cp*Re($\eta^3$-C$_3$H$_5$)(NH$_2$CH$_2$CH$_3$)$_2$][BF$_4$] (4.4) with PMe$_3$

When complex **4.4** was treated with PMe$_3$ in CH$_2$Cl$_2$ or acetone at room temperature overnight, one ethylamine ligand in **4.4** was substituted by PMe$_3$ to produce complex [Cp*Re($\eta^3$-C$_3$H$_5$)(NH$_2$CH$_2$CH$_3$)(PMe$_3$)][BF$_4$] (**4.6**). A small impurity due to the bis-PMe$_3$ complex [Cp*Re($\eta^3$-C$_3$H$_5$)(PMe$_3$)$_2$][BF$_4$] (M$^+$ = 515, very weak intensity) can be observed in the FABMS of isolated **4.6**, but no matter how much excess PMe$_3$ was utilized or for how long the reaction was conducted at room temperature, all attempts to prepare the bis-PMe$_3$ complex were unsuccessful.

The FABMS spectrum of **4.6** showed M$^+$ for the cation at m/z = 484 and a base peak at m/z = 439 which is in agreement with the loss of CH$_3$CH$_2$NH$_2$ from M$^+$. A comparison of the $^1$H NMR spectrum of **4.6** with that of **4.5** showed that the CH$_3$CN resonance for **4.5** at $\delta$ 2.84 had disappeared and there were two new broad resonances at $\delta$ 3.15 and $\delta$ 2.58 which are assigned to the NH$_2$ protons of the newly generated ethylamine ligand which also exhibits the expected ethyl resonances. The PMe$_3$ resonance occurred at a similar position to that in **4.5**, $\delta$ 1.39 ($J_{PH}$ = 7.4 Hz). The presence of the PMe$_3$ ligand in **4.5** and **4.6** resulted in long range coupling to the $\eta^3$-allyl protons, causing especially the resonance of the proximal H$_a$ protons to be a multiplet rather than the usual doublet. In **4.5** even the CH$_3$CN ligand methyl protons were weakly coupled to phosphorus resulting in a doublet of separation 2.2 Hz (Figure 4.3).

### 4.3.4. Reaction of [Cp*Re($\eta^3$-C$_3$H$_5$)(PMe$_3$)(CH$_3$CN)][BF$_4$] (4.5) with NaBH$_4$

As in complexes **2.2** and **2.3**, the CH$_3$CN ligand in complex **4.5** can also be reduced by NaBH$_4$ in THF/H$_2$O solution to give the corresponding ethylamine complex [Cp*Re($\eta^3$-C$_3$H$_5$)(PMe$_3$)(CH$_3$CH$_2$NH$_2$)][BF$_4$] (**4.6**). Complex **4.6** was first synthesized from the substitution of one CH$_3$CH$_2$NH$_2$ ligand in complex **4.4** by PMe$_3$, which was mentioned previously in section 4.3.3.

## 4.4. Discussion

### 4.4.1. Mass Spectra of Complexes 4.1-4.6

The FAB mass spectrum of **4.1** gave four fragments, where m/z 436 is the parent peak of the cation, m/z 391 and m/z 389 are consistent with the loss of $CH_3CH_2NH_2$ and $[CH_3CH_2NH_2 + 2H]$ from $M^+$ separately, and m/z 361 is a fragment from losing $[CH_3CH_2NH_2 + CO + 2H]$. The $M^+$ peak is 60% intensity in comparison with the base peak of m/z 389. This is probably an indication of the stability of **4.1** under FAB conditions. For a comparison with the other two amine complexes **4.4** and **4.6**, $M^+$ of **4.6** (m/z 484) is about 12% of the base peak m/z 439, while $M^+$ of **4.4** (m/z 453) is 10% of the base peak m/z 362. This is in a good agreement with the reactivity of complexes **4.1-4.4**, since the $CH_3CH_2NH_2$ in **4.4** was easily replaced by $PMe_3$ to give **4.6**, while attempts at replacing $CH_3CH_2NH_2$ in **4.1** were not successful.

The parent peak of **4.2**, m/z 508, is 9% of the base peak m/z 432 which results from loss of $PMe_3$ from $M^+$. The mass spectrum of **4.5** showed a preference for losing $CH_3CN$ to give a base peak at m/z 439 [$Cp*Re(C_3H_5)(PMe_3)$], while for **4.1**, **4.4** and **4.6**, loss of $CH_3CH_2NH_2$ was preferred. The fragments $Cp*Re(C_3H_5)$ (m/z = 363) or $[Cp*Re(C_3H_5) - 2H]$ (m/z = 361) were the most stable species in all cases for the mass spectra of **4.1-4.6**.

### 4.4.2. $^1$H NMR Spectroscopy

The room temperature 400 MHz $^1$H NMR spectra of complexes **4.1-4.6** were recorded in different solvents as reported in Tables 4.1, 4.2 and 4.3. There are several aspects which are typical for these allyl complexes. First of all, the allyl group in complexes **4.1**, **4.2**, **4.3**, **4.5** and **4.6** is bound to a chiral rhenium center, so all five allyl protons are inequivalent. This leads to the *syn* protons exhibiting multiplets from coupling with $H_c$, *anti* $H_a$ and the other *syn* proton $H_{s'}$. "W conformation" long range coupling is observed for the *syn* protons. Especially in **4.3** (Figure 4.1), one *syn* proton is a doublet of

107

doublets with $J_{sc}$ = 5.6 Hz, $J_{ss'}$ = 3.4 Hz, and the other *syn* proton showed a clear doublet of doublets of doublets pattern with *syn-anti* coupling of 0.6 Hz. In complex **4.4**, the symmetry results in both *syn* and *anti* protons from the allyl ligand being doublets (Figure 4.2).

Complexes **4.1**, **4.4** and **4.6** gave strong NH$_2$ proton signals at 2.5-4.0 ppm in CDCl$_3$, which are broad triplets with a coupling of 10.5 Hz from the adjacent CH$_2$ group. In **4.4**, when one NH$_2$ proton signal at δ 3.38 was saturated, the other one at δ 3.50 decreased also; the same thing occurred for the resonance at δ 3.38 when δ 3.50 was saturated. This is because the two signals are so close that when one was saturated, the other one was unavoidably saturated also. No exchange is expected to occur between the two NH$_2$ protons, and we do not consider this is responsible for the intensity changes observed. The CH$_2$ group in the ethylamine ligand gave a complicated multiplet from coupling with both NH$_2$ and CH$_3$, while CH$_3$ is a typical triplet with a separation of 7.0 Hz in all the ethylamine complexes.

### 4.4.3. Reactivity of [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(NH$_2$CH$_2$CH$_3$)][BF$_4$] (4.1)

When **4.1** was treated with PMe$_3$ at room temperature for 72 h, no substitution of EtNH$_2$ by PMe$_3$ occurred, nor was the $\eta^3$-allyl group attacked by PMe$_3$. Thus, the replacement of CH$_3$CN by EtNH$_2$ has made the complex inactive toward nucleophilic attack by PMe$_3$, probably due to the increased electron density at the rhenium center as reflected by the ν(CO) values (1956 cm$^{-1}$ for **2.2**, and 1937 cm$^{-1}$ for **4.1**, in KBr).

Attempts to deprotonate the CH$_3$CH$_2$NH$_2$ ligand in this cationic complex were carried out by using DBU or *t*-BuLi. In each case, loss of ν(CO) in the IR spectrum and the disappearance of the Cp* resonance in the $^1$H NMR spectrum indicated decomposition. Presumably the expected product Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(NHCH$_2$CH$_3$) is unstable. This is a visualized intermediate in the stepwise reduction of **2.2**. The result is therefore consistent with the fact that in the attempted stepwise reduction of **2.2** to **4.1** intermediates were not observed (see section 4.2.1).

### 4.4.4. Reactivity of $[Cp*Re(\eta^2-C_3H_5PMe_3)(CO)(CH_3CN)][BF_4]$ (4.2)

Reactions of **4.2** with PhIO or $Me_3NO$ in $CH_3CN$ or $CH_2Cl_2$ were attempted to see if CO could be oxidatively removed and lead to further $CH_3CN$ coordination or possibly a transfer of $PMe_3$ to the rhenium center. These resulted in loss of $v(CO)$ in the IR spectrum indicating oxidative removal of CO was successful, but the $^1H$ NMR appeared to indicate loss of the Cp* signal and no identifiable products could be isolated from the resulting oily material obtained.

A reversible reaction of **4.2** to **2.2** was detected from the $^1H$ NMR spectrum of **4.2** after the sample was kept at -78 °C in $CD_2Cl_2$ for 72 h without the presence of excess $PMe_3$ (Equation 4.1). Besides all the signals for **4.2**, the Cp* signal at $\delta$ 1.94, and $CH_3CN$ signal at $\delta$ 2.74 for **2.2** occurred. A multiplet $H_c$ at $\delta$ 4.85, two doublets of doublets at $\delta$ 3.16, 3.02 for the two $H_s$, and two doublets at $\delta$ 2.00 and $\delta$ 1.37 for the $H_a$ were unambiguously assigned to **2.2** by comparison with the $^1H$ NMR data from the pure **2.2**. A doublet at $\delta$ 1.46 with a coupling of 12.8 Hz was assigned to $Me_3PO$ which was produced from the oxidation of the free $PMe_3$ dissociated from **4.2**. The removing of $PMe_3$ in this way induced further dissociation of $PMe_3$ in complex **4.2**, and the stability of it decreased. The ratio of **4.2/2.2** = 1.0/1.5 according to the intensity of the Cp* signals when the $^1H$ NMR spectrum of the sample was recorded.
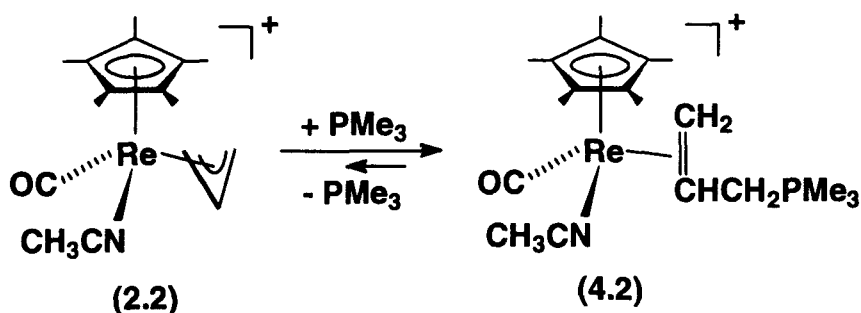


Equation 4.1. Reversible reaction of **4.2** to **2.2** in $CD_2Cl_2$ at -78 °C.

## 4.5. X-ray Structure Determination of [Cp*Re($\eta^3$-C$_3$H$_5$)(NH$_2$CH$_2$CH$_3$)$_2$][ReO$_4$]

Crystals for the X-ray structure determination were grown from a solution of **4.4** in acetone-toluene over a period of three months. The structure determination was kindly carried out by Dr. F. W. B. Einstein and Dr. R. J. Batchelor, and confirmed the presence of the cation of **4.4**, [Cp*Re($\eta^3$-C$_3$H$_5$)(NH$_2$CH$_2$CH$_3$)$_2$]$^+$ (Figure 4.4), but the anion could not be satisfactorily modeled as the expected ion [BF$_4$]$^-$ based on the analysis and IR spectrum of the original material. The anion present in the crystal was best interpreted as [ReO$_4$]$^-$, and we presume that this has arisen from an unidentified reaction during the long period in solution prior to growth of crystals. The allyl group adopts the *endo* orientation, just as it has previously been shown to do in the crystal structures of **2.2** and **2.3**.[110]

The molecular structure of [*endo*-Cp*Re($\eta^3$-C$_3$H$_5$)(NH$_2$CH$_2$CH$_3$)$_2$]$^+$ is shown in Figure 4.4, and the selected intramolecular distances and angles are given in Table 4.4. The structure of the cation is closely comparable to that of complex [Cp*Re($\eta^3$-C$_3$H$_5$)(NCMe)$_2$]$^+$,[110] and in fact there are no significant differences in the internal dimensions of the Cp*Re($\eta^3$-C$_3$H$_5$) fragments in the two structures. Even the placement of the nitrogen atoms in the Re-atom coordination sphere is closely similar, with the exception that the Re-N bond lengths, as expected, are longer (2.228(7) Å), for ethylamine, than acetonitrile (2.089(7) and 2.086(10) Å).

## 4.6. Stereochemical Considerations

The X-ray structure determination shows that the allyl ligand adopts the *endo* configuration in the bis-ethylamine complex cation [Cp*Re($\eta^3$-C$_3$H$_5$)(NH$_2$CH$_2$CH$_3$)$_2$]$^+$ of **4.4**, just as it does in the mono- and bis-acetonitrile complex cations [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(NCCH$_3$)]$^+$ and [Cp*Re($\eta^3$-C$_3$H$_5$)(NCCH$_3$)$_2$]$^+$ in **2.2** and **2.3**.[110] The $^1$H NMR spectra of **4.4** indicate the presence of only one isomer in solution also, and because the chemical shifts and coupling constants of the allyl protons in **4.4** are very similar to those of **2.2** and **2.3** which have been previously established to be *endo* isomers in solution by
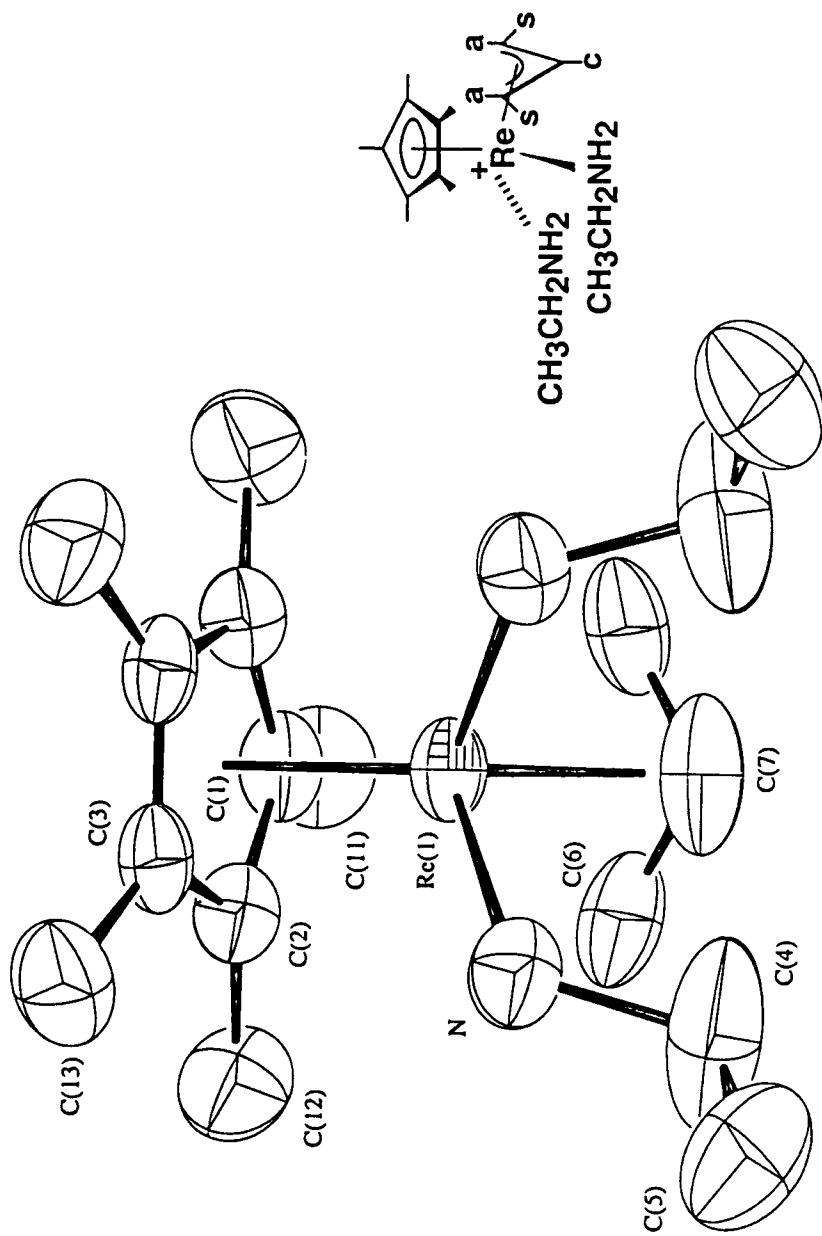
Figure 4.4. The structure of the cation $[Cp^*Re(\eta^3\text{-}C_3H_5)(NH_2CH_2CH_3)_2]^+$ in (4.4).

Table 4.4. Selected Intramolecular Distances (Å) and Angles ($^{\circ}$) for

$[Cp*Re(\eta^3\text{-}C_3H_5)(NH_2CH_2CH_3)_2][ReO_4]$ solv.

| Distances (Å) | | Distances (Å) | |
|---|---|---|---|
| Re(1) - N | 2.228(7) | Re(1) - C(7) | 2.090(13) |
| Re(1) - C(1) | 2.160(11) | Re(1) - Allyl [b] | 1.884 |
| Re(1) - C(2) | 2.215(8) | N - C(4) | 1.470(10) |
| Re(1) - C(3) | 2.333(8) | C(4) - C(5) | 1.495(12) |
| Re(1) - Cp* [a] | 1.892 | C(6) - C(7) | 1.412(12) |
| Re(1) - C(6) | 2.177(9) | | |

| Angles ($^{\circ}$) | | Angles ($^{\circ}$) | |
|---|---|---|---|
| N - Re(1) - N' | 79.8(4) | C(4) - N - Re(1) | 125.2(6) |
| N - Re(1) - Cp* | 114.5 | C(5) - C(4) - N | 114.5(9) |
| N - Re(1) - Allyl | 101.7 | C(6) - C(7) - C(6)' | 114.1(13) |
| Cp* - Re(1) - Allyl | 132.0 | | |

a. Cp* denotes the center of mass of the carbon atoms of the cyclopentadienyl ring.

b. Allyl denotes the center of mass of the carbon atoms of the allyl group.

NOE,[110] it is highly probable that **4.4** is present as the *endo* isomer in solution. Similarly, we assign all the other allyl complexes in this study, i.e., **4.1, 4.3, 4.5** and **4.6**, to be *endo* isomers. Therefore, there seems to be a general tendency for the *endo* isomer to be preferred when the electron withdrawing CO groups in **2.1** are replaced by the better donors MeCN, EtNH₂ etc.

Where the allyl group in **2.2** has been converted to a substituted propene complex as in **4.2**, and the ancillary ligands are inequivalent (i.e., CO and CH₃CN), four possibilities exist for the stereochemistry of the resulting complex **4.2** which will depend on the site of nucleophilic attack and the most stable alkene rotamer. These possibilities are shown in Scheme 4.6 (**a-d**). In this case, the C=C axis of the alkene is expected to be tilted toward the poorest π-accepting substituent, which is MeCN. There is both theoretical [113] and experimental support for alkene tilting in this way in, for example, CpMo(NO)(CO) (alkene) [113c] and, more importantly, the rhenium complexes [CpRe(NO)(PPh₃)(alkene)]⁺ [121] and [Cp*Re(NO)(PPh₃)(alkene)]⁺.[122] For complex [CpMo(NO)(CO)(allyl)]⁺, the nucleophilic addition to the allyl group results in the formation of only a single diastereomer, and the product observed is that which could result from nucleophilic addition *syn* to the better π-accepting nitrosyl group in the *exo* isomer or *anti* to the nitrosyl in the *endo* isomer.[90,113c,121] If this regioselectivity can legitimately be extended to the present rhenium carbonyl acetonitrile complexes, it would predict that nucleophilic addition to the *endo*-allyl would occur *anti* to the carbonyl, as depicted in Scheme 4.6, and would lead for **4.2** to formation of the diastereomer **c** (or its rotamer **d**) rather than configurations **a** or **b** (which would arise from addition *syn* to CO in the *endo* allyl group).

The pattern of allyl proton chemical shifts that we observe, i.e., $\delta H_2 < \delta H_1 < \delta H_3$ (for numbering scheme see Scheme 4.7 **e**) is similar to the pattern carefully established for the thermodynamically preferred conformer in [Cp*Re(NO)(PPh₃)(alkene)]⁺ by Gladysz (shown in Scheme 4.7 **f**), and on this basis we propose that the observed rotamer is **c**. However, we cannot rule out rapid interconversion of isomer **c** and **d**. (Notably, complex

Rotamers



(a)

(b)

Diastereomers

Rotamers



(c)

(d)
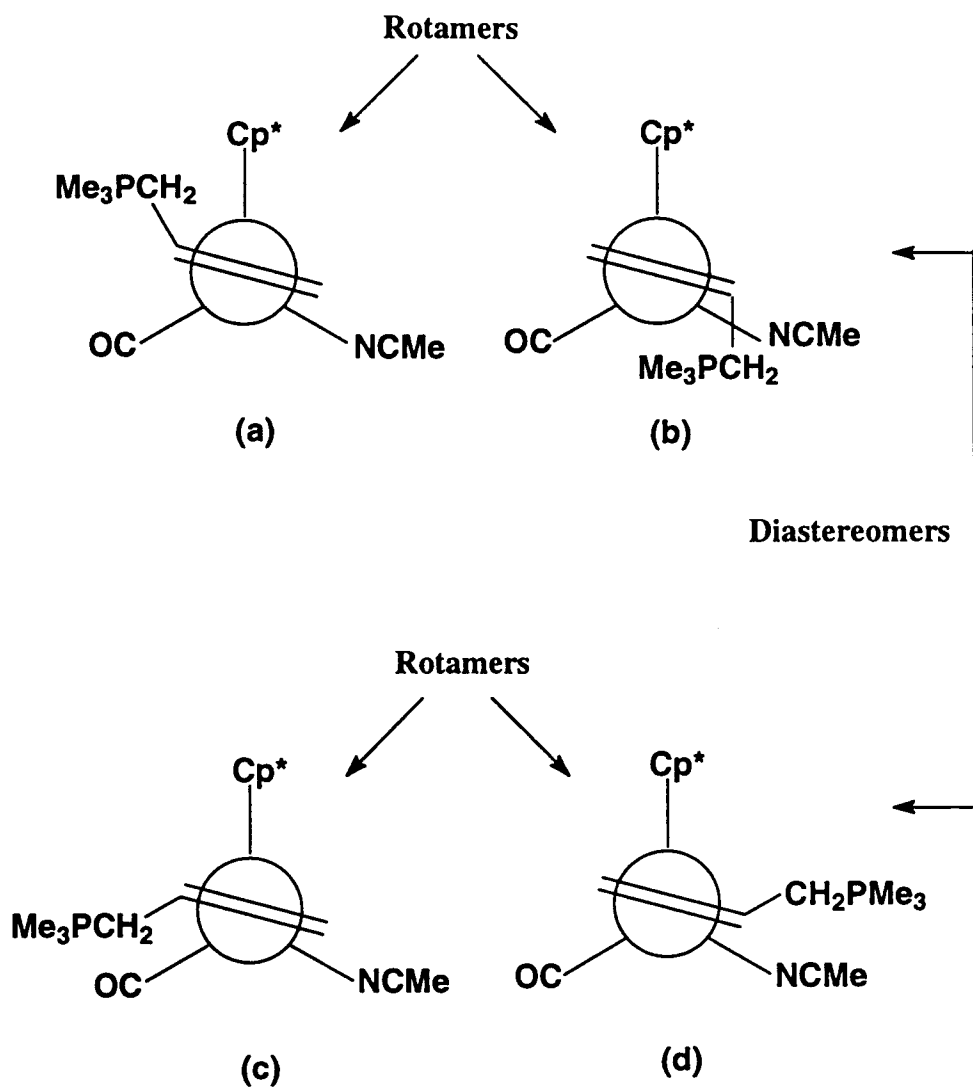
Scheme 4.6. Isomers of **4.2** produced from $PMe_3$ attacking different side of the $\eta^3$-allyl in **2.2**.

**(e)**                        **(f)**
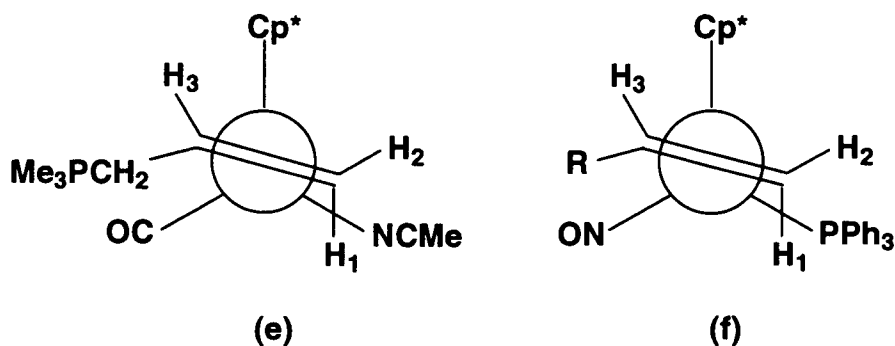
Scheme 4.7. e. Preferred isomer for $[Cp*Re(NCMe)(CO)(\eta^2\text{-}C_3H_5PMe_3)]^+$ **4.2**.

f. Preferred isomer for $[Cp*Re(NO)(PPh_3)(alkene)]^+$.

CpMo(NO)(CO)(propene) was observed to give a single set of propene resonances at room temperature indicating a single diastereomer, but two sets of resonances corresponding to individual propene rotamers at -80 °C ).[113c]

## 4.7. Conclusions

The acetonitrile ligands in complexes $[Cp*Re(\eta^3\text{-}C_3H_5)(CO)(NCMe)][BF_4]$ **(2.2)** and $[Cp*Re(\eta^3\text{-}C_3H_5)(NCMe)_2][BF_4]$ **(2.3)** are strong competitors with the allyl ligand as targets in the regiochemistry of nucleophilic attack and are a poor choice of leaving group as regards ligand substitution at the metal.

The coordinated acetonitrile has been observed to be reduced to coordinated ethylamine without showing any intermediates for stepwise reduction, and indeed both such groups were reduced in the case of the bis-acetonitrile complex **2.3**.

The only displacement of $CH_3CN$ by $PMe_3$ we have observed is from **2.3** and even then only one of the acetonitriles could be easily substituted. This is in stark contrast with what might be thought (on the basis that $N_2Ar$ and $C_3H_5$ are both 3e-donor ligands) to be rather closely related aryldiazenido complexes $[Cp*Re(CO)(NCMe)(N_2Ar)][BF_4]$ and $[Cp*Re(NCMe)_2(N_2Ar)][BF_4]$ that we have studied. In these complexes, one or both

acetonitrile groups can be readily substituted by a range of trialkyl or triaryl phosphines.[123,124]

Clearly, replacing one or two CO groups by MeCN dramatically lowers the electrophilicity of the allyl group and it is decreased further in the bis ethylamine complex **4.4**, to the point that now no attack of PMe₃ occurs at the allyl group. Even so, only one of the two possible $CH_3CH_2NH_2$ ligands is substituted by PMe₃. One of the target compounds that prompted this work is the interesting stable hydrido allyl complex $Cp^*ReH(CO)(\eta^3-C_3H_5)$ [1d] and we were seeking a possible alternative method of synthesis by substituting acetonitrile in **2.2** by hydride. In view of the outcome, other strategies for its synthesis needed to be developed, and will be reported in Chapter V.

## 4.8. Experimental Details

### 4.8.1. General Procedure

All reactions were carried out under dry nitrogen in Schlenk apparatus. Solvent purification, spectroscopic measurements, and the crystal structure analysis were carried out as described in Chapter II.

## 4.8.2. Preparation of [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(NH$_2$Et)][BF$_4$] (4.1)

Complex **2.2** (63.9 mg, 0.12 mmol) was dissolved in THF (5 mL) at 0 °C. NaBH$_4$ (6.0 mg, 0.16 mmol) and two drops of H$_2$O were added to the solution. The $\nu$(CO) band from **2.2** disappeared after the solution was stirred for 3 h at 0 °C and was replaced by a new $\nu$(CO) absorption at 1937 cm$^{-1}$. The reaction mixture was filtered through Celite, and the solvent pumped off. The residue was extracted with THF/hexane (5/1) and recrystallized from THF/hexane (1/6). A yellowish solid was obtained in analytical purity. Yield: 30.0 mg (0.058 mmol, 48%), m. p.: at 180 °C, the sample decomposed and gave black solid. IR (cm$^{-1}$, THF): $\nu_{CO}$ = 1937. FABMS (m/z): 436 (M$^+$ of cation), 391 (M$^+$ - EtNH$_2$), 389 (M$^+$ - EtNH$_2$ - 2H, base), 361 (M$^+$ - EtNH$_2$ - CO - 2H). $^1$H NMR (acetone-d$_6$, $\delta$): 5.00 (1H, m, H$_c$), 3.95 (1H, br, NH$_2$), 3.76 (1H, br, NH$_2$), 3.12 (1H, m, H$_s$), 2.73 (1H, m, H$_s$), 2.55 (2H, m, CH$_2$), 2.05 (1H, d, $J_{a'c}$ = 9.7 Hz, H$_{a'}$), 1.98 (15H, s, Cp*), 1.48 (1H, d, $J_{ac}$ = 8.5 Hz, H$_a$), 1.05 (3H, t, CH$_3$). Anal. Calcd. for C$_{16}$H$_{27}$BF$_4$NRe: C, 36.79; H, 5.20; N, 2.67; Found: C, 37.01; H, 5.15; N, 2.62.

## 4.8.3. Preparation of [Cp*Re($\eta^2$-CH$_2$CHCH$_2$PMe$_3$)(CO)(NCMe)][BF$_4$] (4.2)

Complex **2.2** (20.0 mg, 0.04 mmol) was dissolved in CH$_2$Cl$_2$ (4 mL), and PMe$_3$ (0.1 mL, 0.97 mmol) was added to this solution. The mixture was stirred at room temperature for 30 min, at the end of which the IR showed a $\nu$(CO) band at 1823 cm$^{-1}$. Excess PMe$_3$ and solvent were pumped off and the residue was recrystallized from THF/hexane (2/5). A yellow solid was obtained, m. p.: 85-86 °C. Yield: 15.6 mg (0.026 mmol, 65%). IR (CH$_2$Cl$_2$, cm$^{-1}$): $\nu_{CO}$ = 1823. FABMS (m/z): 508 (M$^+$ of cation), 467 (M$^+$ - MeCN), 432 (M$^+$ - PMe$_3$, base), 391 (M$^+$ - PMe$_3$ - MeCN), 389 (M$^+$ - PMe$_3$ - MeCN - 2H). $^1$H NMR (CD$_2$Cl$_2$, $\delta$): 3.01 (1H, m, H$_4$), 2.70 (3H, s, CH$_3$CN), 1.93 (1H, m, H$_3$), 1.89 (9H, d, $J_{PH}$ = 14.0 Hz, PMe$_3$), 1.82 (1H, m, H$_5$), 1.79 (15H, s, Cp*), 1.71 (1H, m, H$_1$), 1.43 (1H, m, H$_2$). $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$, $\delta$): 128.50 (s, CN), 96.14 (s, $C_5$Me$_5$), 31.78 (s, =CH−), 26.02 (s, =CH$_2$), 25.85 (d, $J_{PC}$ = 44.2 Hz, -$C$H$_2$PMe$_3$), 9.75 (s,

$C_5\{CH_3\}_5$), 8.02 (d, $J_{PC}$ = 53.2 Hz, PMe$_3$), 5.13 (s, $CH_3CN$). Anal. Calcd. for $C_{19}H_{32}BF_4NOPRe$: C, 38.39; H, 5.43; N, 2.36; Found: C, 38.35; H, 5.54; N, 2.11.

### 4.8.4. Preparation of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(NHCOCH$_3$) (4.3)

Complex 2.2 (30.0 mg, 0.058 mmol) was dissolved in MeOH (4 mL), at –78 °C, NaOH (10.0 mg, 0.25 mmol) was added to the solution which was then stirred for 2 h. The solvent was pumped off, and the residue was extracted with hexane (2 mL × 3). The hexane solution was cooled to -78 °C and pumped overnight to give the analytically pure product as a white solid, m. p.: 148-149 °C. Yield: 24.0 mg (0.054 mmol, 92%). IR (hexane, cm$^{-1}$): $\nu_{CO}$ = 1952, 1595. EIMS (m/z): 449 (M$^+$), 421 (M$^+$ - CO), 379 (M$^+$ - CO - C$_3$H$_6$, base), 360 (M$^+$ - NH$_2$COMe - CO - 2H). $^1$H NMR (C$_6$D$_6$, δ): 4.39 (1H, m, H$_c$), 3.34 (1H, br, NH), 2.48 (1H, ddd, J$_{s'c}$ = 5.6 Hz, J$_{ss'}$ = 3.4 Hz, J$_{s'a'}$ = 0.6 Hz, H$_s$), 2.08 (3H, s, CH$_3$CO), 1.92 (1H, dd, J$_{sc}$ = 5.6 Hz, J$_{ss'}$ = 3.4 Hz, H$_s$), 1.60 (1H, d, $J_{ac}$ = 5.5 Hz, H$_a$), 1.54 (15H, s, Cp*), 0.76 (1H, d, $J_{a'c}$ = 4.2 Hz, H$_{a'}$). Anal. Calcd. for C$_{16}$H$_{24}$NO$_2$Re: C, 42.84; H, 5.39; N, 3.12. Found: C, 43.12; H, 5.59; N, 3.11.

### 4.8.5. Preparation of [Cp*Re($\eta^3$-C$_3$H$_5$)(NH$_2$CH$_2$CH$_3$)$_2$][BF$_4$] (4.4)

Complex 2.3 (50.0 mg, 0.094 mmol) was dissolved in THF (2 mL), and NaBH$_4$ (15.0 mg, 0.40 mmol) and two drops of H$_2$O were added and the solution was stirred for 4 h. The reaction mixture was filtered through Celite, and solvent was pumped off. The residue was extracted with THF/hexane (6/1), and recrystallized from THF/hexane (1/5), m. p.: 132-133 °C. Yield: 46.0 mg (0.085 mmol, 90%). FABMS (m/z): 453 (weak, M$^+$ of cation), 408 (M$^+$ - NH$_2$Et), 406 (M$^+$ - NH$_2$Et - 2H), 362 (M$^+$ - 2NH$_2$Et - H, base). $^1$H NMR (acetone-d$_6$, δ): 3.77 (1H, m, H$_c$), 3.50 (1H, br, NH$_2$), 3.38 (1H, br, NH$_2$), 2.50 (2H, m, CH$_2$), 2.44 (1H, d, J$_{sc}$ = 4.9 Hz, H$_s$), 1.67 (15H, s, Cp*), 1.52 (1H, d, $J_{ac}$ = 6.7 Hz, H$_a$), 1.10 (3H, t, $J_{H-H}$ = 7.0 Hz, CH$_3$). Anal. Calcd. for C$_{17}$H$_{34}$BF$_4$N$_2$Re: C, 37.85; H, 6.35; N, 5.19; Found: C, 37.62; H, 6.07; N, 4.86.

### 4.8.6. Preparation of [Cp*Re($\eta^3$-C$_3$H$_5$)(NCMe)(PMe$_3$)][BF$_4$] (4.5)

PMe$_3$ (0.5 mL, 4.83 mmol) was added to a solution of complex **2.3** (50.2 mg, 0.097 mmol) in CH$_2$Cl$_2$, then stirred for overnight at room temperature, to give a yellow solution. The solvent and excess PMe$_3$ were pumped off and the residue was recrystallized from THF/hexane (1/6) to give a pale yellow solid, m. p.: 133-134 °C. Yield: 32.7 mg (0.058 mmol, 60%). FABMS (m/z): 480 (M$^+$ of cation), 439 (M$^+$ - CH$_3$CN, base), 437 (M$^+$ - MeCN - 2H), 419 (M$^+$ - PMe$_2$), 405 (M$^+$ - PMe$_2$CH$_2$). $^1$H NMR (CDCl$_3$, $\delta$): 3.68 (1H, m, H$_c$), 2.84 (3H, d, $J_{PH}$ = 2.2 Hz, CH$_3$CN), 2.26 (1H, m, H$_s$), 2.14 (1H, m, H$_s$), 1.73 (15H, s, Cp*), 1.45 (1H, m, H$_a$), 1.38 (9H, d, $J_{PH}$ = 8.8 Hz, PMe$_3$), 1.03 (1H, m, H$_a$). Anal. Calcd. for C$_{18}$H$_{32}$BF$_4$NRe: C, 38.17; H, 5.70; N, 2.47; Found: C, 38.06; H, 5.85; N, 2.20.

### 4.8.7. Preparation of [Cp*Re($\eta^3$-C$_3$H$_5$)(NH$_2$Et)(PMe$_3$)][BF$_4$] (4.6)

**Method A:**

Complex **4.5** (36.0 mg, 0.064 mmol) was dissolved in THF (3 mL), NaBH$_4$ (10.0 mg, 0.26 mmol) and two drops of H$_2$O were added to the solution, which was then stirred for 3 h. The solvent was pumped off and the residue was extracted with THF, and recrystallized from THF/hexane (1/5) to give a yellowish solid, m. p.: 163-164 °C. Yield: 31.0 mg (0.054 mmol, 84%). FABMS (m/z): 484 (M$^+$ of cation), 439 (M$^+$ - NH$_2$Et, base), 437 (M$^+$ - NH$_2$Et - 2H). $^1$H NMR (CDCl$_3$, $\delta$): 3.67 (1H, m, H$_c$), 3.15 (1H, br, NH$_2$), 2.58 (1H, br, NH$_2$), 2.25-2.20 (2H, m, CH$_2$), 1.92 (1H, m, H$_s$), 1.83 (1H, m, H$_s$), 1.69 (15H, s, Cp*), 1.43 (1H, m, H$_a$), 1.39 (9H, d, $J_{PH}$ = 7.4 Hz, PMe$_3$), 1.17 (3H, t, $J_{H-H}$ = 7.0 Hz, CH$_3$), 1.13 (1H, m, H$_a$). Anal. Calcd. for C$_{18}$H$_{36}$BF$_4$NPRe: C, 37.90; H, 6.36; N, 2.46; Found: C, 37.75; H, 6.63; N, 2.35.

**Method B:**

PMe$_3$ (0.25 mL, 2.4 mmol) was added to a solution of **4.4** in CH$_2$Cl$_2$ (22.0 mg,

0.04 mmol), stirred at room temperature for overnight. Solvent was pumped off, the residue was recrystallized from $CH_2Cl_2$/hexane (1/8) to give pure product which gave the spectroscopic data identical to that of complex **4.6**.

# Chapter V

# Photochemical Reactions of Cp*Re(CO)$_3$ with Allyl Halides. Synthesis, Characterization and Reactivity of the Rhenium Allyl Chloride Complex Cp*Re($\eta^3$-C$_3$H$_5$)(CO)Cl and Its Alkyl Derivatives

## 5.1. Introduction

The rhenium $\eta^3$-allyl hydrido complex Cp*Re($\eta^3$-C$_3$H$_5$)(CO)H (**5.7**) was first reported from our group in 1989.[1d,e] It was discovered to result from a photochemical C-H activation reaction of the rhenium propene complex Cp*Re(C$_3$H$_6$) (CO)$_2$ (**3.1**) in a very low yield. In order to investigate the chemistry of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)H, an efficient method to synthesize this complex needed to be developed. As was mentioned in Chapter IV, all efforts to make complex Cp*Re($\eta^3$-C$_3$H$_5$)(CO)H (**5.7**) by transformation of either [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(MeCN)][BF$_4$] (**2.2**) or [Cp*Re($\eta^3$-C$_3$H$_5$)(MeCN)$_2$][BF$_4$] (**2.3**) were not successful. Therefore, it became necessary to search in a different direction in order to synthesize **5.7**. According to the literature, the chemistry of an iridium $\eta^3$-allyl hydrido complex had been very well established by Bergman's group.[125,126] The synthetic method they reported is described in Scheme 5.1. Addition of allylmagnesium chloride to [($\eta^5$-C$_5$Me$_5$)IrCl$_2$]$_2$ in ether gave Cp*Ir($\eta^3$-C$_3$H$_5$)Cl which was easily reduced by LiBEt$_3$H to give the $\eta^3$-allyl hydrido complex Cp*Ir($\eta^3$-C$_3$H$_5$)H.[127,128] This suggested that a suitable rhenium halide complex could also be a precursor for the formation of the rhenium $\eta^3$-allyl hydrido complex Cp*Re($\eta^3$-C$_3$H$_5$)(CO)H (**5.7**). The problem then became how to make the rhenium halide complex Cp*Re($\eta^3$-C$_3$H$_5$)(CO)X if we wanted to simulate the chemistry established for the iridium complex.

Transition metal allyl halide complexes can be synthesized in many different ways depending upon the available starting metal compounds.[1a,7,9,19-23] For example, allyl halides

react with metals or low valent metal complexes to afford allyl complexes by formal oxidative-addition (Equations 5.1-5.2):[129,130]
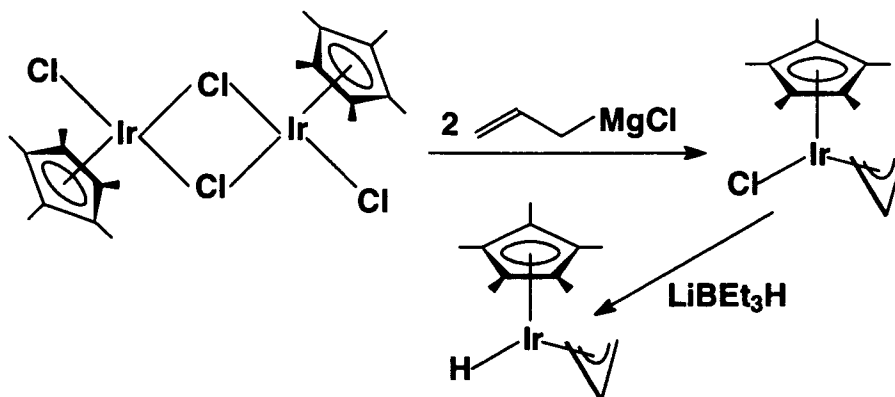


Scheme 5.1. Synthesis of $Cp^*Ir(\eta^3\text{-}C_3H_5)Cl$.

$$Pd^0 \quad + \quad C_3H_5Br \quad \xrightarrow{\Delta} \quad [(\eta^3\text{-}C_3H_5)PdBr]_2 \qquad (\text{Eq. } 5.1)^{129}$$

$$Ru_3(CO)_{12} + C_3H_5Br \quad \xrightarrow{\Delta} \quad (\eta^3\text{-}C_3H_5)Ru(CO)_3Br \quad (\text{Eq. } 5.2)^{130}$$
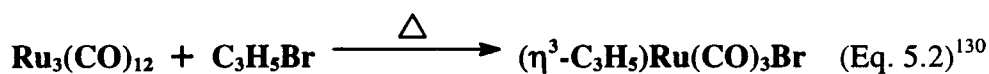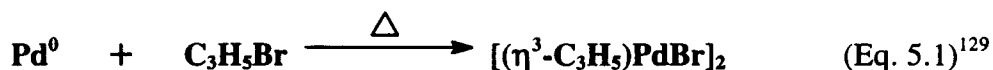
For a metal complex which contains a CO ligand, the CO can be removed in a photochemical reaction, in the presence of the allyl halide, and the $\eta^3$-allyl halide complex can be obtained. For example, $CpMo(CO)_3Cl$ reacted with allyl chloride under photolysis to produce the $\eta^3$-allyl complex $CpMo(CO)(\eta^3\text{-}C_3H_4R)Cl_2$ (R = H, Me, Equation 5.3).[131]

$$CpMo(CO)_3Cl \quad + \quad C_3H_4RCl \quad \xrightarrow[-2CO]{h\nu} \quad CpMo(CO)(\eta^3\text{-}C_3H_4R)Cl_2$$

(Eq. 5.3)
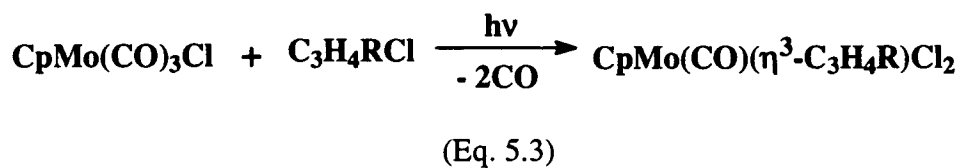
In this Chapter, we report both photochemical and thermal syntheses of $Cp*Re(\eta^3\text{-}C_3H_5)(CO)Cl$ (**5.1**). The syntheses of its $\eta^3$-allyl alkyl derivatives $Cp*Re(\eta^3\text{-}C_3H_5)(CO)R$ (**5.8 - 5.12**) and the hydride derivative $Cp*Re(\eta^3\text{-}C_3H_5)(CO)H$ (**5.7**) through the reactions of **5.1** with $C_6H_5Li$, $RMgX$ ($X = Cl$, $R = C_4H_9$; $X = Br$, $R = CH_3$, $C_2H_5$, $C_3H_5$) or $LiBEt_3H$, and the characterization of these new complexes, are also reported. The attempts to synthesize **5.1** or its bromide derivative by means of photochemical reactions of $Cp*Re(CO)_3$ with allyl chloride and allyl bromide will be also discussed.

## 5.2. Photochemical Reactions of $Cp*Re(CO)_3$ with $CH_2=CHCH_2X$ ($X = Br$, $Cl$)

### 5.2.1. Photochemical Reaction of $Cp*Re(CO)_3$ with $CH_2=CHCH_2Br$ in Hexane

Complex $Cp*Re(\eta^3\text{-}C_3H_5)(CO)Br$ was obtained when $Cp*Re(\eta^3\text{-}C_3H_5)(CO)H$ (**5.7**) was stirred with $CHBr_3$ for overnight.[1e] It was easily reduced by $LiBEt_3H$ in ether to give **5.7** again (Equation 5.4). Therefore, the hydride complex **5.7** could be synthesized if a high yield synthesis of the bromide complex was available. According to the method used for the synthesis of $(\eta^3\text{-}C_3H_5)Ru(CO)_3Br$ (Equation 5.2),[130] treatment of $Ru_3(CO)_{12}$ with allyl bromide at 60-70 °C for a few hours to produce the corresponding $\eta^3$-allyl bromide complex, the reaction of $Cp*Re(CO)_3$ with $CH_2=CHCH_2Br$ was studied under both thermal and photochemical conditions in an attempt to make $Cp*Re(\eta^3\text{-}C_3H_5)$ $(CO)Br$, and then reduce it to the hydride compound **5.7**.



(Eq. 5.4)

*(endo + exo)*         *(endo)*
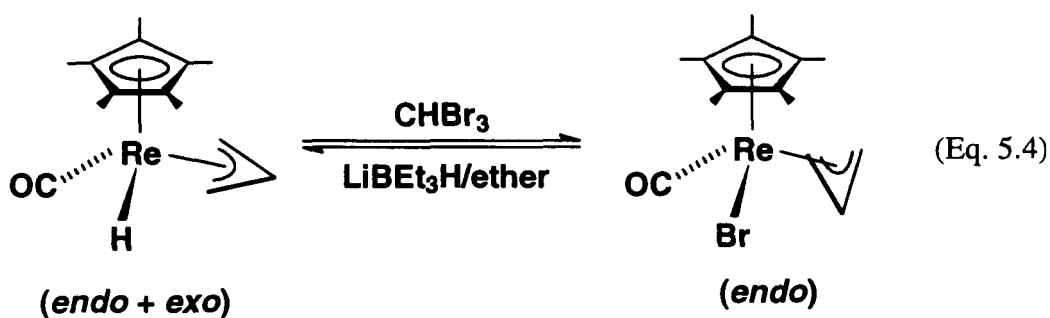
When Cp*Re(CO)$_3$ was treated with CH$_2$=CHCH$_2$Br in hexane, toluene or as neat allyl bromide under refluxing condition for 48 h, no reaction occurred. When a hexane solution of Cp*Re(CO)$_3$ with allyl bromide was photolyzed under UV light at 0 °C for 1 hour in a quartz tube, reaction occurred and both *cis* **5.4a** and *trans* **5.4b** isomers of Cp*Re(CO)$_2$Br$_2$ were obtained (Equation 5.5), but no Cp*Re($\eta^3$-C$_3$H$_5$)(CO)Br was produced. Except for **5.4a** and **5.4b**, only some oil and poorly soluble material, thought likely to be organic polymer, was formed as the byproduct. The $^1$H NMR spectrum of this could not be obtained owing to the low solubility in common solvents. The mass spectrum by EIMS or FABMS was of poor quality and was uninformative.
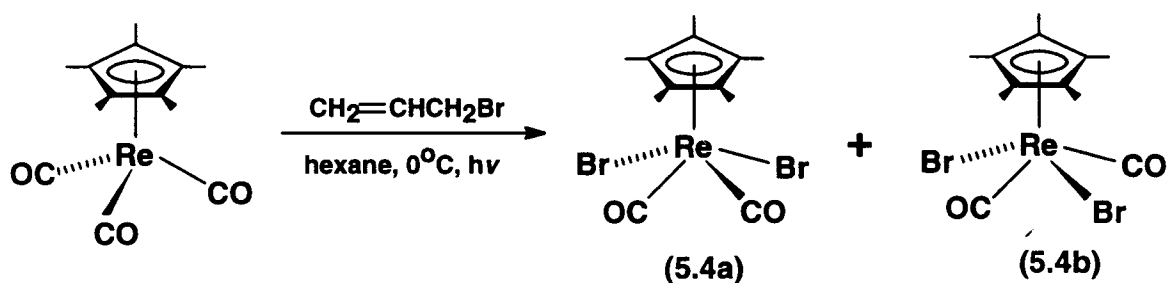


Equation 5.5

The $^1$H NMR of **5.4a** gave a singlet at $\delta$ 2.07 for Cp*, while the Cp* signal for **5.4b** occurred at $\delta$ 2.01. The IR spectra for the mixture of **5.4a** and **5.4b** in CH$_2$Cl$_2$ showed four strong v(CO) bands, assigned as 2035 cm$^{-1}$, 1960 cm$^{-1}$ for **5.4a**, and 2049 cm$^{-1}$, 1981 cm$^{-1}$ for **5.4b**. These assignments are in agreement with data reported in the literature.[132]

## 5.2.2. Photochemical Reaction of Cp*Re(CO)$_3$ with CH$_2$=CHCH$_2$Cl in Benzene

It was reasoned that the formation of the dibromide complex was a result of facile photolysis of allyl bromide and the production of bromine radicals. Allyl chloride is less susceptible to photolysis,[133] so the experiment was repeated using allyl chloride. The

124

solvent was also changed from hexane to benzene in this experiment in view of the potential coordination ability of benzene to stabilize a "Cp*Re(CO)$_2$" intermediate, while hexane can not normally act as a ligand.

Irradiation of Cp*Re(CO)$_3$ with CH$_2$=CHCH$_2$Cl in benzene at 10-15 °C afforded the two products **5.1** and **5.2** (Scheme 5.2). About 20% conversion of Cp*Re(CO)$_3$ into products was obtained after the solution was photolyzed for 2 h, and approximately equal amounts (ca 10%) of **5.1** and **5.2** were formed. Extending the irradiation time did increase the yield of the desired complex **5.1**, but the solution turned a darker color, and the formation of organic polymers made the recovery of unreacted Cp*Re(CO)$_3$ very difficult.

Characterization of **5.2** gave data in agreement with the literature.[134-136] The Cp* resonance in the $^1$H NMR spectrum in C$_6$D$_6$ occurred at δ 2.01 ppm. Absorptions in the IR spectrum in ether for the terminal ν(CO) were at 2010 and 1919 cm$^{-1}$, and for bridging ν(CO) at 1887 cm$^{-1}$. The mass spectrum showed a parent peak at m/z 784, and the fragment (M$^+$ - 2H) at m/z 782, while the base peak at m/z 726 is in agreement with [M$^+$ - 2CO - 2H]. The characterization of **5.1** will be discussed in Section 5.4.

### 5.2.3. Photochemical Reaction of Cp*Re(CO)$_3$ with Pure CH$_2$=CHCH$_2$Cl

The irradiation of Cp*Re(CO)$_3$ with CH$_2$=CHCH$_2$Cl in benzene produced **5.1** only in a low yield. The byproduct, **5.2,** is not useful in this research work, so this method of preparing **5.1** is not an efficient method. We thought that the reason might be the polymerization of CH$_2$=CHCH$_2$Cl. This would decrease the concentration of the allyl chloride, and make the reaction not favored for the formation of **5.1**. Based on this idea, a solution of Cp*Re(CO)$_3$ in pure allyl chloride was photolyzed under UV light at 0 °C for 2 h. The conversion of Cp*Re(CO)$_3$ to the product **5.1** was increased to 25-35%. As indicated in Scheme 5.2, two major products were again obtained, **5.1** and **5.3**. During the separation of **5.1** from the crude product by chromatography on a neutral alumina column, a trace amount of Cp*Re(η$^2$-C$_3$H$_5$Cl)(CO)$_2$ (**5.5**) was also isolated, but complex **5.2** was not obtained. Complex **5.1** was obtained as pure *endo* isomer, and **5.3** (total *ca* 5%) was
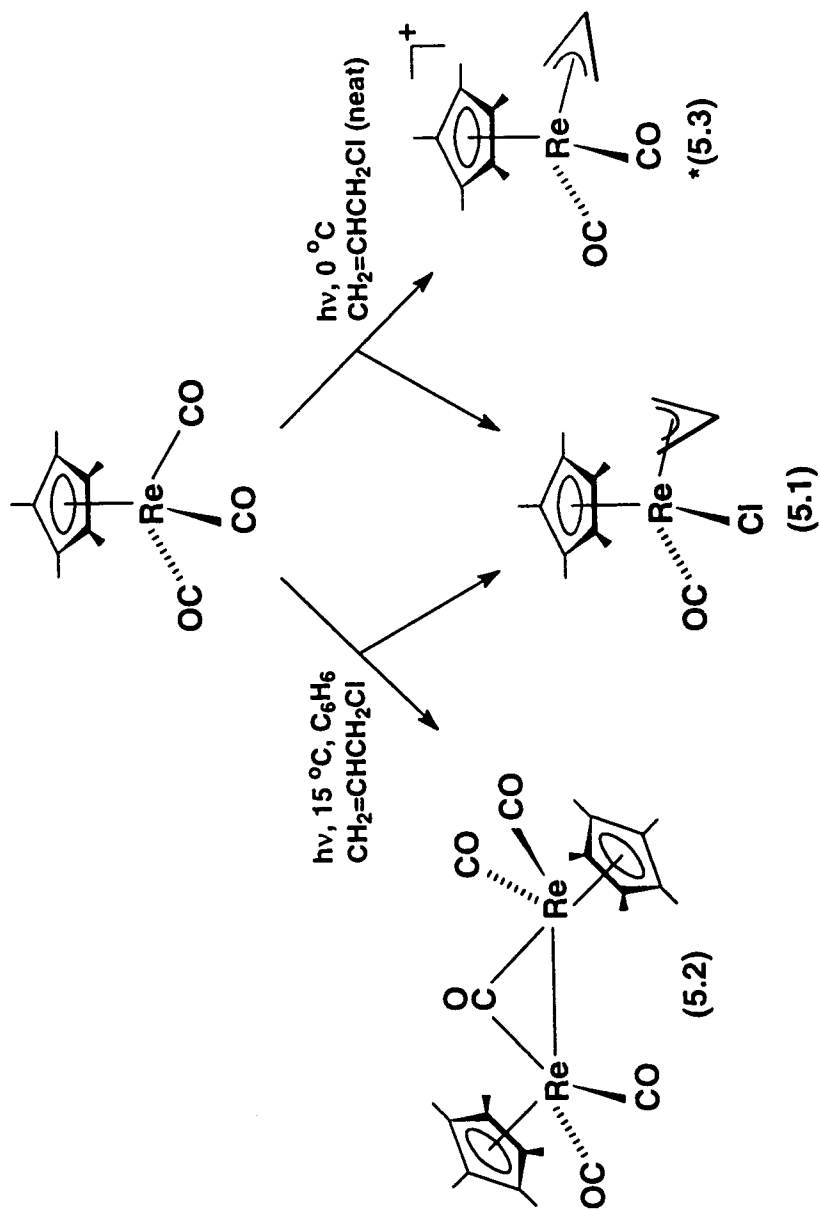
Scheme 5.2. Irradiation of Cp*Re(CO)$_3$ with allyl chloride under UV light. * Mixture of *endo* and *exo* isomers.

produced as a mixture of both the *endo* and *exo* isomers. Except that the counter anion is Cl⁻, the cation of **5.3** is exactly the same as that of **2.1**. The $\nu(CO)$ absorptions in the IR spectrum, and the proton chemical shifts and coupling patterns in the $^1H$ NMR, and the FABMS of **5.3** are identical to those of complex **2.1**. This method of synthesis of **5.1** is an improvement by comparison with that of using benzene as solvent. Not only the overall yield is increased, but also the byproduct **5.3** from the reaction is a useful starting material, as is **2.1**. The problem is that even though 30% of the Cp*Re(CO)₃ was converted into the product, the remainder was mixed with organic polymers, so the recovery of the valuble Cp*Re(CO)₃ was not as effective as we had expected.

When allyl chloride was replaced by $CH_2=C(Me)CH_2Cl$, the irradiation of Cp*Re(CO)₃ with pure $CH_2=C(Me)CH_2Cl$ gave the methallyl complex $Cp*Re(\eta^3-C_4H_7)(CO)(Cl)$ (**5.6**), and no other product was obtained from this reaction. The IR spectrum of **5.6** gave a strong absorption at 1954 cm⁻¹ for $\nu(CO)$, which is in a similar position to that of complex **5.1**. EIMS showed a parent peak at m/z 440. Two fragments at m/z 412 and m/z 356 are consistent with the loss of CO from the parent ion, and the loss of one CO followed by isobutene. The $^1H$ NMR spectrum of **5.6** in $C_6D_6$ clearly exhibited all the resonances for the methallyl protons. Two doublets at $\delta$ 3.20, $\delta$ 2.65 were assigned to the two $H_s$ protons, and two singlets at $\delta$ 2.00 and $\delta$ 1.04 to the two $H_a$ ones. The methyl gave a singlet at $\delta$ 2.90, and the Cp* resonance occurred at $\delta$ 1.48. Only one isomer was observed. This is assigned as the *endo* isomer by the similarity of the methylene proton resonances to those of **5.1**, which was identified to be the *endo* isomer by NOE experiments (see section 5.4).

### 5.2.4. Discussion of the Photoreactions of Cp*Re(CO)₃ with Allyl Chloride

According to the literature, CO substitution reactions occur under high-energy irradiation of carbonyls, which leads to dissociation of CO and formation of coordinatively unsaturated compounds (possessing vacant coordination sites for other ligands to

coordinate).[137-141] This is at least one of the reasons that led us to attempt the synthesis of **5.1** by irradiating Cp*Re(CO)$_3$ in the presence of allyl halide. The allyl halide is a potential ligand which can coordinate to the coordinatively unsaturated metal center either using the double bond or by oxidative addition.

The photoreactions of CpMn(CO)$_3$ with allyl chloride were studied by Hill's group.[142] Their results indicated that the dicarbonyl $\eta^2$-alkene complex CpMn($\eta^2$-C$_3$H$_5$Cl)(CO)$_2$ was first formed, and further irradiation led to the conversion of the $\eta^2$-alkene to $\eta^3$-allyl to give complex [CpMn($\eta^3$-C$_3$H$_5$)(CO)$_2$][Cl]. The photoreactions of complexes CpM(CO)$_3$X (M = Mo, W; X = Cl, Br, I) with allyl halides were also studied by the same group; the $\eta^2$-alkene complexes CpM($\eta^2$-C$_3$H$_5$X)(CO)$_2$X were confirmed to be the intermediates in the formation of the $\eta^3$-allyl compounds CpM($\eta^3$-C$_3$H$_5$)(CO)X$_2$.[143]

In our case, when Cp*Re(CO)$_3$ was irradiated with allyl chloride, the experimental data suggested that the irradiation of Cp*Re(CO)$_3$ did lead to the dissociation of one CO first to produce [Cp*Re(CO)$_2$],[135] followed by coordination of the allyl chloride to [Cp*Re(CO)$_2$] to give complex **5.5**. Further irradiation of **5.5** afforded the dissociation of the second CO, followed by a C–Cl bond activation, similar to what occurred in the case of the C–H bond activation in Cp*Re($\eta^2$-C$_3$H$_6$)(CO)$_2$ giving Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H), to afford a $\eta^3$-allyl chloride complex **5.1** (Scheme 5.3).[1d,1e]

The IR spectrum of **5.5** showed two $\nu$(CO) bands at 1950 and 1875 cm$^{-1}$, which are in the same region for the CO absorptions in other substituted propene dicarbonyl complexes mentioned in Chapter III. The EIMS of **5.5** gave a parent peak at m/z 454, while the fragment of m/z 419, which corresponds to the loss of Cl from the parent ion, strongly supports the structure of **5.5** instead of the other possibility of a $\eta^1$-allyl complex Cp*Re($\eta^1$-C$_3$H$_5$)(CO)$_2$(Cl) (which could be formed by oxidative addition of the allyl chloride to [Cp*Re(CO)$_2$] intermediate), since the coordinated Cl normally remains with the metal center in the MS process to form the base peak. The $^1$H NMR of **5.5** could not be obtained because of insufficient sample.
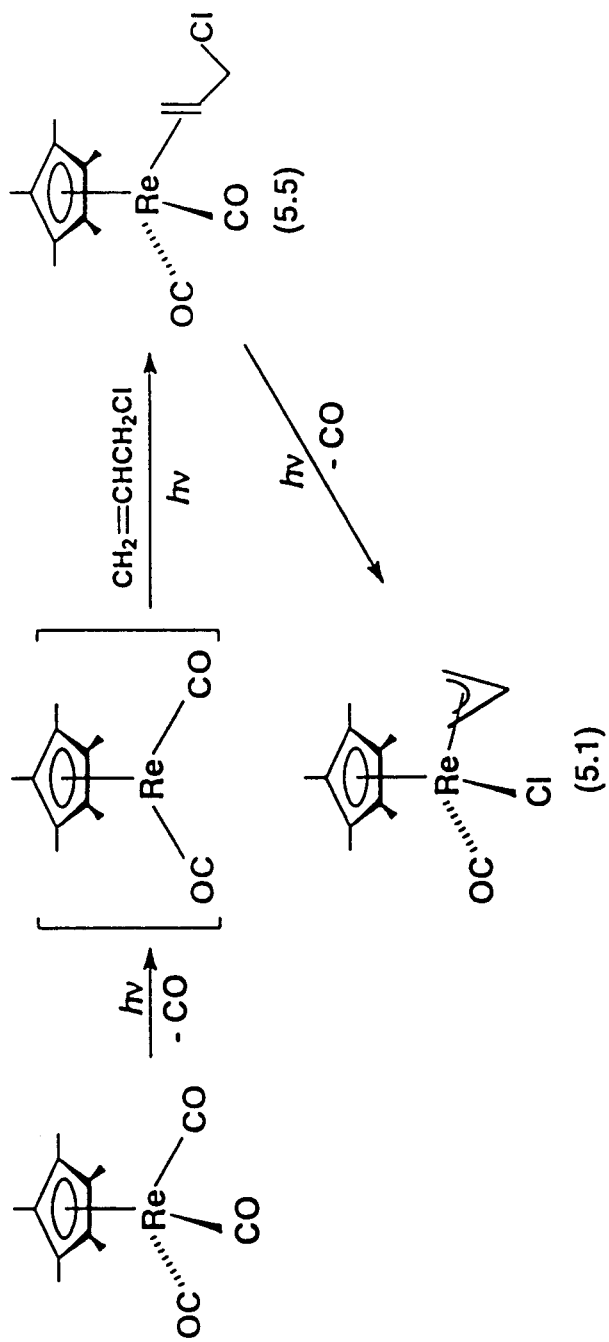
Scheme 5.3. Proposed mechanism for the formation of complex 5.1.

## 5.3. Synthesis of Complex 5.1 from [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] (2.1)

The reaction of CpRe(NO)(CH$_3$)(PPh$_3$) with HBF$_4$ in CH$_2$Cl$_2$ has been studied by Gladysz's group. The characterization of a CH$_2$Cl$_2$ complex [CpRe(NO)(ClCH$_2$Cl)(PPh$_3$)][BF$_4$] was reported.[144] The CH$_2$Cl$_2$ ligand in this complex was easily substituted by either one or two electron ligands to generate the desired compounds (Scheme 5.4).
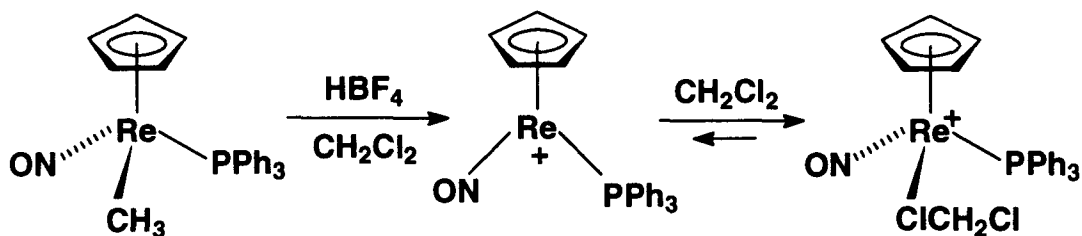


Scheme 5.4. Synthesis of [CpRe(NO)(PPh$_3$)(ClCH$_2$Cl)][BF$_4$].

We have studied the reaction of **2.1** with PhIO in pure CH$_2$Cl$_2$ in an attempt to simulate the chemistry of the rhenium nitrosyl complex in order to make the CH$_2$Cl$_2$ complex [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(CH$_2$Cl$_2$)][BF$_4$], then by replacing the CH$_2$Cl$_2$ with Cl$^-$ or H$^-$ to get **5.1** or **5.7**. The experimental result indicated that PhIO did react with **2.1** in CH$_2$Cl$_2$. The solution (**2.1** in CH$_2$Cl$_2$) changed color from yellow to purple after PhIO was added to the solution for 0.5 h. When an aliquot of this purple colored solution was removed to record the IR spectrum (without protecting under N$_2$), the color changed back to yellow, and the IR spectrum observed consisted of the two $\nu$(CO) bands for complex **2.1**. No other $\nu$(CO) band was observed. The recovery of **2.1** was almost quantitative when the purple colored solution was exposed to the air and returned to the yellow color. We propose that the purple color is that of an associative intermediate of PhIO with **2.1** instead of the expected CH$_2$Cl$_2$ complex.

As mentioned in section 5.2, the synthesis of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)Cl (**5.1**) is possible by using photochemical reactions, but none of them is very effective. The

isolation and purification of **5.1** from organic impurities were very difficult, and the recovered yield of the unreacted Cp*Re(CO)$_3$ was low. It is still necessary to find a better method to synthesize **5.1**. While studying the nucleophilic reaction of X$^-$ (X = Cl, Br, I) with [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] (**2.1**), it was found that X$^-$ did not attack the allyl, and no reaction occurred. However the reaction of [Cp*Mn($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] with KI was reported to give Cp*Mn($\eta^2$-C$_3$H$_5$I)(CO)$_2$ quantitatively.[108] We reasoned that [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] may preferentially coordinate X$^-$ to the metal center if a prior coordinatively unsaturated intermediate is formed. We knew that PhIO can oxidatively remove CO from this cationic complex, as it was used in the syntheses of complexes **2.2** and **2.3**. So a reaction was designed in which complex **2.1** was treated with PhIO in the presence of Me$_4$NCl in CH$_2$Cl$_2$.

Scheme 5.5 shows this one-step synthetic route for the preparation of complex **5.1**. The separation of the neutral compound **5.1** from the excess PhIO and Me$_4$NCl was easily achieved by extracting the product with hexane or ether from the reaction mixture, since neither PhIO nor Me$_4$NCl was soluble in these solvents. Although the starting material for the synthesis of **5.1** is a mixture of the *exo* and *endo* isomers of **2.1**, the $^1$H NMR experiments for the product indicated that **5.1** was obtained as the pure *endo* isomer only.

The presence of Cl$^-$ is necessary in this reaction. Complex **5.1** was not obtained by simply treating [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$]Cl (**5.3**) with PhIO in CH$_2$Cl$_2$. We assume that the concentration of Cl$^-$ present as a counter anion in complex **5.3** is probably insufficient to favour the coordination to the vacant site after CO was removed by PhIO, or if the reaction occurred in an associative process (i.e. S$_N$2 reaction). When Me$_4$NCl was added to the reaction, complex **5.1** was produced quantitatively within one hour at room temperature.

## 5.4. Characterization of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)Cl (5.1)

Complex **5.1**, synthesized by using either photochemical or thermal methods just described, was found to give identical analytical and spectroscopic data. The IR spectrum
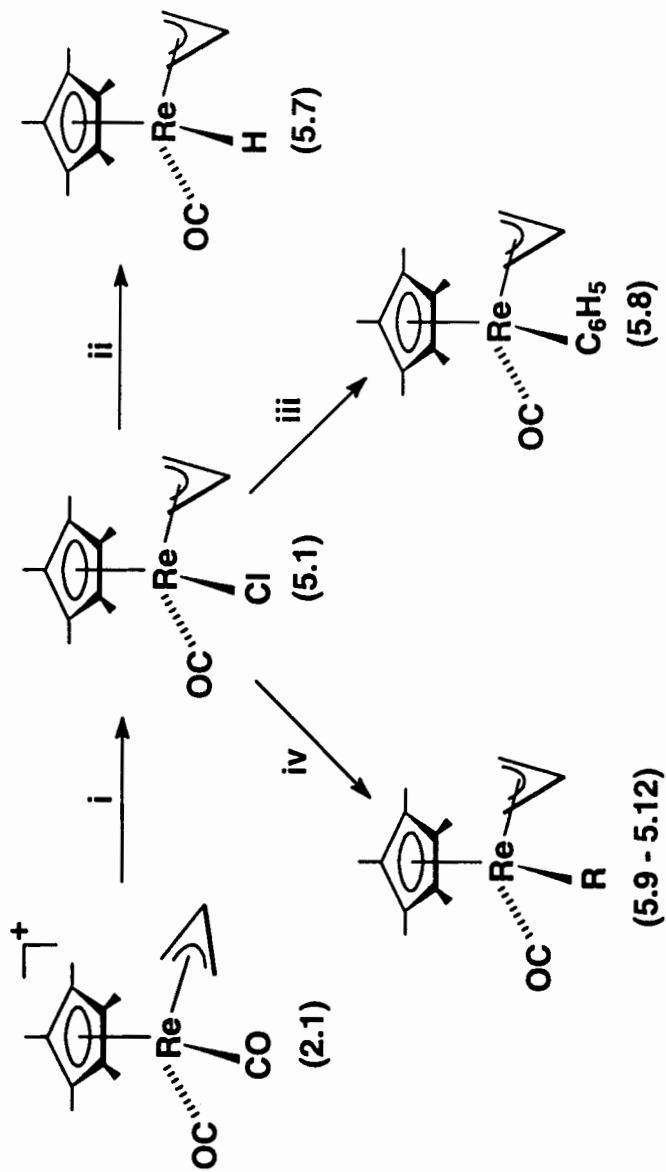
Scheme 5.5. Synthesis and reactions of complex (5.1). i. PhIO/Me$_4$NCl/CH$_2$Cl$_2$; ii. LiBEt$_3$H/ether; iii. C$_6$H$_5$Li/ether; iv. RMgBr/ether, R = CH$_3$, C$_2$H$_5$, C$_3$H$_5$, C$_4$H$_9$.

of **5.1** gave only one strong $\nu$(CO) absorption at 1960 cm$^{-1}$ in hexane, indicating the loss of two CO ligands from Cp*Re(CO)$_3$. The EIMS spectrum gave a parent peak at m/z 426. The base peak at m/z 356 corresponds to [M$^+$ - CO - C$_3$H$_5$ - H].

The $^1$H NMR spectrum of **5.1** (Figure 5.1) clearly showed $\eta^3$-allyl coordination to the rhenium center, with resonances at $\delta$ 4.78 (m, H$_c$), $\delta$ 3.21 (dd, H$_s$), $\delta$ 2.80 (ddd, H$_{s'}$) and $\delta$ 1.76, $\delta$ 0.85 (d, H$_a$ and H$_{a'}$). The Cp* resonance is a singlet at $\delta$ 1.46. This is upfield from the Cp* resonances in cationic complexes such as **2.1** ($\delta$ 2.17 in CD$_2$Cl$_2$), **2.2** and **2.3** ($\delta$ 1.98 and 1.71 in CDCl$_3$), and is in the region for other subsequently synthesized neutral complexes such as **5.8**-**5.12** (Tables 5.2, 5.3). No matter which method was used for the synthesis of **5.1**, the $^1$H NMR Overhauser experiment indicated that only the *endo* isomer was obtained, same as its bromide analog.[1e] Saturation of Cp* at $\delta$ 1.46 induced enhancements for both H$_a$ signals at $\delta$ 1.76 and $\delta$ 0.85, which indicated a short distance from Cp* to the two H$_a$ protons through space as expected for the *endo* structure but not for *exo*. Saturation of H$_c$ at $\delta$ 4.78 gave enhancements for both H$_s$ at $\delta$ 3.21 and $\delta$ 2.80, which confirmed the assignments of H$_c$ and H$_s$, but there was no enhancement of the Cp* resonance, which would be expected to occur for an *exo* structure.

## 5.5. Chemical Reactions of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(Cl) (5.1)

### 5.5.1. Reaction of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(Cl) (5.1) with LiBEt$_3$H

Complex **5.1** reacted with LiBEt$_3$H in freshly distilled ether at 0 °C for 2 h to give complex **5.7** (Scheme 5.5), which had previously been produced in very low yield from photochemical C-H activation of the rhenium propene complex Cp*Re(C$_3$H$_6$)(CO)$_2$.[1e] The conversion of complex **5.1** to **5.7** is about 90% in the presence of excess LiBEt$_3$H. The reaction must be conducted in dry ether, otherwise the yield of **5.7** is very low because the reverse reaction of **5.7** in the presence of both moisture and LiCl, which was produced from the reaction of **5.1** with LiBEt$_3$H, gave **5.1** again. At 0 °C, the IR spectrum of the initial product showed the presence of only *endo* **5.7**, which gave a strong $\nu$(CO)
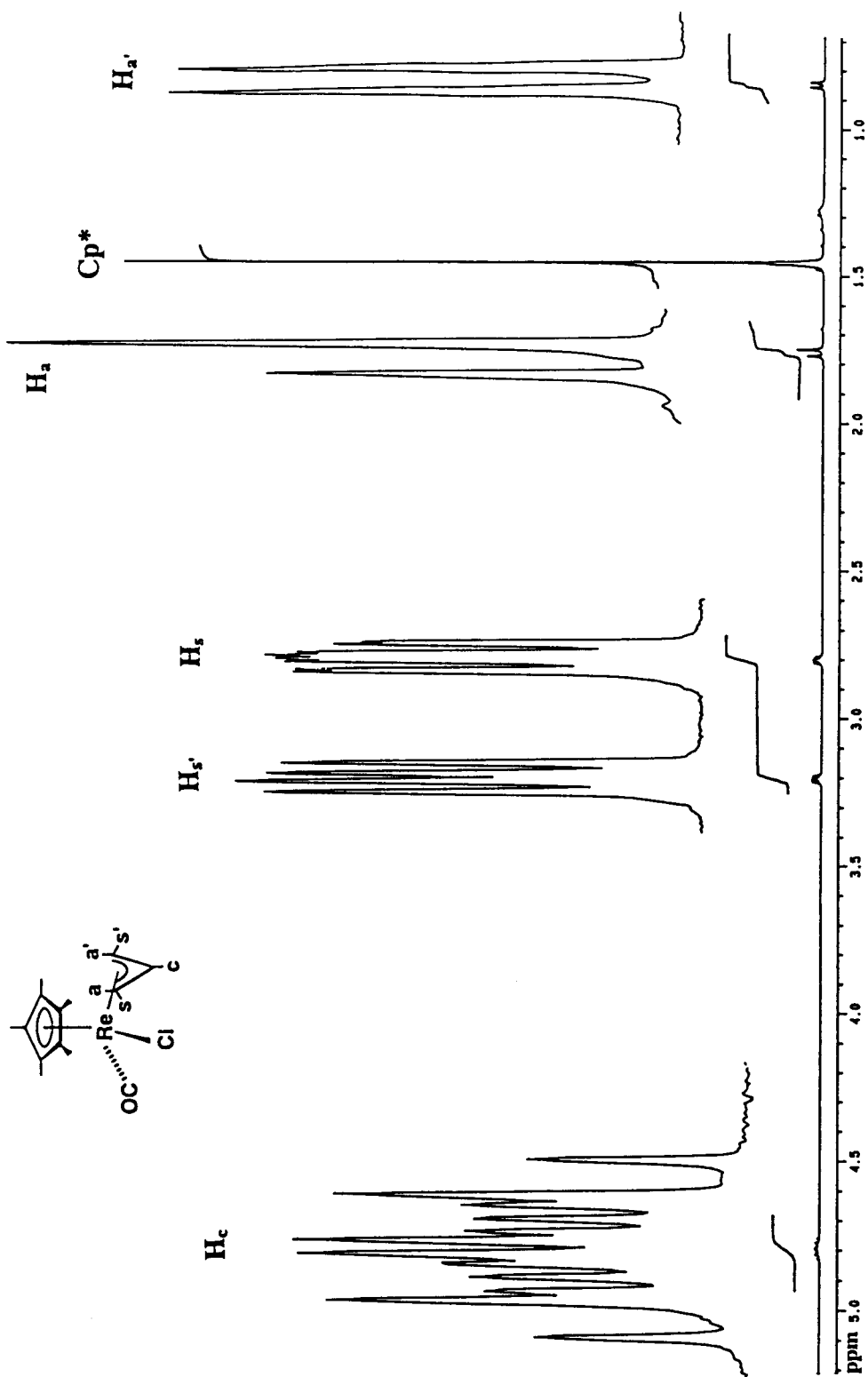
Figure 5.1. $^1$H NMR spectrum of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(Cl) (5.1) in C$_6$D$_6$.

134

band at 1900 cm$^{-1}$ in ether. Then ether was pumped off, and the crude product was extracted with hexane. This hexane solution was checked by IR again and also showed pure *endo* isomer. The hexane solution was pumped to dryness, the residue was dissolved in a little hexane, then transferred to a neutral alumina column. Eluting with hexane again gave only the *endo* isomer. Upon eluting with ether, a mixture of both the *endo* and *exo* isomers was obtained, for which the *exo* isomer showed a ν(CO) band at 1906 cm$^{-1}$ in hexane in the IR spectrum. It appears there is some isomerization of the *endo* isomer during the purification.

Although complex **5.7** reacted with CHBr$_3$ to give the bromo substituted compound Cp*Re(η$^3$-C$_3$H$_5$)(CO)Br,[1e] **5.7** is stable in CD$_2$Cl$_2$, and the $^1$H NMR spectrum of it was recorded in this solvent. For the *endo* isomer, the Cp* resonance occurred at δ 2.01, and the Re–H signal appeared at δ –12.2. For the *exo* isomer, the Cp* resonance occurred at δ 1.98, and the Re–H signal occurred at δ –9.75. The chemical shifts of the allyl protons for both the *endo* and the *exo* isomers are given in the experimental section 5.9.8. Both the proton chemical shift and the coupling pattern of the allyl group $^1$H NMR data of **5.7** recorded in CD$_2$Cl$_2$ are similar to the C$_6$D$_6$ data reported in the previous work,[1e] but the Cp* resonances for both isomers are slightly downfield shifted in CD$_2$Cl$_2$, and the Re–H signals are upfield shifted compared with the data recorded in C$_6$D$_6$. The reactivity investigation of complex **5.7** will be discussed in Chapter VI.

### 5.5.2. Reaction of Cp*Re(η$^3$-C$_3$H$_5$)(CO)(Cl) (5.1) with C$_6$H$_5$Li

Complex **5.1** reacted with C$_6$H$_5$Li in dry ether at 0 °C to produce complex **5.8**. The IR spectrum showed a strong ν(CO) absorption at 1919 cm$^{-1}$ in hexane, which is much lower compared with complex **5.1** (1960 cm$^{-1}$ in hexane), indicating more electron donation to the metal center from C$_6$H$_5$ than Cl. The EIMS spectrum of **5.8** gave a parent peak at m/z 468, and a base peak at m/z 440 which is consistent with the loss of CO from the molecule. The $^1$H NMR spectrum of **5.8** in C$_6$D$_6$ (Figure 5.2) showed two sets of multiplets at δ 7.86 and δ 7.14 for the five protons of the coordinated phenyl group. The
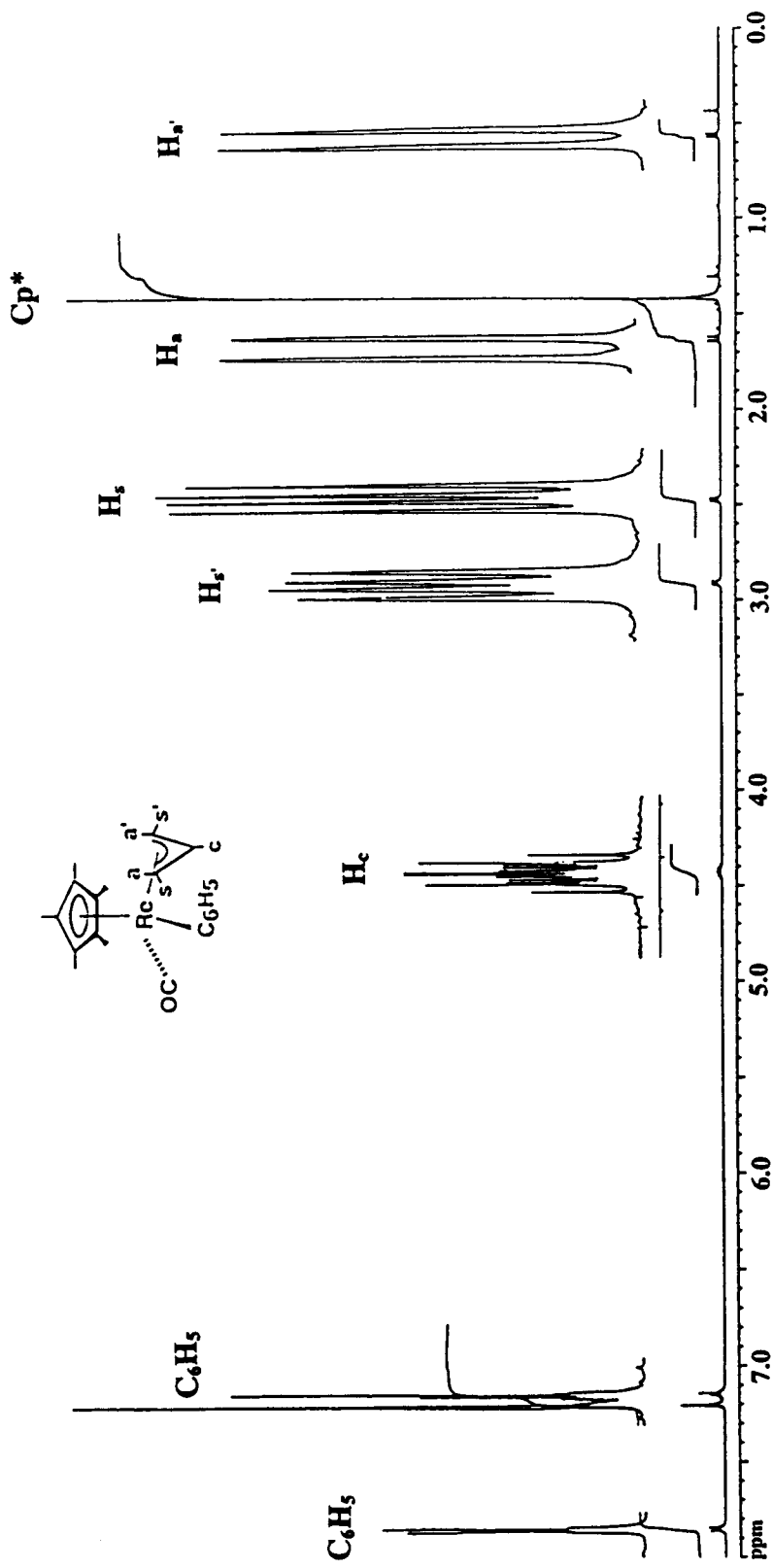
Figure 5.2. $^1$H NMR spectrum of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(C$_6$H$_5$) (5.8) in C$_6$D$_6$.

136

allyl ligand gave resonances at δ 4.42 for $H_c$ (multiplet), δ 2.90 and δ 2.48 for $H_s$ (doublet of doublets), and δ 1.61, δ 0.58 for $H_a$ (doublet). The Cp* showed a singlet at δ 1.43. Saturation at δ 1.43 for Cp* caused an NOE enhancement of the $H_a$ resonances at δ 0.58 and δ 1.61, which indicated an *endo* structure for the $\eta^3$-allyl ligand in complex **5.8**. Since one $H_a$ proton at δ 1.61 is very close to the Cp* signal at δ 1.43, when the Cp* resonance at δ 1.43 was saturated, this $H_a$ resonance was also partially saturated. This is why the enhancement of one $H_a$ resonance at δ 0.58 was stronger than the other one at δ 1.61, and the $H_s$ signals at δ 2.48 also experienced a small enhancement. No enhancement was observed for $H_c$ when Cp* was saturated. This indicated a long distance between the Cp* to the central proton $H_c$ of the allyl ligand, which is the case for the *endo* isomer. Saturation at δ 4.42 for $H_c$ induced an enhancement for both $H_s$ signals, and decoupled $H_s$ from a doublet of doublets to a doublet, but no enhancement of the Cp* resonance was observed. All the evidence from the $^1H$ NMR experiment supported an *endo* structure for complex **5.8**.

### 5.5.3. Reaction of Cp*Re($\eta^3$-C₃H₅)(CO)(Cl) (5.1) with RMgX (X = Br, R = CH₃, C₂H₅, C₃H₅; X = Cl, R = C₄H₉)

Although the rhenium nitrosyl methyl complex [Cp*Re(NO)(PPh₃)(CH₃)][BF₄] has been reported from the stepwise reduction of [Cp*Re(NO)(PPh₃)(CO)][BF₄] with NaBH₄,[100] we have not found any report of rhenium $\eta^3$-allyl alkyl complexes in the literature. Complex **5.1** reacted with an excess of RMgBr or RMgCl (R = CH₃, CH₂CH₃, CH₂CH=CH₂, and CH₂CH₂CH₂CH₃) at 0 °C in freshly distilled ether to produce rhenium $\eta^3$-allyl alkyl complexes **5.9-5.12**. The spectroscopic data for complexes **5.8-5.12** are listed in Tables 5.1 and 5.2.

Complexes **5.9 - 5.12** gave strong single ν(CO) absorptions in the IR spectra in the region of 1915±5 cm⁻¹. This is about 40 cm⁻¹ lower in comparison with the value for complex **5.1** because of the substitution of the Cl by an alkyl group. Compared with Cl, an alkyl group is a better σ donor and by supplying more electron density to the metal center,

causes back-donation from the metal to CO to increase, and a decrease in the CO bond order.

Table 5.1. Spectroscopic Data for Complexes **5.8-5.12**.

| Complex | IR {ν(CO), cm⁻¹}[a] | MS (m/z) M⁺ | MS (m/z) Base | ¹H NMR of Cp* (ppm)[b] |
|---|---|---|---|---|
| **5.8** | 1919 | 468 | 440 | 1.43 |
| **5.9** | 1917 | 406 | 374 | 1.51 |
| **5.10** | 1912 | 420 | 359 | 1.48 |
| **5.11** | 1914 | 432 | 400 | 1.47 |
| **5.12** | 1912 | 448 | 374 | 1.50 |

a. In hexane; b. All samples were measured in $C_6D_6$ at 400 MHz.

The EIMS spectra of **5.9-5.12** showed clear parent peaks. For complexes **5.9**, **5.10** and **5.12**, fragments [M⁺ − 2H] was even stronger than M⁺ (Figure 5.3). These may indicate that the C-H bond in a coordinated alkyl group is easy to be activated in the MS experiment. We have not found this character in our other rhenium cationic complexes.[110,145] Both CO and RH fragments are found to be lost very easily from the molecule, and lead to strong intensities for the fragments [M⁺ − RH] or [M⁺ − CO] which are the observed base peaks for compounds **5.9-5.12**.

In the ¹H NMR spectrum of **5.9**, the η³-allyl protons were assigned as: δ 3.96 (multiplet) $H_c$, δ 2.59, δ 2.10 (doublet of doublets) $H_s$, and δ 1.04, δ 0.40 (doublet) $H_a$. The Re–CH₃ gave a singlet at δ 0.20, which is in the typical region for methyl directly coordinated to a metal center in neutral compounds.[100] According to the results from the ¹H NMR NOE study of **5.8**, we assume that the major isomer of **5.9** is *endo*, because both

138

the coupling pattern and the chemical shift of the allyl protons of **5.9** are similar to those of **5.8**. But we did find about 20% of the *exo* isomer of **5.9** to be present according to the expanded $^1$H NMR spectrum (at room temperature in $C_6D_6$, integration for Cp*), which showed a multiplet for $H_c$ at $\delta$ 3.27 and a singlet at $\delta$ 1.40 for Cp* of the *exo* isomer. Other signals for the *exo* isomer are not clear enough to be assigned. This is different in comparison with the case of **5.8**. We did not find any signals attributable to the presence of the *exo* isomer from the expanded $^1$H NMR spectrum of **5.8**.

Table 5.2. Allyl Proton Chemical Shifts and Coupling Constants of **5.8-5.12**.

| Complex | Chemical Shifts $\delta$ (ppm) and Coupling Constants J (Hz)[a] |
|---|---|
| **5.8** | 4.42 (m, $H_c$); 2.90, 2.48 (dd, $J_{sc} = 5.6$, $J_{ss'} = 3.2$, $H_{s'}$, $H_s$); 1.61 (d, $J_{ac} = 8.0$, $H_a$); 0.58 (d, $J_{a'c} = 7.2$, $H_{a'}$) |
| **5.9** | 3.96 (m, $H_c$); 2.59, 2.10 (dd, $J_{sc} = 5.4$, $J_{ss'} = 3.1$, $H_{s'}$, $H_s$); 1.04 (d, $J_{ac} = 9.0$, $H_a$); 0.40 (d, $J_{a'c} = 7.5$, $H_{a'}$) |
| **5.10** | 4.16 (m, $H_c$); 2.60, 2.17 (dd, $J_{sc} = 5.4$, $J_{ss'} = 3.2$, $H_{s'}$, $H_s$); 1.05 (d, $J_{ac} = 7.7$, $H_a$); 0.51 (d, $J_{a'c} = 7.7$, $H_{a'}$) |
| **5.11**[b] | 4.11 (m, $H_c$); 2.53, 2.29 (dd, $J_{sc} = 5.3$, $J_{ss'} = 3.4$, $H_{s'}$, $H_s$); 1.09 (d, $J_{ac} = 9.1$, $H_a$); 0.57 (d, $J_{a'c} = 6.4$, $H_{a'}$) |
| **5.12** | 4.18 (m, $H_c$); 2.59, 2.17 (dd, $J_{sc} = 5.4$, $J_{ss'} = 3.3$, $H_{s'}$, $H_s$); 1.38 (d, $J_{ac} = 5.5$, $H_a$); 0.50 (d, $J_{a'c} = 7.1$, $H_{a'}$) |

a. All samples were measured in $C_6D_6$ at 400 MHz;  b. For $\eta^3$-allyl protons only.
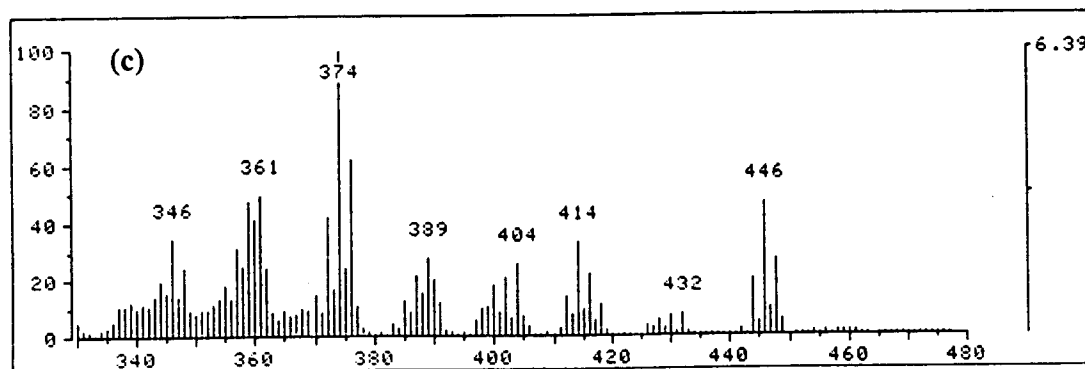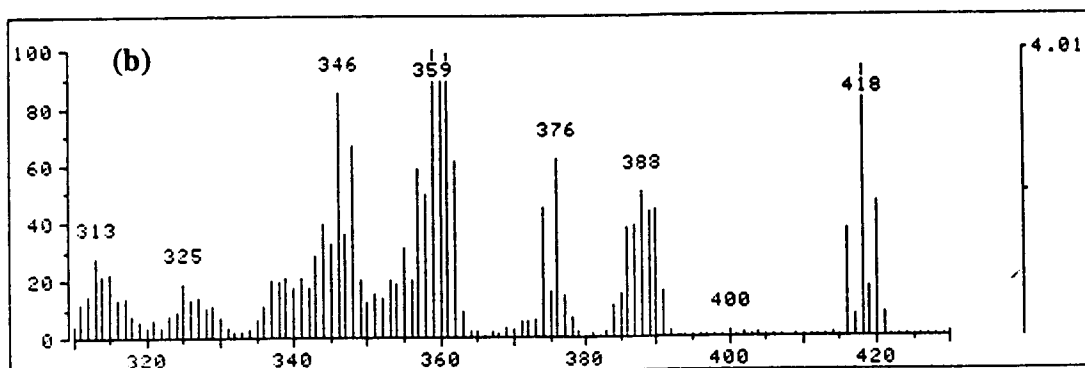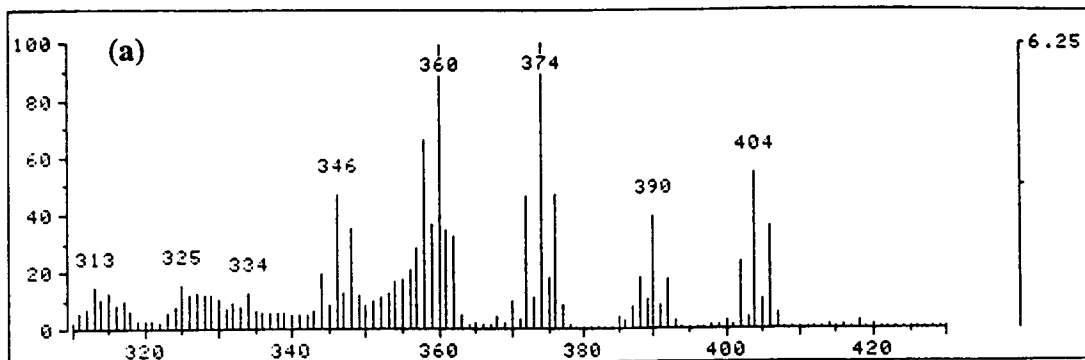
Figure 5.3. Mass spectra of complexes **5.9, 5.10** and **5.12**.
(a). Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(CH$_3$) (**5.9**); (b). Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(CH$_2$CH$_3$) (**5.10**);
(c). Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(C$_4$H$_9$) (**5.12**).

The $^1$H NMR spectrum of **5.10** gave resonances for *endo* allyl group protons at δ 4.16 (multiplet to $H_c$), δ 2.60, δ 2.17 (doublet of doublets to $H_s$), and δ 1.05, δ 0.51 (doublet to $H_a$). Re-$CH_2CH_3$ showed a triplet for $CH_3$ at δ 1.53 with a coupling of 7.7 Hz from the $-CH_2-$ group, and a multiplet at δ 0.91 for Re-$CH_2$ protons. In the $^1$H NMR spectrum of complex **5.10**, there was no evidence for the presence of the *exo* isomer.

The $^1$H NMR spectrum of **5.11** showed resonances for $\eta^1$-allyl at δ 6.02 (multiplet for the central proton), δ 5.17 (multiplet for the two terminal protons), and δ 2.30 (multiplet for Re-$CH_2-$); the *endo* $\eta^3$-allyl gave the signals at δ 4.11 (multiplet for $H_c$), δ 2.53, δ 2.29 (doublet of doublets to $H_s$), and δ 1.09, δ 0.57 (doublet for $H_a$). The assignments were confirmed by $^1$H NMR decoupling experiments, and by a comparison of our data with the data reported in the literature for other $\eta^1$-allyl complexes.[146]

Variable temperature $^1$H NMR experiments have been conducted in toluene-$d_8$ for **5.11** in order to study the exchange of the $\eta^1$-allyl with $\eta^3$-allyl in **5.11**. There is no evidence supporting the exchange of the $\eta^1$-allyl with $\eta^3$-allyl even after complex **5.11** was heated to 335 K in toluene-$d_8$. We were also expecting the loss of coordinated CO at high temperature (335 K in this case) from **5.11**, followed by a conversion of the $\eta^1$-allyl to the $\eta^3$-allyl to give Cp*Re($\eta^3$-$C_3H_5$)$_2$. The experiment showed that **5.11** decomposed when it was heated to 335 K in toluene-$d_8$; the IR showed that the $\nu$(CO) absorption disappeared and the $^1$H NMR of this solution showed no signals for the Cp* and the allyl protons, except some unassigned signals in the region of 3.0-1.0 ppm, which could be resonances from the decomposition products.

$^1$H NMR spectrum of **5.12** showed the same allyl proton patterns as in the complexes **5.8-5.11**. The multiplet at δ 4.18 is assigned to $H_c$; the two multiplets at δ 2.59, δ 2.17 to $H_s$, and the two doublets with the coupling of 7.1 Hz at δ 1.38, δ 0.50 to $H_a$. The coordinated butyl gave many overlapping multiplets at δ 1.50-δ 0.8. The spectroscopic data for complexes **5.8-5.12** are summarized in Tables 5.2 and 5.3.

## 5.6. Discussion

### 5.6.1. *Endo-Exo* isomerization of 5.7

When **5.7** was stored for eventual use in further reactions, the *exo* isomer of **5.7** was kept in the pure solid state at 0-5 °C for three days, at the end of which no *endo* isomer was detected from the $^1$H NMR spectrum in $CD_2Cl_2$. The *endo* isomer was kept under the same condition for the same reason, but its $^1$H NMR in $CD_2Cl_2$ showed the appearance of the *exo* isomer, with the ratio of *endo/exo* ≈ 3/1 in $CD_2Cl_2$ at room temperature (the sample was dissolved in $CD_2Cl_2$ at 18-22 °C and kept at this temperature for about 2 hours before the spectrum was recorded). This solution was cooled down to 213 K (within 4 hours) and the $^1$H NMR spectrum was recorded. The chemical shift of the hydride and other protons changed as the temperature changed, but the ratio of the *endo/exo* isomers showed no obvious change.

The *exo-endo* isomerization process of **5.7** had been studied in the previous work in our group.[1d-e,116] The results are not in good agreement with the result obtained from this work. The conclusions from the previous work are: the *endo* isomer in hexane did not isomerize to the mixture of the *endo* and *exo* isomers if no UV irradiation was employed but did so when irradiated; but the *exo* isomer converted to the mixture of the *exo* and *endo* isomers thermally in $C_6D_6$ (Equation 5.6).[1e]



(Eq. 5.6)

(**5.7**, *endo*)                    (**5.7**, *exo*)
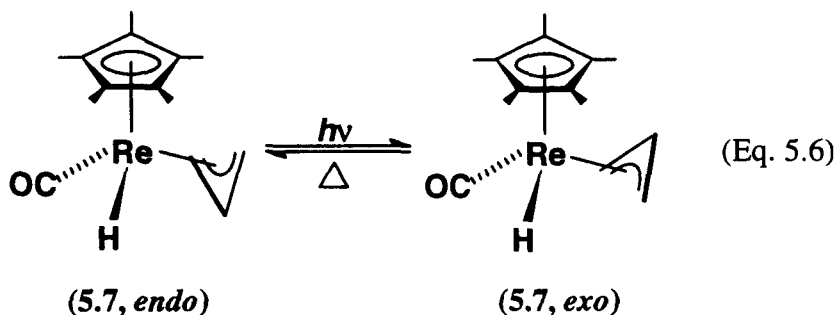
In the previous work, **5.7** was obtained in a photochemical reaction, and the *exo* isomer was the one which had the higher population compared with the *endo* isomer initially. The thermal conversion of the *exo* isomer to an *exo/endo* mixture was studied at different temperatures in $C_6D_6$. The ratios of the *exo* to the *endo* isomer are listed in Table 5.3. In our work, the conversion is from the pure *endo* isomer to an *exo/endo* mixture (the spectrum was recorded in $CD_2Cl_2$), but the ratio of the *exo* to the *endo* isomer in the same temperature region is almost the same as the result obtained from the previous work (Table 5.3).[116] This suggests that the isomerization is a thermally reversible process, and the observed *endo/exo* ratio at 20 °C (*endo/exo* ≈ 3/1) in $CD_2Cl_2$ is the equilibrium ratio at that temperature. The factors that affect the *exo-endo* isomerization of **5.7** have not been thoroughly studied yet, and more work will be necessary in order to understand the isomerization of **5.7** under various conditions.

Table 5.3. Data for the Ratio of the *Exo* to *Endo* isomers.

| exo/endo | 0.34[a] | 0.32[a] | 0.32[a] | 0.33[b] |
|---|---|---|---|---|
| t °C | 31 | 25 | 5 | ~20 |
| days | 7 | 14 | 40 | |

a. Results from the previous work.[116] The sample was dissolved in $C_6D_6$ in a sealed NMR tube and kept at the temperature and time indicated. b. Result from this work. The sample was dissolved in $CD_2Cl_2$ and kept at about 20 °C for 2 h till the $^1H$ NMR spectrum was recorded.

## 5.6.2. Mass Spectra of Complexes 5.1-5.13

The mass spectra of complexes **5.1-5.13** gave us some information about the process of the molecular fragmentation, and the stability of the fragments in the MS

experiment.[147] For complexes **5.1**, **5.6**, and **5.13**, the mass spectra gave mainly three fragments. Except for the parent ions, the second fragments are loss of CO from the parent, which gave m/z 398 for **5.1**, m/z 412 for **5.6**, and m/z 490 for **5.13**. The third fragments are generated from loss of both CO and allyl ligands from the parent ions to give Cp*ReX (X = Cl for **5.1** and **5.6**, X = I for **5.13**), which are the base peaks for these three complexes. This is different in comparison with our other rhenium allyl complexes. When no halide ligand is coordinated to the rhenium center, such as in complexes **5.8**-**5.12**, the base peaks for these complexes are the fragments of [Cp*Re(allyl) - 2H].

Complex **5.8** showed a base peak at m/z 440, which is the fragment from loss of CO from the parent ion. Another fragment at m/z 425 is consistent with loss of the allyl ligand and two H from the parent ion [$M^+$ - $C_3H_5$ - 2H], in which the two H atoms are supposed to come from the Cp* ring. It has been reported in the literature that loss of two H from the Cp* ring is very common in Cp* rhenium complexes.[135]

The common character of the mass spectra for complexes **5.9**, **5.10** and **5.12** is that the [$M^+$ - 2H] fragment is stronger than the parent peak. This is not in a good agreement with the computer simulated spectra for these complexes, and it could be the reflection of the stability of these compounds in MS experiment. We assume that these two H atoms come from the alkyl ligand instead of the Cp* ring, since loss of two H atoms from the Cp* ring did not affect the intensity of the parent ion for the complexes according to the result from other rhenium compounds obtained in this work.[110,145] For **5.11**, to eliminate two H atoms from the coordinated $\eta^1$-allyl is difficult compared with in complexes **5.9**, **5.10** and **5.12**. For this reason, the [$M^+$ - 2H] fragment in **5.11** is not as strong as in cases of **5.9**, **5.10** and **5.12**.

### 5.6.3. $^1$H NMR Spectra of Complexes 5.1-5.13

The $^1$H NMR spectra of complexes **5.1**, **5.6** and **5.13** showed only the *endo* isomer to be present. The two *syn* protons from two different carbon termini in each complex gave different coupling patterns, since the allyl is bonded to a chiral metal center, and the

two carbon atoms from the different allyl terminus are in the different chemical environment. In complex **5.1**, one *syn* proton showed a doublet of doublets with the coupling of $J_{s'c} = 6.0$ Hz, $J_{ss'} = 3.1$ Hz. (The W pattern long range coupling of the two *syn* protons was observed for all the neutral rhenium $\eta^3$-allyl complexes, as it was in the cationic rhenium allyl compounds).[110,145,148] The other *syn* proton showed a doublet of doublets of doublets pattern. An extra coupling of 0.77 Hz for this *syn* proton could not be ignored. The *syn* protons in complex **5.13** have the same coupling pattern as in **5.1**, one is doublet of doublets with the separation of $J_{s'c} = 6.0$ Hz, and $J_{ss'} = 3.1$ Hz, the other one is doublet of doublets of doublets, with an extra coupling of 0.6 Hz. We propose that this extra coupling is the coupling of the *syn* and *anti* protons from the same carbon terminus, which is not always resolved in the only proton resonance.

In complex **5.6**, since the central proton was replaced by the methyl group, the coupling from the central proton disappeared. The *syn* protons in this case showed only a doublet coupled to the other *syn* proton with $J_{ss'} = 4.7$ Hz, and the *anti* protons gave a simple singlet.

The NOE experiment for **5.8** indicated that the allyl group in this compound adopted the *endo* structure. The $^1$H NMR spectra of complexes **5.9-5.12** showed the similar allyl proton patterns to those of **5.8**, and the chemical shifts of the allyl protons are in the same region. The central protons $H_c$ gave multiplet resonances at $\delta$ 4.5-$\delta$ 4.0 (Table 5.2), the *syn* protons at $\delta$ 3.0-$\delta$ 2.0 are doublet of doublets, and the *anti* protons appeared at the higher field as a doublet. One is at $\delta$ 0.6-0.4, the other is at $\delta$ 1.7-1.0 ppm. Because the characters of these allyl protons are similar compared with those of **5.8**, we assume that the observed isomers of complexes **5.9-5.12** are also the *endo* isomers.

We had tried to distinguish the two *syn* and the *anti* protons by $^1$H NMR experiments using NOE and $^1$H-$^1$H correlation experiments. The NOE experiments for complexes **5.1** and **5.8** indicated that the *syn* proton at the lower field and the *anti* proton at the higher field are from the same carbon terminus. For example, saturation for the *anti* proton at $\delta$ 1.61 caused an enhancement for the *syn* proton at $\delta$ 2.48 instead of the one at

δ 2.90. It indicated a short distance of these two protons, which is the case of the two protons are from the same carbon center. Since the metal centers in complexes **5.1-5.13** are chiral centers, it is understandable that the two carbon termini of the allyl ligand have different chemical environment, and this is reflected in the $^1$H NMR spectra from both the chemical shifts and the coupling patterns of the protons connected to the different carbon atoms. But we can not tell which terminus is closer to the carbonyl ligand, and which one is towards the halide in complexes **5.1**, **5.6** and **5.13**, or alkyl ligand in cases of complexes **5.8-5.12**.

## 5.7. Reactivity of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(CH$_3$)

### 5.7.1. Reaction of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(CH$_3$) with CO

Carbon monoxide is among the most studied ligands in transition metal organometallic chemistry. Its insertion into metal-carbon bonds may lead to esters, aldehydes, alcohols, ketones and other products after work up.[149,150]

This insertion reaction was expected to occur for complexes **5.8-5.12** to give Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(COR). Complex **5.9** was dissolved in hexane, and CO was bubbled through the solution till saturated. This solution was stirred at room temperature for 48 h. The IR spectrum showed no new ν(CO) absorption, and the $^1$H NMR showed only pure **5.9**. The same experiment was conducted with complexes **5.8** and **5.11**, and again CO did not insert into the Re–R bonds (R = C$_6$H$_5$, CH$_3$, C$_3$H$_5$) under the experimental conditions employed.

### 5.7.2. Substitution of Methyl by Iodide

For complex **5.9**, the coordinated methyl group was easily substituted by iodide to give **5.13**. When **5.1** was treated with CH$_3$MgI at room temperature in ether, the IR spectrum showed the ν(CO) absorptions for complex **5.9** and remaining **5.1** when the reaction was conducted for 1h. But **5.9** was completely converted to complex **5.13** after

the reaction was continued for 5 h in an attempt to complete the conversion of **5.1** to **5.9**, no **5.9** was obtained.

## 5.8. Conclusions

The reactions of Cp*Re(CO)$_3$ with CH$_2$=CHCH$_2$Br under different conditions were studied. Refluxing Cp*Re(CO)$_3$ with CH$_2$=CHCH$_2$Br in hexane, toluene or neat allyl bromide did not lead to any reaction. Irradiation of Cp*Re(CO)$_3$ with CH$_2$=CHCH$_2$Br under UV light in hexane did not give the desired allyl complex Cp*Re($\eta^3$-C$_3$H$_5$)(CO)Br. Instead, the reaction afforded only the bis-bromo complex Cp*Re(CO)$_2$Br$_2$ (Equation 5.5).

Complex Cp*Re($\eta^3$-C$_3$H$_5$)(CO)Cl (**5.1**) was synthesized by both photochemical and thermal reactions. In addition to **5.1**, the byproducts from the irradiation of Cp*Re(CO)$_3$ with allyl chloride (in benzene or using neat allyl chloride) under UV light were also characterized. The synthesis of **5.1** provided a crucial precursor for further study of the rhenium $\eta^3$-allyl neutral compounds by substituting Cl with various one or two electron donor ligands. Especially, the reaction of **5.1** with LiBEt$_3$H in ether to give Cp*Re($\eta^3$-C$_3$H$_5$)(CO)H (**5.7**) is an efficient method to make this complex. The new high yield synthesis of **5.7** now makes it possible to study the chemistry of this stable allyl hydride complex.

The reactivity of complex **5.1** with RMgX (X = Br, R = CH$_3$, C$_2$H$_5$, C$_3$H$_5$; X = Cl, R = C$_4$H$_9$) or C$_6$H$_5$Li were studied. The syntheses and characterization of the rhenium $\eta^3$-allyl alkyl complexes **5.8-5.12** are reported for the first time. The $^1$H NMR spectra data indicated that the allyl ligand in these complexes adopts *endo* structure.

## 5.9. Experimental Section

### 5.9.1. General Procedure

All reactions were carried out under dry nitrogen in Schlenk apparatus. Solvents were purified by standard methods and were freshly distilled under dry nitrogen. All reagents were obtained from Aldrich except where mentioned. The RMgX (X = Cl, Br; R = $CH_3$, $C_2H_5$, $C_3H_5$ and $C_4H_9$) reagents were synthesized by the standard method according to the organic text book.[151] Irradiation was carried out by using a water-jacketed 200 W Hanovia Model 654A-0360 high pressure mercury vapour lamp. FTIR spectra were recorded on a Bomem Michelson-120 instrument. The $^1H$ NMR spectra were recorded at the SFU NMR service by Mrs. M. M. Tracey using a Bruker WM-400 instrument operating at 400.13 MHz. Mass spectra were obtained by Mr. G. Owen 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). Masses are given for $^{187}Re$, $^{35}Cl$ and $^{80}Br$ isotope. Correct isotopic distribution patterns were observed for all parent peaks. Microanalyses were performed by Mr. M. K. Yang of the SFU Microanalytical Laboratory.

### 5.9.2. Preparation of Cp*Re($\eta^3$-$C_3H_5$)(CO)Cl (5.1)

**Method I:**

Cp*Re(CO)$_3$ (44.8 mg, 0.11 mmol) was dissolved in benzene (20 mL) in a quartz tube, and 3 mL allyl chloride was transferred into this solution by syringe. The solution was cooled to 10-15 °C by cold water bath, then irradiated under UV light for 2 h. A dark red solution was produced. The IR spectrum showed this to be a mixture of **5.1, 5.2** and unreacted Cp*Re(CO)$_3$. Solvent was pumped off under vacuum, the residue was dissolved in $CH_2Cl_2$, and then transferred to a neutral alumina column. Eluting with hexane gave recovered Cp*Re(CO)$_3$, eluting with hexane/ether/$CH_2Cl_2$ in a 1:1:1 ratio gave complex

5.2. Finally, eluting with ether gave complex **5.1**. The crude product **5.1** was purified again by chromatography with $CH_2Cl_2$/ether, then dissolved in hexane, and cooled to -78 °C overnight. The pure product was obtained as yellow crystals (13.0 mg, 0.03 mmol, 27%), m. p.: 144-145 °C. IR ($cm^{-1}$, hex): $\nu_{CO}$ = 1960 (s). EIMS (m/z): 426 ($M^+$), 398 ($M^+$ - CO), 356 ($M^+$ - CO - $C_3H_6$, base), 354 ($M^+$ - CO - $C_3H_8$). $^1$H NMR ($\delta$, $C_6D_6$): 4.78 (1H, m, $H_c$), 3.21 (1H, dd, $J_{s'c}$ = 6.0 Hz, $J_{ss'}$ = 3.1 Hz, $H_{s'}$), 2.80 (1H, ddd, $J_{sc}$ = 6.0 Hz, $J_{ss'}$ = 3.1 Hz, $J_{as}$ = 0.8 Hz, $H_s$), 1.76 (1H, d, $J_{ac}$ = 9.1 Hz, $H_a$), 1.46 (15H, s, $C_5Me_5$), 0.85 (1H, d, $J_{a'c}$ = 6.9 Hz, $H_{a'}$). Anal. Calcd. for $C_{14}H_{20}ClORe$: C, 39.47; H, 4.73; Found: C, 39.72; H, 4.89.

**Method II:**

Cp*Re(CO)$_3$ (800 mg; 1.97 mmol) was dissolved in pure allyl chloride (20 mL, 0.25 mmol) in a quartz tube. At 0 °C, the solution was irradiated under UV light for 2 h, and a dark red solution and some precipitate were obtained. Volatiles were pumped into a clean trap cooled in a liquid nitrogen bath to recover the unreacted allyl chloride. The residue was extracted with ether. The soluble part was dissolved in $CH_2Cl_2$ and transferred to a neutral alumina column. Eluting with hexane gave unreacted Cp*Re(CO)$_3$, eluting with ether gave complex **5.1** (203.0 mg; 0.48 mmol, 24%) as the first fraction, and a trace amount of **5.5** as the second fraction. The residue after ether extraction was recrystallized from $CH_2Cl_2$/ether to give complex **5.3**, which is a mixture of both *endo* and *exo* isomers (*endo/exo* = 5/3 in CDCl$_3$ according to the integration of $^1$H NMR spectrum for Cp* protons).

**Method III:**

[Cp*Re($\eta^3$-C$_3$H$_5$)(CO)$_2$][BF$_4$] (**2.1**, 50.6 mg, 0.1 mmol) was dissolved in $CH_2Cl_2$ (5 mL) at room temperature, and PhIO (44.0 mg, 0.2 mmol) and Me$_4$NCl (33.0 mg, 0.3 mmol) were added to the solution. This mixture was stirred for 1 h to give a dark brown solution. At this time, the IR showed only one $\nu$(CO) band at 1948 $cm^{-1}$ (in $CH_2Cl_2$) for

complex **5.1**. The solution was pumped to dryness, and the residue was extracted with hexane (0.5 mL × 5). Solvent was pumped off, the residue was dissolved in $CH_2Cl_2$, then transferred to a neutral alumina column. Eluting with hexane removed organic impurities, eluting with ether gave complex **5.1** (39.2 mg, 0.092 mmol, 92%) as a yellow solid after recrystallization from hexane at -78 °C.

### 5.9.3. Characterization of {Cp*Re(CO)₂}₂-μ-(CO) (5.2)

As mentioned in method I for the preparation of complex **5.1**, complex **5.2** was isolated as a byproduct from the irradiation of Cp*Re(CO)₃ with allyl chloride in benzene under UV light. It is present in the fraction eluted with hexane/ether/$CH_2Cl_2$ = 1/1/1 ratio. The pure product was obtained by crystallization of the hexane solution at -78 °C. IR (ether, cm$^{-1}$): $\nu_{CO}$ = 2010, 1919, 1887; EIMS (m/z): 782 (M$^+$), 726 (M$^+$ - 2CO, base), 698 (M$^+$ - 3CO), 638 (M$^+$ - 5CO - 4H); $^1$H NMR (δ, C₆D₆): 2.01 (15H, s, C₅Me₅).

### 5.9.4. Characterization of [Cp*Re(η³-C₃H₅)(CO)₂]Cl (5.3)

Complex **5.3** was isolated as a byproduct from the irradiation of Cp*Re(CO)₃ with pure allyl chloride (see method II). It precipitated during the reaction and was the insoluble fraction in subsequent ether extraction of **5.1**. Recrystallization from $CH_2Cl_2$/ether gave the pure product as a white solid. IR ($CH_2Cl_2$, cm$^{-1}$): $\nu_{CO}$ = 2052, 2000; FABMS (m/z): 419 (M$^+$), 389 (M$^+$ - CO), 359 (M$^+$ - 2CO - 4H); $^1$H NMR (δ, CDCl₃, *endo* isomer): 4.61 (1H, m, H$_c$), 3.80 (2H, d, J$_{sc}$ = 6.0 Hz, H$_s$), 2.23 (15H, s, C₅Me₅), 1.97 (2H, d, J$_{ac}$ = 9.0 Hz, H$_a$).

### 5.9.5. Characterization of Cp*Re(CO)₂Br₂ (5.4)

Cp*Re(CO)₃ (16.3 mg, 0.04 mmol) was dissolved in 10 mL hexane, at 0 °C, and 0.01 mL (14.0 mg, 0.12 mmol) allyl bromide was added to the solution. This solution was irradiated under UV light for 10 min and a precipitate formed, which is a mixture of the *trans* and *cis* isomers of **5.4**. The solution IR showed ν(CO) absorptions for only

Cp*Re(CO)₃. Irradiating for a further 1 h formed more precipitate. Cp*Re(CO)₃ was recovered from the solution. The precipitate was recrystallized from $CH_2Cl_2$/ether to give the pure product as a brown solid (mixture of the *trans* and *cis* isomers). EIMS (m/z; mixture of both *cis* and *trans* isomers): 538 ($M^+$), 510 ($M^+$ - CO), 482 ($M^+$ - 2CO), 400 ($M^+$ - 2CO - HBr, base). IR ($CH_2Cl_2$, cm⁻¹): *cis* isomer, $\nu_{CO}$ = 2035, 1960; *trans* isomer, $\nu_{CO}$ = 2049, 1981. ¹H NMR ($\delta$, CDCl₃): *cis* isomer, 2.07 (15H, s, Cp*); *trans* isomer, 2.01 (15H, s, Cp*).

### 5.9.6. Characterization of Cp*Re($\eta^2$-C₃H₅Cl)(CO)₂ (5.5)

Complex **5.5** was isolated in very small yield from the irradiation of Cp*Re(CO)₃ with pure allyl chloride. It was present in the second fraction when ether was used as the elutant (see **5.9.1** method II). The IR showed two $\nu$(CO) absorptions at 1950, 1875 cm⁻¹ in C₆D₆. EIMS (m/z): 454 ($M^+$), 419 ($M^+$ - Cl), 398 ($M^+$ - 2CO), 356 ($M^+$ - 2CO - C₃H₆, base). The ¹H NMR and microanalysis were not obtained because of insufficient sample.

### 5.9.7. Preparation of Cp*Re($\eta^3$-C₄H₇)(CO)Cl (5.6)

Cp*Re(CO)₃ (100.0 mg, 0.25 mmol) was dissolved in pure 2-methyl-3-chlorobutene (20 mL, 202.0 mmol) in a quartz tube. At 0 °C, the solution was irradiated under UV light for 2 h and a dark red solution was obtained. Excess of methallyl chloride was pumped off, and the residue was chromatographed on a neutral alumina column. Eluting with hexane gave the first fraction which was Cp*Re(CO)₃, eluting with ether gave complex **5.6**. This crude product was recrystallized from hexane at -78 °C to give **5.6** (30.0 mg, 0.068 mmol, 27%), m. p.: 145-146 °C. IR (cm⁻¹, hex): $\nu_{CO}$ = 1954 (s). EIMS (m/z): 440 ($M^+$), 412 ($M^+$ - CO), 356 ($M^+$ - CO - C₄H₈, base), 354 ($M^+$ - CO - C₄H₁₀). ¹H NMR ($\delta$, C₆D₆): 3.20 (1H, d, $J_{ss'}$ = 5.0 Hz, H$_s$), 2.90 (3H, s, CH₃), 2.65 (1H, d, $J_{ss'}$ = 5.0 Hz, H$_s$), 2.00 (1H, s, H$_a$), 1.48 (15H, s, C₅Me₅), 1.04 (1H, s, H$_a$). Anal. Calcd. for C₁₅H₂₂ClORe: C, 40.95; H, 5.04; Found: C, 41.20; H, 4.96.

### 5.9.8. Preparation of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7)

To a solution of complex **5.1** (15.0 mg, 0.035 mmol) in 2 mL freshly distilled ether was added by syringe 0.2 mL of LiBEt$_3$H in ether solution (1 M). This solution was stirred at 0 °C for 3 h. By this time, the IR showed that the $\nu$(CO) band for complex **5.1** had disappeared, and a new $\nu$(CO) band appeared at 1900 cm$^{-1}$ which is assigned to the *endo* isomer of complex **5.7**.[1e] Solvent was pumped off, and the residue was extracted with hexane, then chromatographed on a neutral alumina column. Eluting with ether/hexane (1/1) gave crude **5.7**. Chromatography was repeated with pure hexane, and the pure product was obtained as a white solid after removing the solvent. This is assigned as the *endo* isomer from the IR spectrum. The residue in the column (after elution with hexane) was eluted again with ether to give very small amount of the *exo* isomer (12.0 mg, 88%, *endo* and *exo*). IR (cm$^{-1}$, hexane): $\nu_{CO}$ = 1914 (*endo* isomer), 1906 (*exo* isomer). $^1$H NMR ($\delta$, CD$_2$Cl$_2$) for the *endo* isomer: 3.78 (1H, m, H$_c$), 3.10 (1H, m, H$_s$), 2.47 (1H, m, H$_s$), 2.01 (15H, s, Cp*), 0.67 (1H, d, J$_{ac}$ = 9.6 Hz, H$_a$), 0.24 (1H, d, J$_{ac}$ = 9.0 Hz, H$_a$), -12.15 (1H, s, Re–H); $^1$H NMR ($\delta$, CD$_2$Cl$_2$) for the *exo* isomer: 2.56 (1H, m, H$_c$), 2.40 (1H, m, H$_s$), 2.15 (1H, m, H$_s$), 1.98 (15H, s, Cp*), 1.54 (1H, d, J$_{ac}$ = 9.0 Hz, H$_a$), 1.33 (1H, d, J$_{ac}$ = 9.6 Hz, H$_a$), -9.75 (1H, s, Re–H).

### 5.9.9. Preparation of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(C$_6$H$_5$) (5.8)

A solution of complex **5.1** (30.0 mg, 0.07 mmol) in 14 mL ether was added to 0.1 mL C$_6$H$_5$Li (1.95 M in THF/ether) at -20 °C. After the solution was stirred for 1 h, the color changed from yellow to colorless and some white solid formed. Two drops of water were added to this solution to destroy excess C$_6$H$_5$Li. The solution was filtered through Celite. Solvent was pumped off, and the residue was dissolved in a small amount of benzene, and transferred to a neutral alumina column. Eluting with hexane gave crude **5.8**, which was recrystallized from hexane at -78 °C to give the pure product as white planar crystals (25.0 mg, 0.053 mmol, 76%), m. p.: 101-102 °C. IR (cm$^{-1}$, hexane): $\nu_{CO}$ = 1919 (s). EIMS (m/z): 468 (M$^+$), 466 (M$^+$ - 2H), 440 (M$^+$ - CO, base), 438 (M$^+$ - CO - 2H),

425 ($M^+$ - $C_3H_6$ - H), 423 ($M^+$ - $C_3H_8$ - H). $^1$H NMR ($\delta$, $C_6D_6$): 7.86-7.14 (5H, m, Re-$C_6H_5$), 4.42 (1H, m, $H_c$), 2.90, 2.48 (2H, dd, $J_{sc}$ = 5.6 Hz, $J_{ss'}$ = 3.2 Hz, $H_{s'}$, $H_s$), 1.61 (1H, d, $J_{ac}$ = 8.0 Hz, $H_a$), 1.43 (15H, s, $C_5Me_5$), 0.58 (1H, d, $J_{a'c}$ = 7.2 Hz, $H_{a'}$). Anal. Calcd for $C_{20}H_{25}ORe$: C, 51.37; H, 5.39; Found: C, 51.38; H, 5.42.

### 5.9.10. Preparation of Cp*Re($\eta^3$-$C_3H_5$)(CO)(CH$_3$) (5.9)

To a solution of **5.1** (40.0 mg, 0.09 mmol) in 5 mL ether was added by syringe 0.4 mL of $CH_3MgBr$ in ether solution (1M, 0.4 mmol). This solution was stirred for 2 h at 0 °C, the solution changed color from yellow to colorless, and a white solid formed at the bottom of the Schlenk, which is the inorganic salt MgClBr. Excess of $CH_3MgBr$ was destroyed by adding three drops of water, then 5 mL hexane was added to the solution to extract the product. The solution was transferred to another Schlenk tube, and the solvent was pumped off. The residue was extracted with hexane, and purified by chromatgraphy (neutral alumina column). Eluting with hexane gave complex **5.9** which was recrystallized from hexane at -78 °C as a white solid (21.0 mg, 0.052 mmol, 58%), m. p.: 114-115 °C. IR ($cm^{-1}$, hex): $v_{CO}$ = 1917 (s). EIMS (m/z): 406 ($M^+$), 404 ($M^+$ - 2H), 392 ($M^+$ - $CH_2$), 390 ($M^+$ - $CH_4$), 376 ($M^+$ - CO - 2H), 374 ($M^+$ - CO - 4H, base), 362 ($M^+$ - CO - $CH_4$), 360 ($M^+$ - CO - $CH_4$ - 2H), 358 ($M^+$ - CO - $CH_4$ - 4H), 348 ($M^+$ - $C_3H_6$ - $CH_4$), 346 ($M^+$ - $C_3H_6$ - $CH_4$ - 2H). $^1$H NMR ($\delta$, $C_6D_6$): 3.96 (1H, m, $H_c$), 2.59, 2.10 (2H, dd, $J_{sc}$ = 5.4 Hz, $J_{ss'}$ = 3.1 Hz, $H_{s'}$, $H_s$), 1.51 (15H, s, $C_5Me_5$), 1.04 (1H, d, $J_{ac}$ = 9.0 Hz, $H_a$), 0.40 (1H, d, $J_{a'c}$ = 7.5 Hz, $H_{a'}$), 0.20 (3H, s, Re-$CH_3$). Anal. Calcd for $C_{15}H_{23}ORe$: C, 44.42; H, 5.72; Found: C, 44.66; H, 5.71.

### 5.9.11. Preparation of Cp*Re($\eta^3$-$C_3H_5$)(CO)(CH$_2$CH$_3$) (5.10)

To a solution of complex **5.1** (30.0 mg, 0.07 mmol) in 5 mL ether was added $CH_3CH_2MgBr$ in ether dropwise by syringe (0.5 mL, 2.55 M). This solution was stirred at 0 °C for 3 h. A white solid was produced and the solution changed color from yellow to colorless. Two drops of water were added to the solution to destroy excess

CH₃CH₂MgBr. The solution was transferred to another Schlenk tube. Ether was pumped off, and the residue was extracted with hexane, then purified by chromatography on a neutral alumina column. Eluting with hexane gave complex **5.10**, which was recrystallized from hexane at -78 °C to give the pure product as a white solid (19.0 mg, 0.045 mmol, 65%), m. p.: 103-104 °C. IR: (cm⁻¹, hexane): $\nu_{CO}$ = 1912 (s). EIMS (m/z): 420 (M⁺), 418 (M⁺ - 2H), 416 (M⁺ - 4H), 390 (M⁺ - CO -2H), 389 (M⁺ - CO - 3H), 388 (M⁺ - CO - 4H), 387 (M⁺ - C₂H₆ - 3H), 386 (M⁺ - C₂H₆ - 4H), 376 (M⁺ - C₃H₆ -2H), 374 (M⁺ - C₃H₆ - 4H), 362 (M⁺ - CO - C₂H₆), 361 (M⁺ - CO - C₂H₆ - H), 360 (M⁺ - CO - C₂H₆ - 2H), 359 (M⁺ - CO - C₂H₆ - 3H, base), 348 (M⁺ - C₂H₆ - C₃H₆), 346 (M⁺ - C₂H₆ - C₃H₆ - 2H). ¹H NMR (δ, C₆D₆): 4.16 (1H, m, $H_c$), 2.60, 2.17 (2H, dd, $J_{sc}$ = 5.4 Hz, $J_{ss'}$ = 3.2 Hz, $H_{s'}$, $H_s$), 1.53 (3H, t, J = 7.7 Hz, CH₃), 1.48 (15H, s, C₅Me₅), 1.05 (1H, d, $J_{ac}$ = 7.7 Hz, $H_a$), 0.91 (2H, m, Re-CH₂), 0.51 (1H, d, $J_{a'c}$ = 7.7 Hz, $H_{a'}$). ¹³C{¹H} NMR (δ, C₆D₆): 95.1 (s, $C_5$Me₅), 77.0 (s, C₃H₅), 30.3 (s, C₃H₅), 28.3 (s, C₃H₅), 27.1 (s, CH₃), 17.5 (s, Re-CH₂), 9.6 (s, C₅{$CH_3$}₅). Anal. Calcd for C₁₆H₂₅ORe: C, 45.80; H, 6.01: Found: 45.50; H, 6.08.

### 5.9.12. Preparation of Cp*Re(η³-C₃H₅)(CO)(η¹-C₃H₅) (5.11)

To a solution of complex **5.1** (30.0 mg, 0.07 mmol) in 5 mL ether was added (η¹-C₃H₅)MgBr by syringe (1 mL, 2.3 M in ether). This solution was stirred at 0 °C for 5 h. A colorless solution and white solid were produced. Three drops of water were added to the solution to destroy excess of (η¹-C₃H₅)MgBr, and the solution was filtered through Celite to remove the solid. The solvent was pumped off, and the product was purified by chromatography (neutral alumina column). Eluting with hexane gave complex **5.11**, which was recrystallized from hexane at -78 °C to give the pure product as a white solid (17.0 mg, 0.039 mmol, 56%). IR (cm⁻¹, hex): $\nu_{CO}$ = 1914 (s). EIMS (m/z): 432 (M⁺), 430 (M⁺ - 2H), 402 (M⁺ - CO - 2H), 400 (M⁺ - CO - 4H) or (M⁺ - C₂H₆ - 2H, base), 398 (M⁺ - C₂H₆ - 4H), 385 (M⁺ - CO - CH₄ - 3H), 374 (M⁺ - CO - C₂H₆), 360 (M⁺ - C₃H₆ - CO - 2H). ¹H NMR (δ, C₆D₆): 6.02 (1H, m, =CH-), 5.17 (2H, m, =CH₂), 4.11 (1H, m, $H_c$), 2.53, 2.29 (2H, dd, $J_{sc}$ = 5.3 Hz, $J_{ss'}$ = 3.4 Hz, $H_{s'}$, $H_s$), 2.30 (1H, m Re-CH₂-), 2.20 (1H, m, Re-CH₂),

1.47 (15H, s, C$_5$Me$_5$), 1.09 (1H, d, J$_{ac}$ = 9.1 Hz, H$_a$), 0.57 (1H, d, J$_{a'c}$ = 6.4 Hz, H$_{a'}$). The elemental analysis of this complex was not determined since not enough sample was obtained.

### 5.9.13. Preparation of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(C$_4$H$_9$) (5.12)

Complex **5.1** (23.6 mg, 0.06 mmol) was dissolved in 5 mL freshly distilled ether, and C$_4$H$_9$MgCl in ether solution (0.2 mL, 1.9 M) was added to it by syringe. This mixture was stirred at 0 °C for 1 h. A colorless solution and white solid were obtained. By using the same purification method as was used for complex **5.11**, **5.12** was obtained as a white solid (18.4 mg, 0.04 mmol, 75%). IR (cm$^{-1}$, hex): ν$_{CO}$ = 1910. EIMS (m/z): 448 (M$^+$), 446 (M$^+$ - 2H), 416 (M$^+$ - C$_2$H$_6$ - 2H), 414 (M$^+$ - C$_2$H$_6$ - 4H), 404 (M$^+$ - C$_3$H$_8$), 402 (M$^+$ - C$_3$H$_8$ - 2H), 389 (M$^+$ - C$_4$H$_{10}$ - H), 376 (M$^+$ - CO - C$_3$H$_8$), 374 (M$^+$ - CO - C$_3$H$_8$ - 2H, base), 361 (M$^+$ - CO - C$_4$H$_{10}$ - H), 359 (M$^+$ - CO - C$_4$H$_{10}$ - 3H), 348 (M$^+$ - C$_3$H$_6$ - C$_4$H$_{10}$), 346 (M$^+$ - C$_3$H$_6$ - C$_4$H$_{10}$ - 2H). $^1$H NMR (δ, C$_6$D$_6$): 4.18 (1H, m, H$_c$), 2.59, 2.17 (2H, dd, J$_{sc}$ = 5.4 Hz, J$_{ss'}$ = 3.3 Hz, H$_{s'}$, H$_s$), 1.50 (15H, s, C$_5$Me$_5$), 1.50-0.8 (m, Re-C$_4$H$_9$), 1.38 (1H, d, J$_{ac}$ = 5.5 Hz, H$_a$), 0.50 (1H, d, J$_{a'c}$ = 7.1 Hz, H$_{a'}$). The elemental analysis of this complex was not determined since not enough sample was obtained.

### 5.9.14. Characterization of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(I) (5.13)

Complex **5.13** was obtained by using the same procedure used for synthesis of **5.9**, but **5.1** was treated with CH$_3$MgI instead of CH$_3$MgBr at room temperature in ether solution for more than 2 h. The pure product was obtained by crystallization from ether as yellow crystals after chromatography on a neutral alumina column (eluting with ether). IR (cm$^{-1}$, ether): ν$_{CO}$ = 1948 (s); EIMS (m/z): 518 (M$^+$), 516 (M$^+$ - 2H), 490 (M$^+$ - CO), 488 (M$^+$ - 2H - CO), 448 (M$^+$ - CO - C$_3$H$_6$, base), 446 (M$^+$ - CO - C$_3$H$_6$ - 2H); $^1$H NMR (δ, C$_6$D$_6$): 4.48 (1H, m, H$_c$), 3.87 (1H, dd, J$_{s'c}$ = 6.0 Hz, J$_{ss'}$ = 3.1 Hz, H$_{s'}$), 2.76 (1H, ddd, J$_{sc}$ = 6.0 Hz, J$_{ss'}$ = 3.1 Hz, J$_{sa}$ = 0.6 Hz, H$_s$), 1.55 (15H, s, C$_5$Me$_5$), 1.42 (1H, d, J$_{ac}$ = 9.2 Hz, H$_a$), 0.56 (1H, d, J$_{a'c}$ = 7.5 Hz, H$_{a'}$).

# Chapter VI

## Reactivity Investigation of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7)

### 6.1. Introduction

Transition metal complexes with M–H bonds are important in stoichiometric and catalytic reactions. The first transition metal hydride complex H$_2$Fe(CO)$_4$ was reported by Hieber in 1931.[152] However, the structures and the chemical natures of the M–H bond were not known until much later.[153] The discovery of the first cyclopentadienyl rhenium hydride complex Cp$_2$ReH was in 1955, which demonstrated that the metal center in this complex can be protonated (Equation 6.1):[154]

$$\text{Cp}_2\text{ReH} \quad + \quad \text{H}^+ \quad \rightleftharpoons \quad \text{Cp}_2\text{ReH}_2^+ \qquad \text{(Eq. 6.1)}$$

Many other rhenium hydride complexes have been reported in the literature, notably those with the general formulae ReHX$_2$L$_4$, ReH$_2$XL$_4$ and ReH$_3$L$_4$, where X is usually a halogen, and L is usually a phosphine ligand.[155] Rhenium hydride complexes were also reported as the products of photochemical or thermal *inter* or *intra* molecular C-H activation of the rhenium pentamethylcyclopentadienyl phosphine carbonyl or dinitrogen complexes Cp*Re(PMe$_3$)(CO)$_2$ or Cp*Re(PMe$_3$)$_2$(N$_2$).[82d,156]

In our group, previous work reported the formation of the first half sandwich rhenium $\eta^3$-allyl hydrido complex Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7), which was obtained in a C–H activation reaction of the coordinated propene ligand in Cp*Re($\eta^2$-C$_3$H$_6$)(CO)$_2$ (3.1).[1d,e] In comparison with other transition metal $\eta^3$-allyl hydrido complexes reported in the literature,[157] complex 5.7 is relatively inert, and the X-ray structure determinations of both isomers (the *endo* and the *exo* isomer) of it were successful. The reactivity

investigation of this complex reported in this Chapter indicates that the Re-H bond in this complex is not as reactive as with other transition metal complexes.

As indicated in Figure 6.1, the reactivity of the metal-hydrogen bond towards unsaturated organic molecules such as olefins and alkynes is essential to many catalytic processes, and can result in the formation of the alkyl, or vinyl metal complexes. Other unsaturated molecules such as diazonium salts can also undergo the similar reactions.[158]
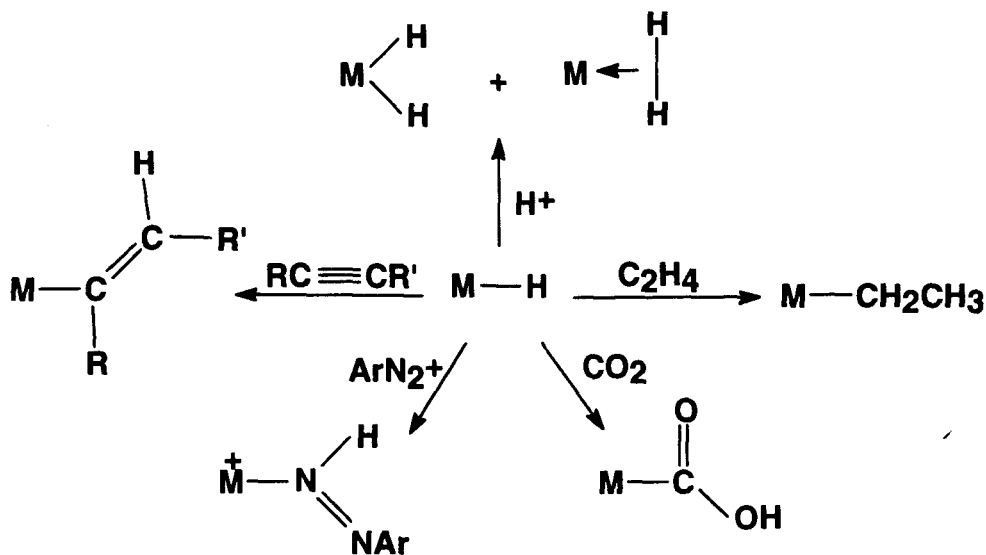
Figure 6.1. Reactions of M-H bond in transition metal hydride complexes.

The protonation of transition metal hydride complexes is a common method for the synthesis of polyhydride complexes. In some cases, the migration of the hydride to an unsaturated ligand, or the elimination of a dihydrogen molecule will create a vacancy in the metal center, and allow the formation of new complexes in the presence of an appropriate ligand.[159] Especially, in the case of an $\eta^3$-allyl hydrido complex, it is possible for the hydride to be transferred to the coordinated allyl by introducing a potential ligand to occupy the vacancy after hydride has migrated.[160]

157

Although several $\eta^3$-allyl hydride complexes have been reported, the study of the reactivity of these complexes has been limited because of the instability of the complexes.[157] The reactivity study of the iridium $\eta^3$-allyl hydride complex Cp*Ir($\eta^3$-C$_3$H$_5$)(H) was reported by Bergman's group in 1988.[160] The result showed that this complex is a precursor for the C-H activation of the solvents, such as C$_6$H$_6$ and C$_3$H$_6$ in the presence of a phosphine ligand. In our group, the similar allyl hydrido rhenium complex **5.7** was reported in 1989, but due to the low yield of **5.7** produced in a secondary photochemical reaction of the propene complex, the investigation of the chemistry associated with **5.7** was not conducted until this work. We have discovered a more efficient method of synthesis of **5.7**, which was reported in Chapter V. In this Chapter, the reactions of **5.7** with various unsaturated bonds and electrophiles will be reported. Especially, the protonation of **5.7** under different conditions will be discussed in detail.

## 6.2. Reactivity of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7)

### 6.2.1. Reaction of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7) with Alkenes and Alkynes

As anticipated for most transition metal hydride complexes, we assumed that complex **5.7** will react with C=C bond to give the corresponding alkyl complexes Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(R). These are known complexes. They were successfully synthesized in this work from the reaction of **5.1** with RMgX, as reported in Chapter V. Complex **5.7** was first treated with CH$_2$=CH$_2$ at room temperature in hexane, and then with hexene or cyclohexene. The IR showed that the $\nu$(CO) absorption of **5.7** did not change over 24 h.

We then replaced the alkenes with alkynes in the same attempt to investigate the reactivity of Re-H bond with a C≡C bond. Complex **5.7** was treated with PhC≡CMe and MeC≡CMe in hexane at room temperature for 24 h but no reaction was observed. We

presume that it is because the $\eta^3$-allyl ligand in complex **5.7** can not be converted to the $\eta^1$-allyl, as this is a requirement for the coordination of the unsaturated bonds.

### 6.2.2. Reaction of Cp\*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7) with CO and CH$_3$CN

Although **5.7** did not react with unsaturated C=C bonds, we expect it may possibly react with C≡O or MeC≡N.[158] Consequently, CO was bubbled through a solution of **5.7** in hexane and the reaction was monitored by IR. The IR showed a decrease of the CO band for **5.7** in intensity, but no new CO absorption resulted. Overnight, the IR showed complete disappearance of $\nu$(CO) for **5.7**, but no new CO band appeared. The $^1$H NMR spectrum of the residue after removing solvent showed no Cp\* or Re-H signals and indicated the decomposition of **5.7**.

The reaction of **5.7** in pure CH$_3$CN was stirred at room temperature for 24 h and was monitored by IR. The result was that the $\nu$(CO) absorption of **5.7** did not change. No reaction occurred.

### 6.2.3. Reaction of Cp\*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7) with PMe$_3$

Complex **5.7** was treated with PMe$_3$ in an attempt to replace the CO with PMe$_3$ to synthesize a $\eta^3$-allyl hydrido phosphine derivative of **5.7**, Cp\*Re($\eta^3$-C$_3$H$_5$)(PMe$_3$)(H). The reaction was carried on overnight, and the result showed that no reaction occurred.

### 6.2.4. Reaction of Cp\*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7) with [NO][BF$_4$]

When complex **5.7** was treated with [NO][BF$_4$] in acetone at -78 °C, in an attempt to coordinate NO at the rhenium center in **5.7**, it reacted to produce complex [Cp\*Re($\eta^2$-C$_3$H$_6$)(CO)(NO)][BF$_4$] (**6.1**). The NO$^+$ attacked the metal, followed by a migration of the hydride to the $\eta^3$-allyl group to give a propene complex **6.1** (Schemes 6.1 and 6.2).

The IR spectrum of **6.1** exhibited a $\nu$(CO) band at 2047 cm$^{-1}$, and $\nu$(NO) at 1765 cm$^{-1}$. These are in the typical regions for coordinated CO and NO absorptions in rhenium cationic compounds.[1d,161] The FABMS of **6.1** gave a peak for the parent ion of the cation

at m/z 422, and this is also the base peak. Two observed fragments are: m/z 380 (loss of $C_3H_6$ from $M^+$), and m/z 350 (consistent with loss of $C_3H_6$, CO and 2H from $M^+$).

The $^1H$ NMR spectrum of **6.1** (Table 6.1) showed resonances for two isomers in a ratio of **a/b** = 1/1.1 ($^1H$ NMR integration for the propene protons; the two Cp* resonances were overlapped), and these were assigned to the isomers **6.1a** and **6.1b** (Scheme 6.2), but the specific structures of these two isomers have not been determined at this stage. For isomer **6.1a**, the propene proton signals are assigned as: $\delta$ 4.27 (multiplet) for $H_3$, $\delta$ 3.59, $\delta$ 3.29 for the two terminal protons $H_1$ and $H_2$, and a doublet at $\delta$ 2.52 for the methyl. The Cp* showed a singlet at $\delta$ 2.23. For isomer **6.1b**, the central proton $H_3$ gave a multiplet at $\delta$ 3.93, and the two resonances at $\delta$ 3.00 and 2.78 were assigned to the terminal protons $H_1$ and $H_2$. The methyl group showed a doublet at $\delta$ 2.12, and the Cp* gave a singlet at $\delta$ 2.22. The $^1H$ NMR sample in $CDCl_3$ was kept at room temperature for one week, and the $^1H$ NMR spectrum indicated that the ratio of **6.1a** and **6.1b** did not change.

We propose that the two isomers resulted from $NO^+$ attacking the different sides of the two (*exo* and *endo*) isomers of **5.7**, since the sample of **5.7** used for this reaction was a mixture of both the *endo* and the *exo* isomers. Theoretically, there are three possible sides for the $NO^+$ to attack at the rhenium, as described in Scheme 6.2, and these are numbered as **1**, **2** and **3**. We assume that a four-legged piano stool intermediate is formed after the $NO^+$ attacked the rhenium, shown in square brackets in Scheme 6.2. The NO ligand must be a bent 1e-donor at this stage, and the $\eta^3$-allyl still adopts the same orientation as it had in **5.7**. If the hydride transfers only to the nearest end of the allyl to produce the propene ligand in the product diastereomer, followed by the conversion of the NO from a 1e-donor to the 3e-donor to give a cationic complex **6.1**, only the reaction of **5.7** with $NO^+$ in positions **1** and **2** will be productive. This is because the hydride will be in a position *trans* to the allyl if $NO^+$ attacked **5.7** at side **3**. This will preclude transfer of the hydride to the allyl, and no propene complex **6.1** would be obtained. Therefore, for the *endo* isomer of **5.7**, diastereomer **6.1a'** and **6.1b'** are obtained, while for the *exo* isomer of
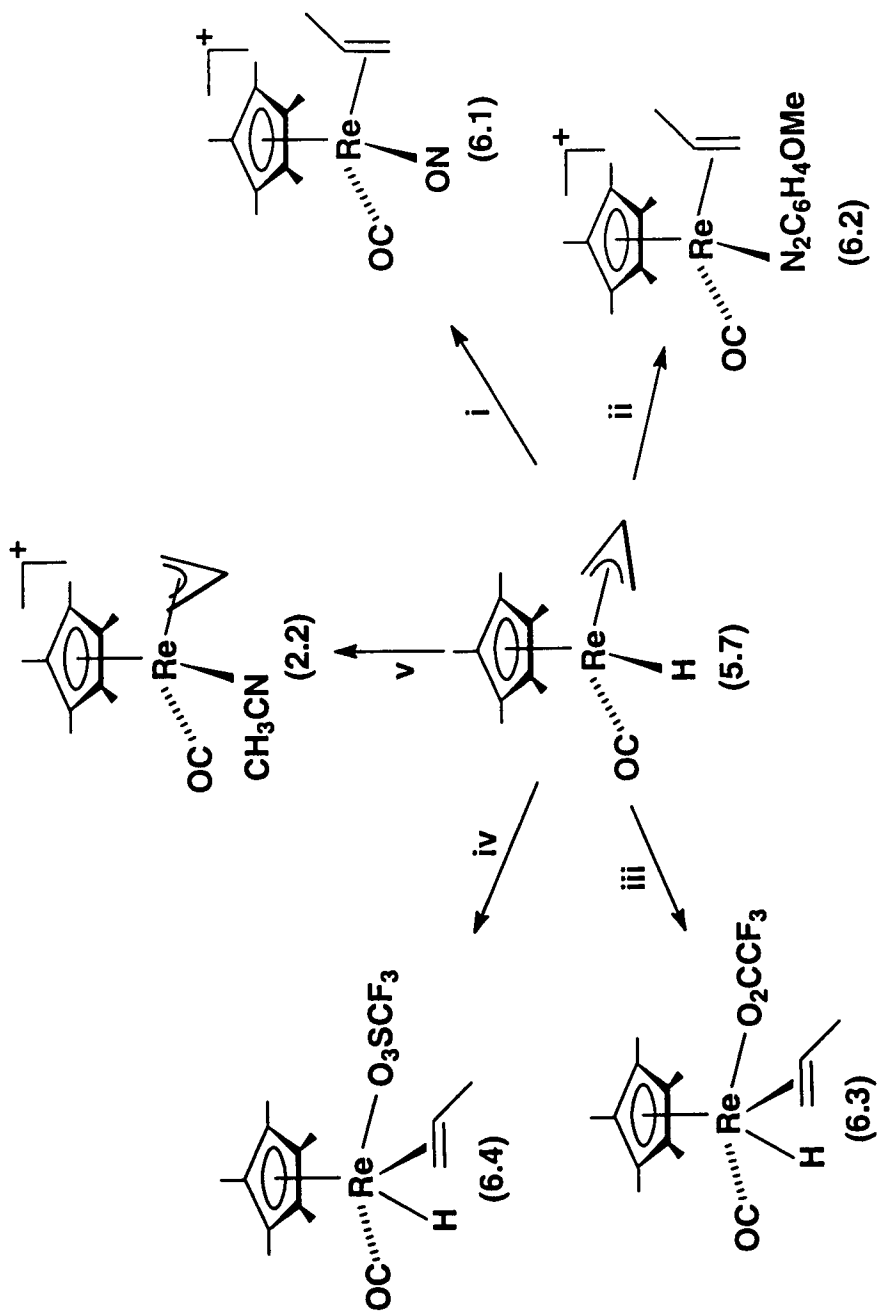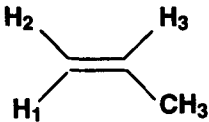
Scheme 6.1. Reactions of **5.7** with electrophiles. i. [NO][BF$_4$]/acetone; ii. [N$_2$C$_6$H$_4$OMe][BF$_4$] /acetone; iii. CF$_3$COOH/acetone-d$_6$; iv. CF$_3$SO$_3$H/C$_6$D$_6$; v. [Ph$_3$Cl][BF$_4$]/CH$_3$CN. For **6.3** and **6.4**, the specific isomer has not been established.

161
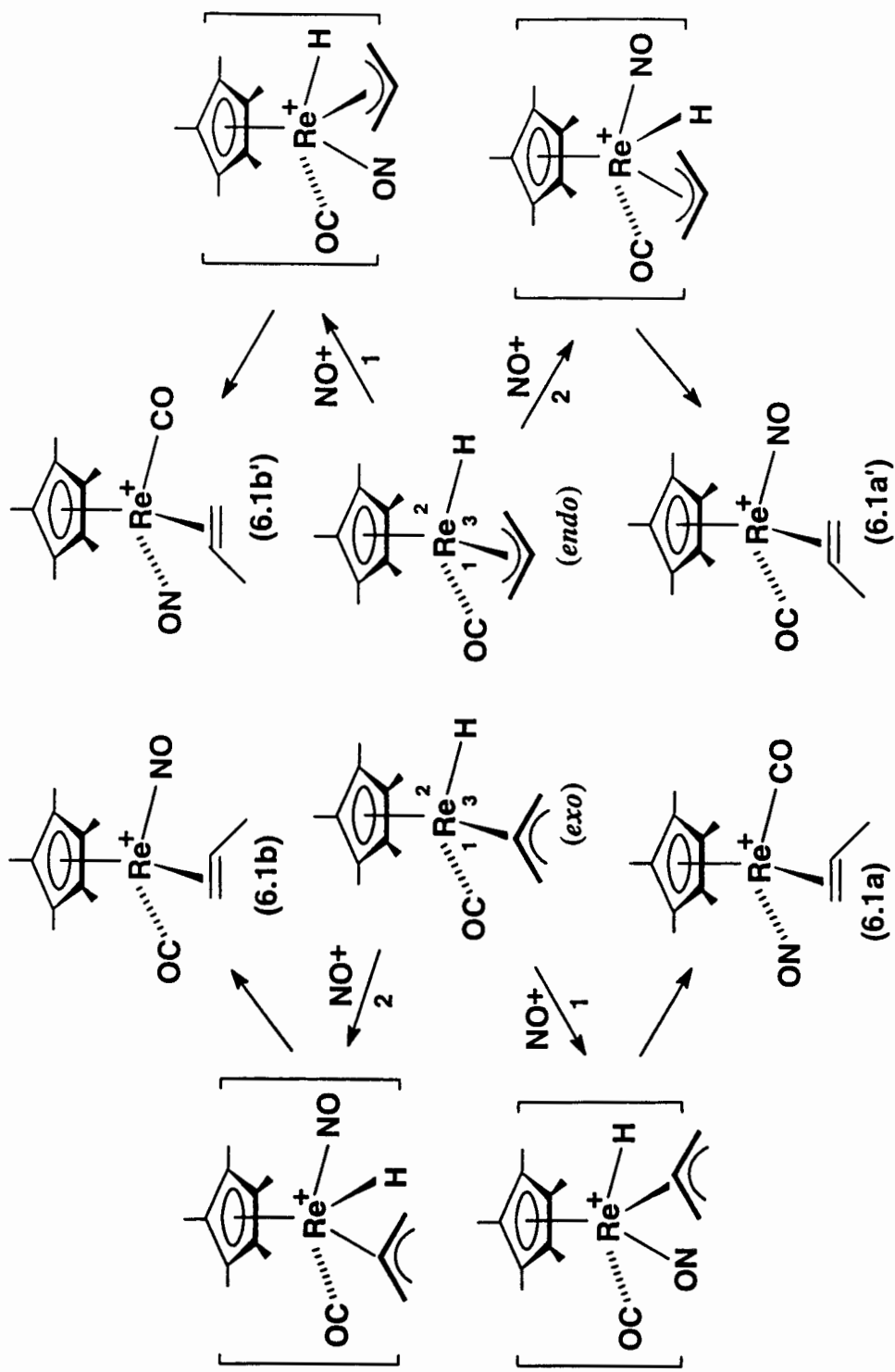
Scheme 6.2. Isomers of **6.1** resulted from the reaction of the two isomers of **5.7** with NO+. Isomers of **6.1a** and **6.1a'**, **6.1b** and **6.1b'** are enantiomers.

**5.7**, **6.1a** and **6.1b** will be formed as the product (Scheme 6.2). The enantiomers **6.1a** and **6.1a'**, as is true also for **6.1b** and **6.1b'** are not distinguishable in the $^1$H NMR, therefore only two sets of $^1$H NMR resonances were obtained, which correspond to the two diastereomers **6.1a** and **6.1b**.

Table 6.1. $^1$H NMR Data of the Propene Ligand in Complexes **6.1-6.4**.



| Complexes | H$_3$ | H$_2$ | H$_1$ | CH$_3$ |
|---|---|---|---|---|
| **6.1a**[a] | 4.27 (m) | 3.29 (d) | 3.59 (dd) | 2.52 (d) |
| **6.1b**[a] | 3.93 (m) | 2.78 (d) | 3.00 (dd) | 2.12 (d) |
| **6.2**[a] | 4.10 (m) | 3.10 (dd) | 3.47 (d) | 2.16 (d) |
| **6.3**[b] | 3.22 (m) | 2.20 (d) | 2.60 (d) | 2.36 (d) |
| **6.4**[b] | 4.00 (m) | 2.19 (dd) | 2.63 (d) | 2.39 (d) |

a. The spectrum was recorded in CDCl$_3$; b. The spectrum was recorded in C$_6$D$_6$. m, multiplet; d, doublet; dd, doublet of doublets. Coupling constants are given in the experimental section.

## 6.2.5. Reaction of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7) with [N$_2$C$_6$H$_4$OMe][BF$_4$]

As shown in Figure 6.1, N$_2$Ar$^+$ can insert into the M-H bond of certain hydrides to give the aryldiazene M-NH=NAr.[155] We reacted **5.7** with [N$_2$C$_6$H$_4$OMe][BF$_4$] in acetone at -78 °C in an attempt to simulate the chemistry reported in the literature. But, the experimental result indicated that [N$_2$C$_6$H$_4$OMe]$^+$ attacked the rhenium instead of inserting into the Re-H bond, and hydride transferred to the $\eta^3$-allyl to produce the propene complex [Cp*Re($\eta^2$-C$_3$H$_6$)(CO)(N$_2$C$_6$H$_4$OMe)][BF$_4$] (**6.2**).

The IR of **6.2** showed $\nu$(CO) at 1982 cm$^{-1}$, and $\nu$(NN) at 1711 cm$^{-1}$, which are in the normal regions for similar cationic rhenium aryldiazenido complexes.[82d] The $^1$H NMR spectrum of **6.2** showed a mutiplet at $\delta$ 7.04 (integration 4H) for the C$_6$H$_4$ protons, the CH$_3$O gave a singlet at $\delta$ 3.87, in the same region observed for Re-N$_2$C$_6$H$_4$OCH$_3$ in cationic rhenium complexes.[82d] The coordinated propene proton resonances were assigned as: $\delta$ 4.10, multiplet for H$_3$; $\delta$ 3.47, $\delta$ 3.10 for the H$_1$ and H$_2$, and the doublet at $\delta$ 2.16 for the methyl group. The Cp* resonance was a singlet at $\delta$ 2.17. The microanalysis of **6.2** was not obtained owing to the decomposition of the sample. But all the information from the spectroscopic data indicated that complex **6.2** was formed. Although iridium aryldiazenido ethylene complexes were reported from our group,[162] there is no previous rhenium aryldiazenido olefin complex reported in the literature.

This complex is not as stable as complex **6.1**, only the IR and $^1$H NMR data of it were obtained. The FABMS of **6.1** was uninformative because of the decomposition, and the subsequent IR on this sample showed no $\nu$(CO) absorption, and the $^1$H NMR spectrum gave no resonance for Cp*.

## 6.2.6. Reaction of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7) with [Ph$_3$C][BF$_4$] in CH$_3$CN

Complex **5.7** reacted with [Ph$_3$C][BF$_4$] in CH$_3$CN at -78 °C to form the acetonitrile complex **2.2**, which was first synthesized from complex **2.1** by using PhIO to remove one

coordinated CO in **2.1** as described in Chapter II. In this reaction, we assume that $Ph_3C^+$ attacked the M-H bond, abstracted $H^-$ to form $Ph_3CH$, which created a 16e intermediate $[Cp*Re(\eta^3-C_3H_5)(CO)]^+$. The acetonitrile then coordinated to this species to produce complex **2.2**. The IR spectrum, FABMS and the $^1H$ NMR spectrum in $CDCl_3$ of this product are identical with those obtained for **2.2** when produced from **2.1** as described in Chapter II.

The reaction of **5.7** with $[Ph_3C][BF_4]$ in $CH_3CN$ was not as selective as in the case of $[NO][BF_4]$, in which complex **6.1** is the only product. In this reaction, complex **2.2** was obtained in only a low yield (31%, according to the integration of the two Cp* resonances in the $^1H$ NMR spectrum). The other product (69%, according to the integration of the two Cp* resonances in the $^1H$ NMR spectrum), for which the structure could not be determined because of instability, showed a Cp* resonance at δ 2.15, and the $CH_3CN$ resonance at δ 2.68. Besides these two resonances, the $^1H$ NMR spectrum of the product also showed a multiplet at δ 3.79, a doublet of doublets at δ 3.04, and a doublet at δ 2.92, which are in the region for the coordinated $\eta^3$-allyl. But the two $H_a$ resonances were overlapped with other resonances, and were unable to be assigned. It was reasonable to assume that this product was the *exo* isomer of **2.2** (especially, the IR of this reaction showed only one ν(CO) at 1971 $cm^{-1}$ in $CH_3CN$), because the **5.7** used for the reaction was a mixture of both the *endo* and the *exo* isomers. Based on this consideration, the $^1H$ NMR sample of this product was kept at room temperature, and the $^1H$ NMR spectrum was recorded. We were expecting a conversion of the *exo* to the *endo*, since the *endo* isomer of **2.2** is the thermodynamic preferred isomer, as described in Chapter II.

The $^1H$ NMR spectrum showed a decrease in the unknown product (according to the intensity of the Cp* signal), but the proportion of *endo* **2.2** did not increase. Instead, more impure resonances appeared. After 5 days, the $^1H$ NMR spectrum showed only complex **2.2**. This result is inconsistent with the assumption that the unknown product is the *exo* isomer of **2.2**. Because the *endo* isomer of **2.2** is thermally stable (no decomposition when it was refluxed at 110 °C), there is no reason to consider the *exo*

isomer of **2.2** would be thermally sensitive. This unknown product could result from the Ph$_3$C$^+$ attacking the metal and hydrogen transfer to the allyl. As well as the signals mentioned above, a doublet at $\delta$ 2.45, integration 3H, could arise from the methyl of propene, and the corresponding resonances at $\delta$ 3.79 (m), $\delta$ 3.04 (dd) and $\delta$ 2.92 (d) could arise from the H$_3$, H$_1$ and H$_2$ in a coordinated propene. But, the resonances in phenyl region ($\delta$ 7.12-7.30) integrated for only five protons. This is not consistent with the coordination of [Ph$_3$C$^+$], but it is in agreement with a coordination of a C$_6$H$_5$ group. The interpretation of the $^1$H NMR of this unknown complex is therefore consistent with a propene complex [Cp*Re($\eta^2$-C$_3$H$_6$)(CO)(CH$_3$CN)(C$_6$H$_5$)][BF$_4$], but based on only the evidence obtained from the $^1$H NMR spectrum, the precise determination of this unknown complex is in some doubt.

## 6.3. Protonation of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7)

### 6.3.1. Protonation of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) with CH$_3$COOH and CF$_3$COOH

An investigation of the protonation reaction of the transition metal hydride complex Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (**5.7**) was considered important for two reasons: i. to test the acidity of the hydride ligand; ii. to determine whether a coordinatively unsaturated cationic complex could be obtained by elemination of H$_2$.[163] When complex **5.7** was reacted with CH$_3$COOH in hexane for 24 h, no reaction occurred. When **5.7** was reacted with the stronger acid CF$_3$COOH at -78 °C in acetone-d$_6$, the IR of the reaction solution after 5 min. showed a $\nu$(CO) band at 1962 cm$^{-1}$, which was assigned to the new complex Cp*Re($\eta^2$-C$_3$H$_6$)(H)(CO)(CF$_3$COO) (**6.3**) (Scheme 6.1). The structure of **6.3** shown in Scheme 6.1 and Figure 6.2 is only one of a possible number of isomers, and the actual isomer has not been established at this stage.

The CIMS (chemical ionization mass spectrum) of **6.3** gave a peak for the parent ion at m/z 506, but a stronger peak at m/z 505 for [M$^+$ - H], and a base peak at m/z 391, which is consistent with loss CF$_3$COOH and one H atom from the parent ion. The EIMS

gave a clear pattern for [M$^+$ - 2H] at m/z 504, and fragments at m/z 476 [M$^+$ - CO - 2H], m/z 434 [M$^+$ - CO - C$_3$H$_6$ - 2H], and m/z 360 [M$^+$ - CF$_3$COOH - CO - 4H].

The $^1$H NMR spectrum of **6.3** (Figure 6.2) in C$_6$D$_6$ showed all the resonances for the propene protons, which were assigned as: a multiplet at δ 3.22 for the central proton of the η$^2$-CH$_2$CHCH$_3$, the two resonances at δ 2.60 and δ 2.20 for the terminal protons, and a doublet at δ 2.36 integrating for three protons for the methyl. The Cp* gave a singlet at δ 1.59. The Re-H gave a singlet at δ -9.28, which was in the expected region for a neutral rhenium hydride complex by comparison with **5.7**.

### 6.3.2. Protonation of Cp*Re(η$^3$-C$_3$H$_5$)(CO)(H) with CF$_3$SO$_3$H

In order to confirm the result obtained from the reaction of **5.7** with CF$_3$COOH, the protonation of **5.7** was conducted again by using CF$_3$SO$_3$H in either acetone-d$_6$ at -78 °C, or C$_6$D$_6$ at room temperature, and complex Cp*Re(η$^2$-C$_3$H$_6$)(H)(CO)(CF$_3$SO$_3$) **(6.4)** was obtained (Scheme 6.1, actual isomer of **6.4** was not determined at this stage). The IR spectrum of **6.4** in C$_6$D$_6$ showed ν(CO) absorption at 1975 cm$^{-1}$. The CIMS of **6.4** gave the parent peak at m/z 542, and the fragments of [M$^+$ + 1] at m/z 543, [M$^+$ - 1] at m/z 541 are even stronger than the parent ion peak. The base peak at m/z 391 is consistent with loss of CF$_3$SO$_3$H and one H atom from the parent ion. The EIMS of both **6.3** and **6.4** did not show the parent peak, but showed the same base peak at m/z 391, which is consistent with the reductive elimination of acid, and loss of one H atom (presumably from the Cp* or propene).

The $^1$H NMR spectrum of **6.4** in C$_6$D$_6$ (Figure 6.3) gave almost the same proton resonances for the propene as in **6.3**. The Cp* signal showed a singlet at δ 1.58, and the major Re-H resonance was at δ -9.68. The five protons of the propene were assigned as: multiplet at δ 4.00 for H$_3$, a doublet at δ 2.39 for the methyl, and the two resonances at δ 2.63 and 2.19 for the H$_1$ and H$_2$. There are two minor hydride resonances at δ -9.51 and δ -9.33, which may be assigned to the different isomers of **6.4**, as discussed in section 6.3.5.1 (Schemes 6.5 and 6.6).
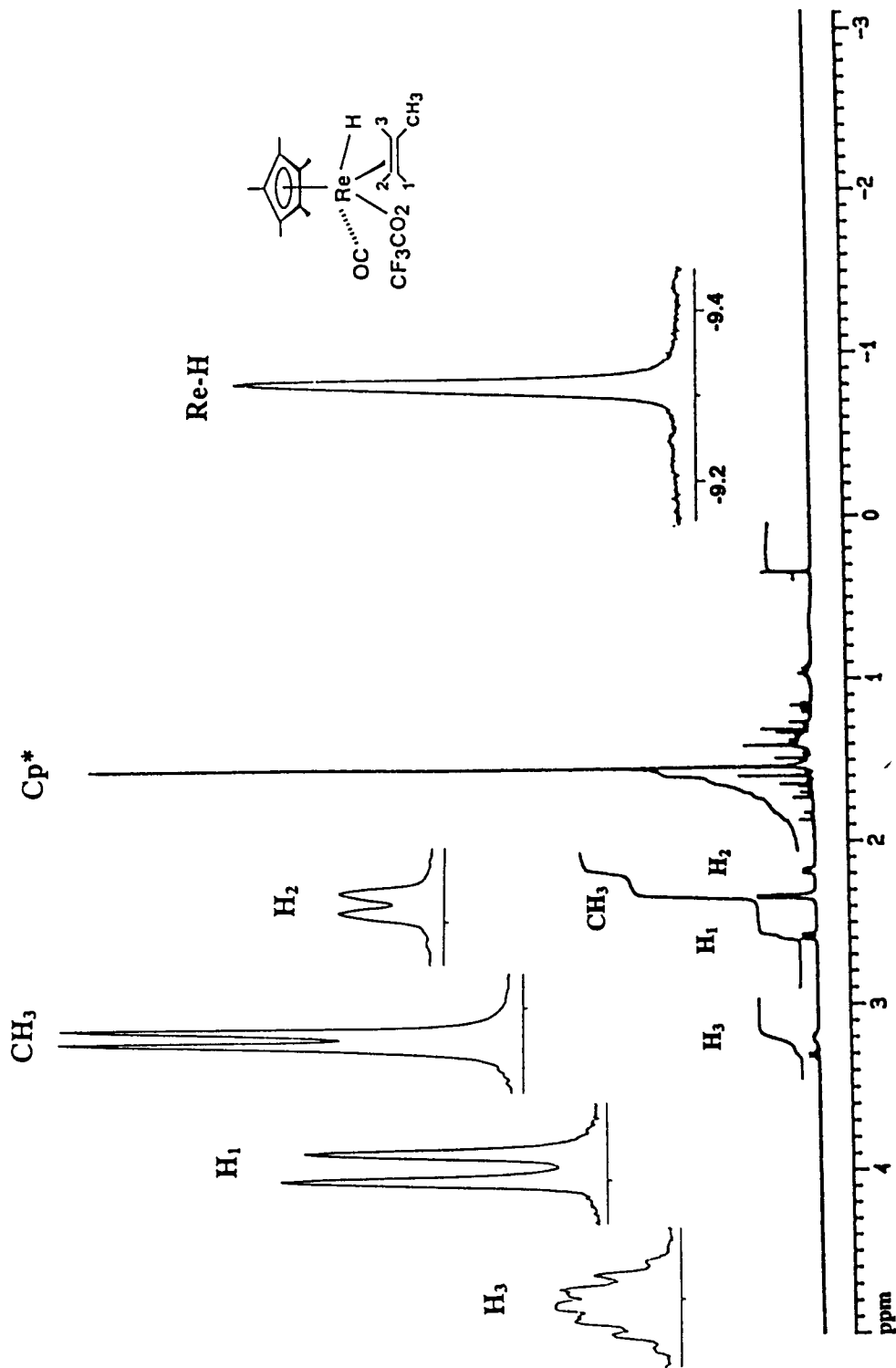
Figure 6.2. $^1$H NMR spectrum of Cp*Re($\eta^2$-C$_3$H$_6$)(H)(CO)(CF$_3$COO) (6.3) in C$_6$D$_6$.

The unlabeled resonances are signals from the impurities.

168
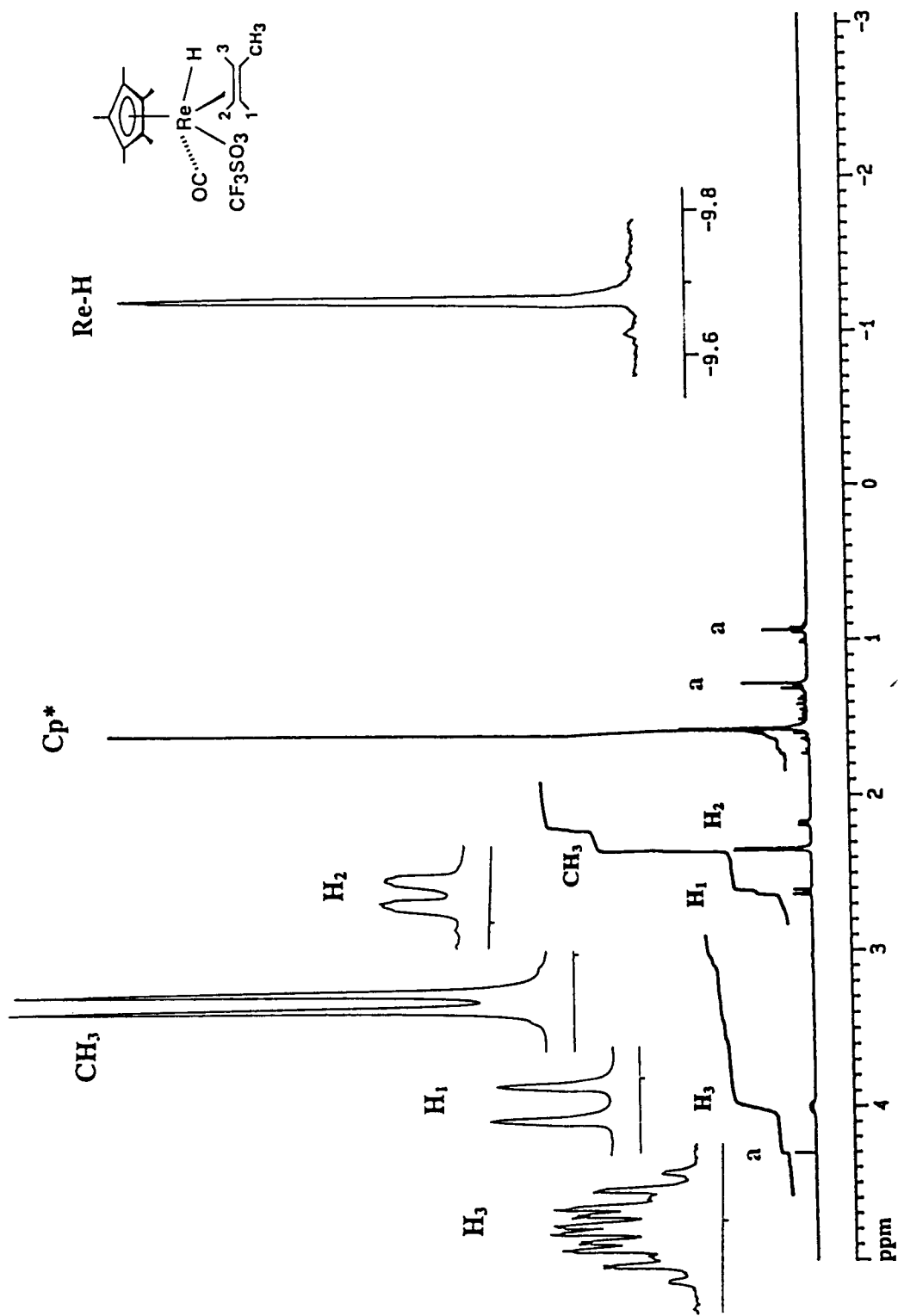
Figure 6.3. $^1$H NMR spectrum of Cp*Re($\eta^2$-C$_3$H$_6$)(H)(CO)(CF$_3$SO$_3$) (6.4) in C$_6$D$_6$. a. impurity.

### 6.3.3. Protonation of Cp*Re(η³-C₃H₅)(CO)(H) with CF₃COOD

The protonation of **5.7** with CF₃COOH may theoretically occur in three different ways (Scheme 6.3): **i.** at the M-H bond; **ii.** at the η³-allyl; **iii.** at the metal center. In the first case, the protonation of the M-H bond would form a molecular dihydrogen intermediate. The coordination of CF₃COO⁻ could then occur with the elimination of H₂ from the intermediate to produce **6.3a**. But, the fact is that the reaction of **5.7** with CF₃COOH did not form complex **6.3a**. This indicated that the protonation of **5.7** with CF₃COOH did not occur at the M-H bond.

If the protonation occurs by pathway **ii** or **iii**, the product will be one of the isomers of complex Cp*Re(η²-C₃H₆)(H)(CO)(CF₃COO) (**6.3**), depending on the attacking position of the H⁺ to the rhenium in **5.7**, which will form different dihydride intermediates in pathway **iii** (the two hydrides can be either *cis* or *trans*), and also depending on the coordination position of the CF₃CO₂⁻ anion in the protonated intermediates in both pathways **ii** and **iii**. As indicated previously, the specific isomer of the propene hydride complexes **6.3** and **6.4** has not been determined, the isomer shown in all Schemes in this Chapter is only representative of the possible isomers. Although pathways **ii** and **iii** give constitutionally the same product when CF₃COOH is used for the protonation of **5.7**, the two mechanisms may be distinguished by employing a deuterated acid to deuterate **5.7**. If the deuteration occurs at the η³-allyl, we would expect deuterium incorporation into the methyl of propene ligand, when formed by deuteration of **5.7** with D⁺, and Cp*Re(η²-CH₂=CHCH₂D)(CO)(H)(O₂CCF₃) (**6.5**) should be the only product. There would be no D incorporation into the hydride. If the protonation occurs at the metal center, to form a hydridodeuteride intermediate first, then by a migration of either D or H to the allyl to give the final product, a mixture of Cp*Re(η²-CH₂=CHCH₂D)(CO)(H)(O₂CCF₃) (**6.5**) and Cp*Re(η²-CH₂=CHCH₃)(CO)(D)(O₂CCF₃) (**6.6**) should be obtained (Scheme 6.4).

The protonation of **5.7** with CF₃COOD was conducted in C₆D₆ at room temperature, and the spectroscopic data were recorded. This reaction did indeed result in
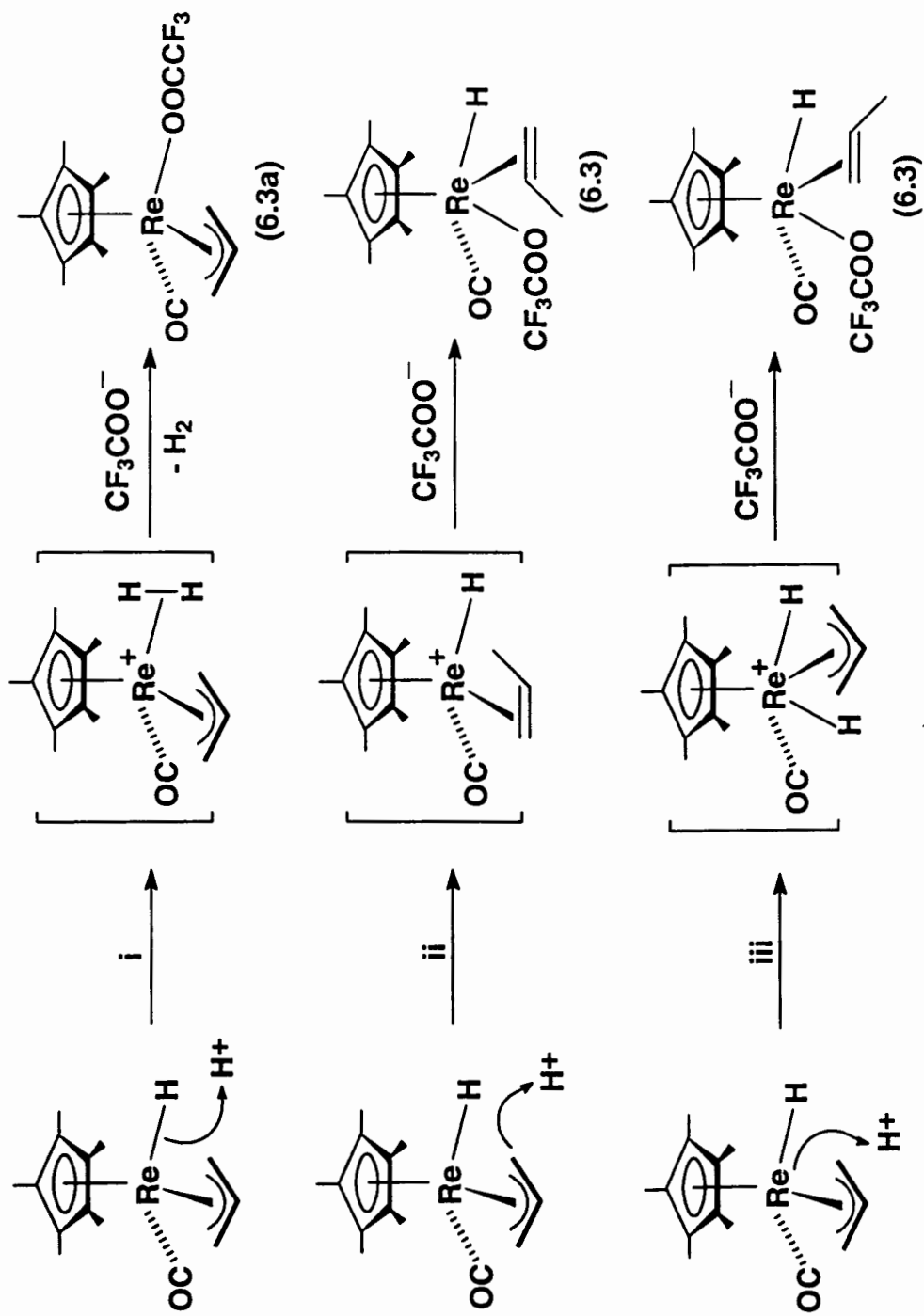
Scheme 6.3. Proposed protonation pathway of **5.7** with CF₃COOH.

171
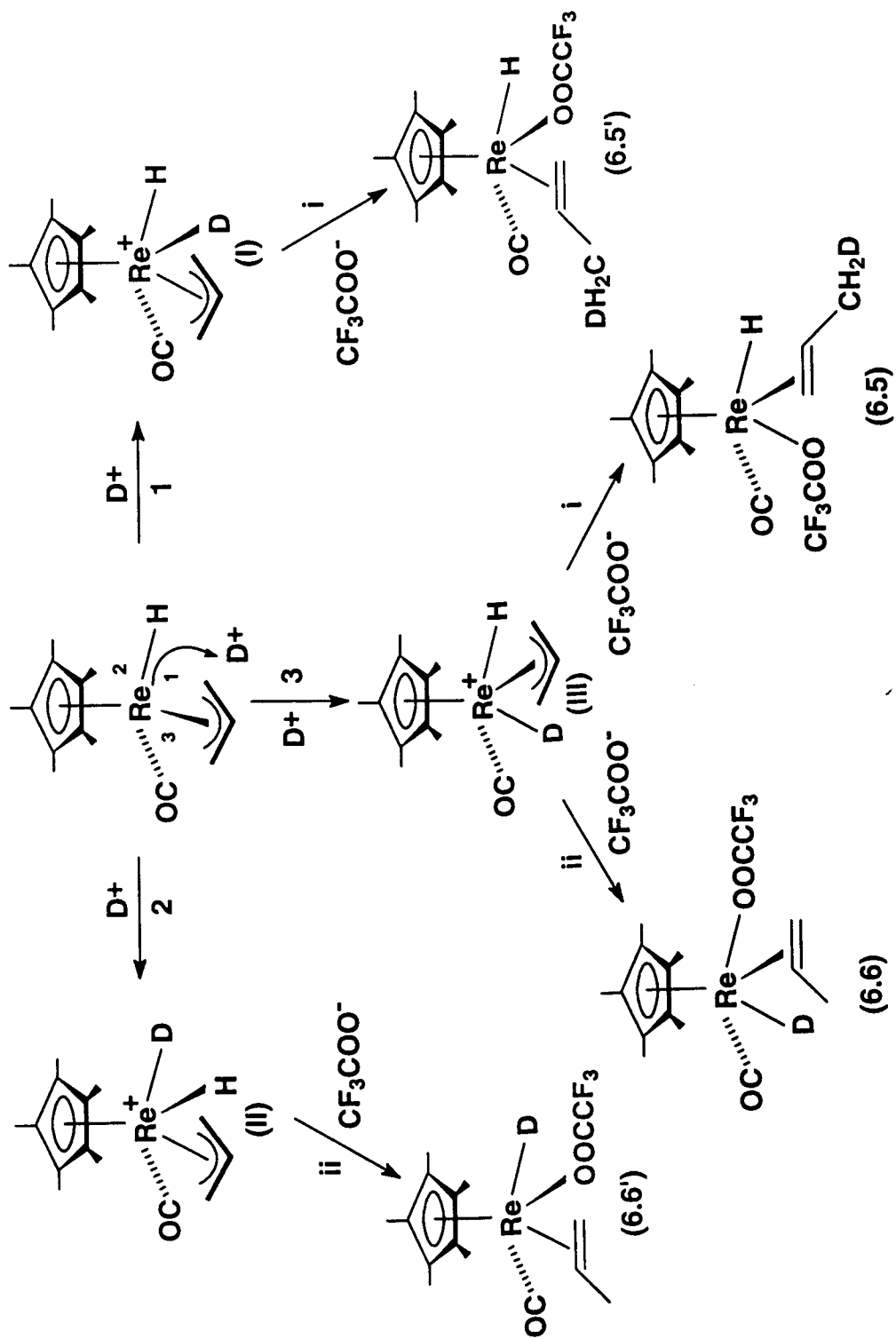
Scheme 6.4. Products produced from the deuteration of **5.7** with CF₃COOD.
i. D migrated to the η³-allyl;  ii. H migrated to the η³-allyl.

a mixture of **6.5** and **6.6**, which suggested that the protonation of **5.7** certainly did occur at the metal center. However, there was an excess of **6.5**. The IR spectrum of the mixture showed only one $\nu(CO)$ absorption at 1971 cm$^{-1}$. The $^1H$ NMR spectrum of the mixture gave almost the same resonances as for complex **6.3**, except that the signal at $\delta$ 2.33 (assigned to $-CH_2D$ and $-CH_3$) is broad because of the coupling of the D atom , and the central proton H$_3$ also showed a broad multiplet at $\delta$ 3.20. The $^2H\{^1H\}$ NMR of this mixture gave a broad signal at $\delta$ 2.24, which corresponds to the deuterium in $-CH_2D$ in **6.5**, and is in a position similar to the proton resonance of this group, indicating the presence of the $-CH_2D$ group in complex **6.5**. A resonance at $\delta$ -9.31, corresponding to Re$-$D, indicated the presence of complex **6.6**. The integration of the $^2H$ resonances for **6.5** and **6.6** is 3.3/1. The excess of **6.5** may be because both mechanisms **ii** and **iii** are operating. Note that mechanism **ii** produces only **6.5**, where **iii** produces both **6.5** and **6.6** (Scheme 6.4). If mechanism **iii** is the only pathway for the protonation of **5.7** to occur, the integration of $^2H$ in the NMR spectrum for $-CH_2D$ in **6.5** and Re-D in **6.6** should be the same. However, the excess **6.5** may also result from the isotope effect of the exchanging of D and H. The estimated equilibrium isotope effect was obtained by calculating $K_H$ / $K_D$ for the equilibrium system between **6.5** and **6.6**, which is 2.02 when the stretching frequencies of Re-H and C-H were used for the calculation (see Appendix). Scheme 6.4 showed only one example of all the possible isomers that may be produced from the protonation of **5.7** with $CF_3COOD$. In order to simplify the situation, the $CF_3COO^-$ anion was assumed to take only the position that the migrated H or D initially occupied. If, in fact the coordination of the $CF_3COO^-$ can occur between any two basal ligands of the dihydride intermediates, and this would lead to further different isomers of **6.5** and **6.6**.

## 6.3.4. Protonation of $Cp^*Re(\eta^3-C_3H_5)(CO)(H)$ with $HBF_4$

The protonation of **5.7** with $CF_3COOD$ suggested that the protonation with $CF_3COOH$ or $CF_3SO_3H$ did occur at the metal center, and a dihydride intermediate was formed. Following this, the nucleophilic anion reacted with the dihydride cationic complex

to produce the final product as shown in Scheme 6.4. We therefore thought that, if HBF$_4$ were used for the reaction, since BF$_4^-$ is a much poorer ligand compared with CF$_3$COO$^-$ or CF$_3$SO$_3^-$, it may be possible to observe the dihydride intermediate. Based on this idea, the protonation of **5.7** was conducted with HBF$_4$ at room temperature in C$_6$D$_6$. However, the product was not the dihydride cationic complex. Although microanalysis was not obtained, the IR and the $^1$H NMR indicated that a propene hydride complex was produced, as in the case when CF$_3$COOH or CF$_3$SO$_3$H were used. We assume that the product was Cp*Re($\eta^2$-C$_3$H$_6$)(H)(CO)(FBF$_3$) (**6.7**).

The IR of the product showed a $v$(CO) absorption at 1971 cm$^{-1}$ in C$_6$D$_6$. The CIMS of the product gave a fragment at m/z 393, which is in agreement with the formula of [Cp*Re($\eta^2$-C$_3$H$_6$)(H)(CO)]$^+$, and is consistent with [M$^+$ - BF$_4$]. The $^1$H NMR of this complex gave resonances at: $\delta$ 2.73 (multiplet) for H$_3$, two doublets at $\delta$ 2.69 and $\delta$ 2.47 for H$_1$ and H$_2$, and a doublet at $\delta$ 2.33, integrated 3H, for the methyl. The Cp* resonance appeared at $\delta$ 1.60, and the major Re-H resonance was a singlet at $\delta$ -9.45, which is in a similar region to the hydride resonances in complexes **6.3-6.6**. There are two minor hydride resonances at $\delta$ -9.30 and $\delta$ -9.26, which may be assigned to the different isomers of **6.7**, as discussed in section 6.3.5.1 (Schemes 6.5 and 6.6). This product was even more sensitive compared with **6.3-6.6**, and it decomposed within 24 h in C$_6$D$_6$ while kept in the refrigerator waiting for the $^{13}$C NMR experiment.

### 6.3.5. Low Temperature $^1$H NMR Study of the Protonation of 5.7

### 6.3.5.1 Protonation of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7) with CF$_3$COOH in CD$_2$Cl$_2$

As described in 6.3.3, the protonation of **5.7** with CF$_3$COOD did indicate the formation of the dihydride intermediate [Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(D)(H)][CF$_3$COO] (*cis*) or [Cp*Re($\eta^3$-C$_3$H$_5$)(D)(CO)(H)][CF$_3$COO] (*trans*) (Scheme 6.4). As just mentioned, the attempt to stabilize the dihydride complex by using HBF$_4$ to protonate **5.7** was not successful, and the hydride propene complex **6.7** was obtained. Therefore, the low

temperature protonation of **5.7** was studied. The purpose of this was to protonate **5.7** at low temperature so as to try to observe any dihydride intermediates produced from the protonation reaction. It was also hoped to observe whether different isomers of the dihydride are produced and lead to different isomers of the product, and by monitoring the conversion of these isomers by $^1$H NMR to attempt to understand the protonation process.

Based on the ideas mentioned above, the protonation of **5.7** with $CF_3COOH$ in $CD_2Cl_2$ at low temperature was studied. $CF_3COOH$ was added to a solution of **5.7** in $CD_2Cl_2$ at 173 K in a $^1$H NMR tube, the sample was put into the probe, and the spectrum was recorded 5 min. later at 183 K. The initial spectrum at 183 K showed the presence of only the *endo* and the *exo* isomers of **5.7** (Figure 6.4). Because $CF_3CO_2H$ was solid at 183 K and not very soluble in $CD_2Cl_2$ at this temperature, it was considered possible that this is the reason for the lack of reaction. The NMR tube was therefore removed from the probe, quickly shaken to mix the reagents, and replaced in the probe. The hydride region of the spectrum now showed two broad signals at $\delta$ -9.32 and $\delta$ -9.13 in a ratio of 3.9/1.0 (Figure 6.4). The spectrum was again obtained at 183 K after a further 10 min. It showed that the resonance at $\delta$ -9 .13 slightly decreased relative to that at $\delta$ -9.32. The $^1$H NMR spectrum was recorded at 203 K, 213 K and 253 K over 3 h (Figure 6.5), and the ratio of these resonances continued to change in favour of the $\delta$ -9.32 resonance. When the temperature was increased to 294 K, the signal at $\delta$ -9.32 shifted to $\delta$ -9.20, and the one at $\delta$ -9.13 shifted to $\delta$ -9.08, and was now of only small intensity (Figure 6.5e). At all temperatures, only one Cp* resonance was observed, and was a singlet at $\delta$ 2.03 at 294 K. The resonances for the propene protons were very broad and were difficult to assign. The sample was then pumped to dryness and redissolved in $C_6D_6$. The $^1$H NMR spectrum in $C_6D_6$ gave a spectrum essentially identical to the one assigned to $Cp*Re(\eta^2\text{-}C_3H_6)(CO)(H)(CF_3CO_2)$ (**6.3**) in section 6.3.1. Only a single hydride resonance occurred at $\delta$ -9.33 ($\delta$ -9.28 in section 6.3.1), and the propene and Cp* resonances were well-resolved.
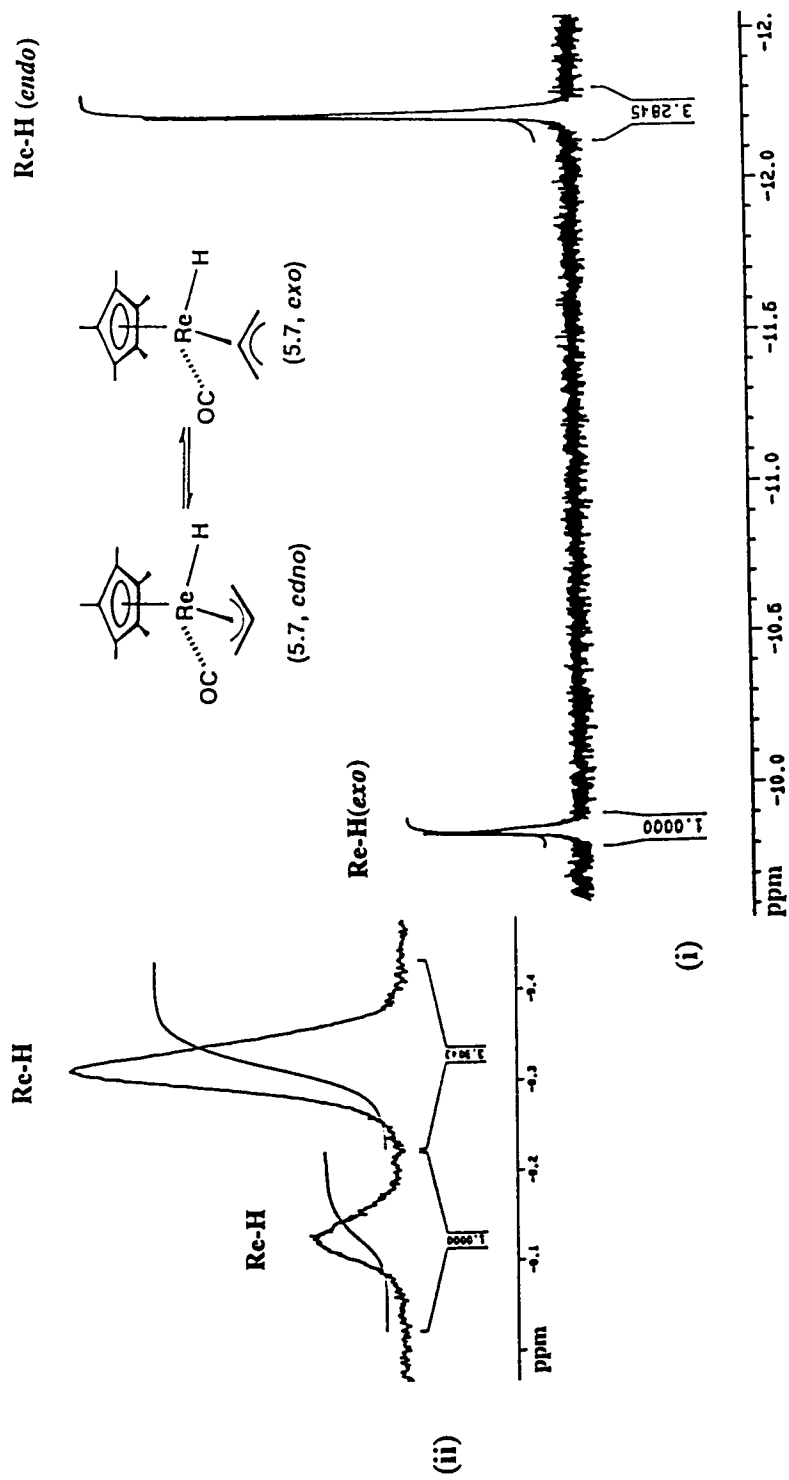
Figure 6.4. $^1$H NMR spectra of **5.7** and the initial product of its protonation with CF$_3$COOH in CD$_2$Cl$_2$ (Re-H resonances).

i. $^1$H NMR spectrum of a mixture of *exo* and *endo* isomers of **5.7** at 183 K in CD$_2$Cl$_2$.

ii. $^1$H NMR spectrum at the time when CF$_3$COOH was added to **5.7** for 5 min. at 183 K in CD$_2$Cl$_2$.

| Spec. | T (K) | T (h) |
|-------|-------|-------|
| a | 183 | 0.08 |
| b | 203 | 1.84 |
| c | 213 | 2.17 |
| d | 253 | 2.96 |
| e | 294 | 3.80 |
| f | 294 | 96.0 |
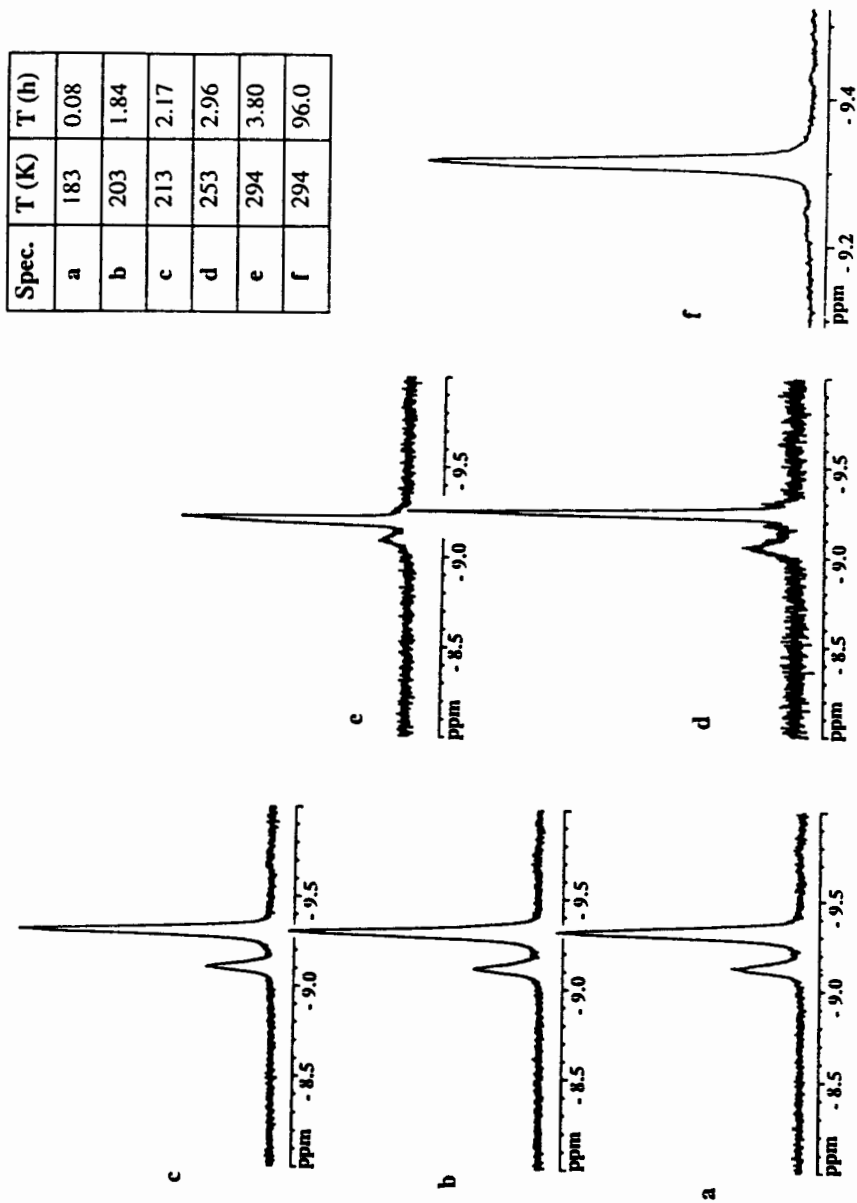
Figure 6.5. Variable temperature $^1$H NMR spectra of **6.3** (Re-H resonances). Spectrum **f** was recorded in $C_6D_6$, all others were in $CD_2Cl_2$.

It is possible that the two inequivalent hydride resonances observed initially result from products formed from the *endo* and *exo* isomers of **5.7** respectively, in view of the relatively similar ratios. However, there is no direct evidence for this. This, of course, could be tested by studying a pure isomer of **5.7**. This was done, as described next, and two isomers of the propene complex again resulted, which tends to discount this idea.

The result of this experiment suggested that the protonation of **5.7** in $CD_2Cl_2$ at low temperature occurred very quickly, and the intermediates were not detected by the $^1H$ NMR experiment. The two observed hydride resonances are considered to correspond to the two different isomers of $Cp^*Re(\eta^2-C_3H_6)(CO)(H)(CF_3COO)$ (**6.3**) that resulted from the protonation of **5.7**. Moreover, the protonation of the mixture of the *endo* and *exo* isomers of **5.7** will theoretically produce three different isomers of the propene hydride complex, in which the hydride ligand can adopt the position of *trans* to CO, propene or the $CF_3CO_2$ anion depending on the attacking position of $CF_3CO_2$. The arrangement of the four ligands in a four-legged piano stool structure of **6.3** or **6.4**, combined with the orientation of the propene ligand will lead to nine isomers of the final product, shown in Schemes 6.5 and 6.6. Although eighteen structures are presented in these two Schemes, among these, **iia** and **iia'**, **iib** and **iib'**, and **iic** and **iic'** are enantiomers, and **ia** and **iia**, **ib** and **iib**, and **ic** and **iic** are diastereomers (Scheme 6.5). Similarly **iva** and **iva'**, **ivb** and **ivb'**, and **ivc** and **ivc'** are enantiomers, and **iiia** and **iva**, **iiib** and **ivb**, and **iiic** and **ivc** are diastereomers (Scheme 6.6). Further, some structures are identical: e.g., **iia** = **iiia**, **iib** = **iiib**, and **iic** = **iiic**. If the hydride $^1H$ NMR resonances of these diastereomers are not distinguishable but those of the geometrical isomers (**i**), (**ii**) and (**iii**) are, there will be only three distinct hydride resonances for isomers H trans to propene, H trans to $CF_3COO$ and H trans to the CO. Three resonances were observed for complexes **6.4** and **6.7** when the $^1H$ NMR spectra of them were first recorded. But, two of them disappeared as the sample was kept in the refrigerator or at room temperature, and only one of them remained. At this stage, it is impossible to determine which of the isomers gave the resonances observed in the $^1H$
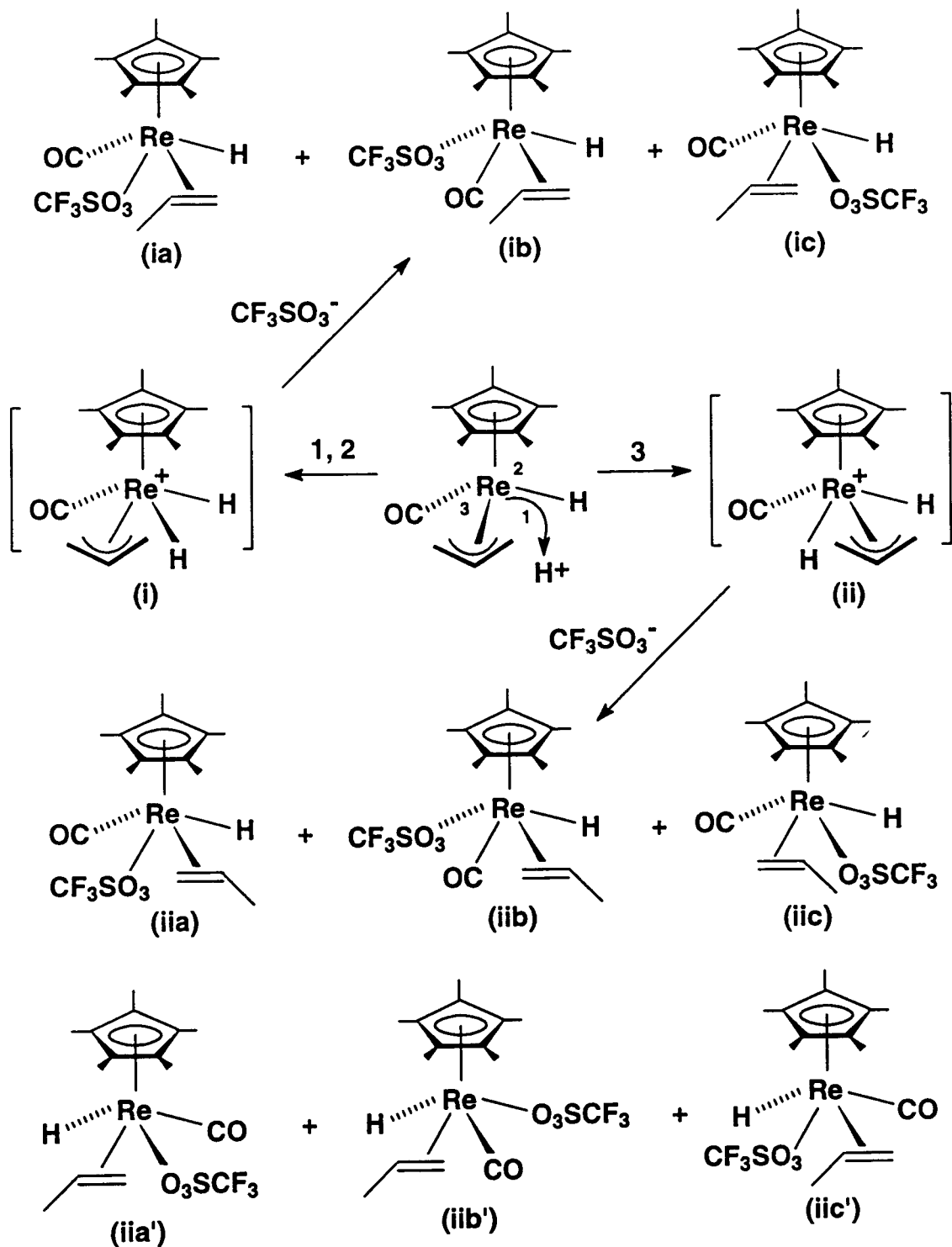
Scheme 6.5. Isomers produced from the protonation of the *endo* isomer of **5.7**.
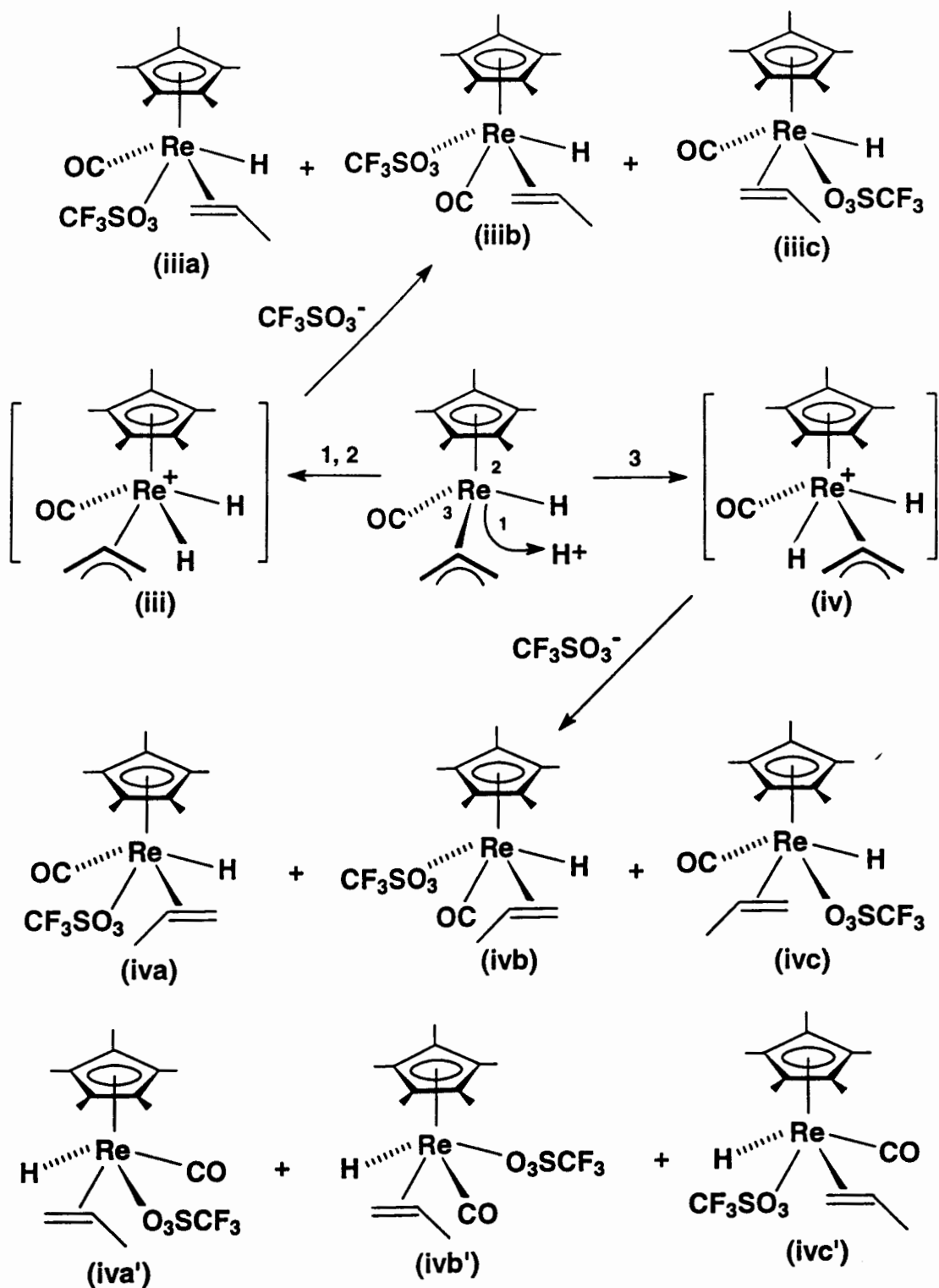
Scheme 6.6. Isomers produced from the protonation of the *exo* isomer of **5.7**.

180

NMR spectrum finally.

### 6.3.5.2. Protonation of Cp\*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7) with CF$_3$SO$_3$H in Acetone-d$_6$

The reaction of **5.7** with CF$_3$SO$_3$H was conducted in acetone-d$_6$ by using the pure *exo* isomer of **5.7**. The $^1$H NMR spectrum of **5.7** in acetone-d$_6$ was recorded at 213 K, and showed only the hydride resonance for the *exo* isomer at $\delta$ -9.68. Then, CF$_3$SO$_3$H was added to a solution of **5.7** in acetone-d$_6$ in an NMR tube at 183 K, then the sample was put into the probe. A spectrum taken at 213 K after CF$_3$SO$_3$H was added to the solution for 5 min showed three hydride resonances. A sequence of spectra with increasing temperature in range 213-273 K were obtained, and showed changes in the hydride resonances as indicated in Table 6.2. At 273 K a further spectrum was obtained 0.8 h later, and showed that a further change in this spectrum occurred with time while the temperature was constant. The temperature was lowered again to 253 K, but the spectrum was not the same as previously obtained at this temperature, indicating that the changes were not reversible with temperature. Instead, it appeared that at 273 K two species were present ($\delta$ -9.24 and $\delta$ -9.44), and both on decreasing the temperature to 253 K, and increasing from 253 K to 294 K, the ratio changed such that the resonance at $\delta$ -9.24 disappeared, and only the one at $\delta$ -9.44 remained. The solvent was removed, and the spectrum re-recorded in C$_6$D$_6$ (some insoluble impurities remained). The $^1$H NMR spectrum of this sample was identical to that of **6.4** obtained in section 6.3.2, and on this basis the products are believed to be the same.

As shown in Scheme 6.6, the protonation of *exo* **5.7** at rhenium can give two possible dihydride intermediates, in which the hydrides are either *cis* or *trans* in a four-legged piano-stool structure. These are shown as **iii** and **iv** in Scheme 6.6. In principle, the final product Cp\*Re($\eta^2$-C$_3$H$_6$)(CO)(H)(CF$_3$SO$_3$) can exist as three stereoisomers. In addition, each of these stereoisomers has a diastereomeric partner where the propene is bound by the opposite enantioface. The final product observed may be a single one of these six isomers or the $^1$H NMR could result from exchange of more than one isomer.

Table 6.2. $^1$H NMR Data of the Isomers Produced from the Protonation of the *Exo* Isomer of **5.7** at Variable Temperature.

| T (K) | Time (h) | Re-H (ppm)[a] Isomers (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | iii | | 6.4 | | iv | | 6.4 | |
| | | δ | % | δ | % | δ | % | δ | % |
| 213 | 0.00 | - 9.19; | 42.1 | - 9.30; | 32.6 | - 9.42; | 25.3 | | |
| 223 | 0.50 | - 9.18; | 36.7 | - 9.30; | 30.1 | - 9.42; | 33.2 | | |
| 233 | 1.18 | - 9.18; | 35.2 | - 9.30; | 36.7 | - 9.39; | 28.0 | | |
| 243 | 1.68 | - 9.18; | 15.4 | - 9.27; | 62.0 | - 9.38; | 22.5 | | |
| 253 | 2.65 | - 9.16; | 13.3 | - 9.24; | 43.8 | - 9.35; | 23.7 | - 9.45; | 19.2 |
| 263 | 2.95 | - 9.16; | 7.5 | - 9.24; | 37.3 | - 9.34; | 22.3 | - 9.44; | 33.0 |
| 273 | 3.32 | - 9.16; | 0.0 | - 9.24; | 65.3 | - 9.34; | 0.0 | - 9.44; | 34.7 |
| 273 | 4.12 | | | - 9.24; | 43.5 | | | - 9.44; | 56.5 |
| 253 | 4.47 | | | - 9.24; | 40.4 | | | - 9.44; | 59.7 |
| 253 | 4.63 | | | - 9.24; | 35.5 | | | - 9.44; | 64.6 |
| 294 | 72.0 | | | | | | | - 9.44; | 100 |

a. The $^1$H NMR spectrum was recorded in acetone-$d_6$. The percentage of the isomers was obtained according to the intensity of the hydride resonances.

The initial spectrum at 213 K showed three hydride resonances at $\delta$ -9.19, $\delta$ -9.30 and $\delta$ -9.42. The $\delta$ -9.19 and $\delta$ -9.42 resonances generally decayed away as the temperature was increased. On this basis, they are tentatively assigned to the two possible dihydride intermediates shown in Scheme 6.6 when the reaction occurred at the rhenium center (Scheme 6.3). The resonance at $\delta$ -9.19 is very broad and could be composed of two inequivalent hydride resonances with unresolved mutual coupling and coupling to the inequivalent allyl terminal protons in the *cis* dihydride structure (iii) in Scheme 6.6. The $\delta$ -9.42 resonance is therefore tentatively assigned to the *trans* dihydride intermediate (iv).

As the temperature was changed, the hydride resonance at $\delta$ -9.30 underwent a complicated change in intensity. It is possible that this arises from one or more isomers of the propene complex $Cp*Re(\eta^2\text{-}C_3H_6)(CO)(H)(CF_3SO_3)$. Overall, this resonance eventually decreases as the resonance of $\delta$ -9.44 increases, and presumably represents an isomer that is unstable with respect to the final product, whichever isomer this is.

This investigation is clearly incomplete. Experiments need to be done to try to establish unambiguously the stereochemical structure of the final products **6.3** and **6.4** and the unstable isomers of the rhenium hydride propene complexes $Cp*Re(\eta^2\text{-}C_3H_6)(CO)(H)$ (A) (A = $CF_3CO_2$ or $CF_3SO_3$).

## 6.4. Discussion

### 6.4.1. Chemical Stability of $Cp*Re(\eta^2\text{-}C_3H_6)(H)(CO)(CF_3COO)$ (6.3)

The hydride ligand in complex **6.3** is inert in chlorinated solvents. Complex **6.3** was stirred in $CD_2Cl_2$ or $CCl_4$ for 24 h, and no reaction occurred. It is also relatively stable in the presence of a strong acid, such as $CF_3COOH$ and $CF_3SO_3H$, but decomposed when a large amount of either $CF_3COOH$ or $CF_3SO_3H$ was added to it. Complex **6.3** decomposed on a neutral alumina column. This is different by comparison with **5.7**, which was purified by chromatography on a neutral alumina column to give the pure product.

### 6.4.2. Protonation of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7) in Different Solvents

The protonation of **5.7** with CF$_3$COOH was first studied in acetone-d$_6$ at -78 °C in an attempt to monitor the reaction by $^1$H NMR spectrum. But, the reaction in acetone-d$_6$ produced some brown color impurity, and the $^1$H NMR resonances of the coordinated propene in complex **6.3** were overlapped with the signals that resulted from the impurity, and this made the assignments of the resonances of the initial product impossible.

We then tried the protonation of **5.7** in hexane at -78 °C. However, after the hexane solution of **5.7** with CF$_3$COOH was stirred for 3 h at this temperature, the IR showed no reaction occurred, but CF$_3$COOH did not dissolve in hexane at this temperature. In this case, the temperature was increased and the reaction was monitored by IR. At room temperature (15-18 °C), the IR showed v(CO) absorption for complex **6.3** at 1981 cm$^{-1}$. This implied that in a nonpolar solvent, the protonation of **5.7** with CF$_3$COOH can proceed at normal temperature (the protonation of **5.7** with CF$_3$COOH in acetone at room temperature did not give a clear product). Due to the lack of deuterated hexane, C$_6$D$_6$ was employed as the solvent for the protonation of **5.7** with CF$_3$COOH at room temperature, and the reaction resulted in a relatively pure product compared with in acetone-d$_6$, and the $^1$H NMR resonances of the product **6.3** were easily assigned because of the clear resolution. Generally, the protonations of transition metal hydride complexes have been studied at low temperature (-78 °C at least), in an attempt to investigate if a dihydrogen or dihydride complex will be formed. Acetone-d$_6$ or CD$_2$Cl$_2$ are the common solvents used in order to monitor the reaction using $^1$H NMR.[164] This is why the protonation of **5.7** with CF$_3$COOH was first studied in acetone-d$_6$. But, in this solvent, the protonation of **5.7** is not very clean. The high solubility of CF$_3$COOH in acetone-d$_6$ may be one of the reasons that leads to the protonation of **5.7** being unselective. In C$_6$D$_6$, although the reaction can not be conducted at low temperature, the solubility of CF$_3$COOH in this solvent is very low, and this can be the reason why the protonation of **5.7** with CF$_3$COOH in C$_6$D$_6$ resulted in relatively pure **6.3**.

### 6.4.3. The Protonation of 5.7 with $CF_3CO_2H$ and $CF_3SO_3H$

The protonation of **5.7** with $CF_3CO_2H$ and $CF_3SO_3H$ resulted in the propene hydride rhenium complexes $Cp*Re(\eta^2-C_3H_6)(CO)(H)(A)$ (A = $CF_3CO_2$, **6.3**; A = $CF_3SO_3$, **6.4**). Although it is impossible to assign the specific structure of the isomer obtained from the protonation of **5.7** based on the evidence obtained, the spectroscopic data clearly indicated the coordination of the propene ligand in complexes **6.3** and **6.4**. This result is consistent with the results reported on the protonation of a molybdenum hydrido allyl complex $Mo(H)(\eta^3-C_3H_5)(dppe)_2$, for which the protonation with HCl was studied by Henderson's group.[165a] The reaction is described in Scheme 6.7. In their case, the protonation was proposed to occur at both the metal center and the allyl ligand, to give a dihydride $\eta^3$-allyl cationic intermediate and a propene hydride cationic intermediate, which resulted from the protonation of the metal center and the $\eta^3$-allyl respectively, and these intermediates lead to the elimination of the propene and propyne. But, the characterization of the proposed intermediates were not reported.
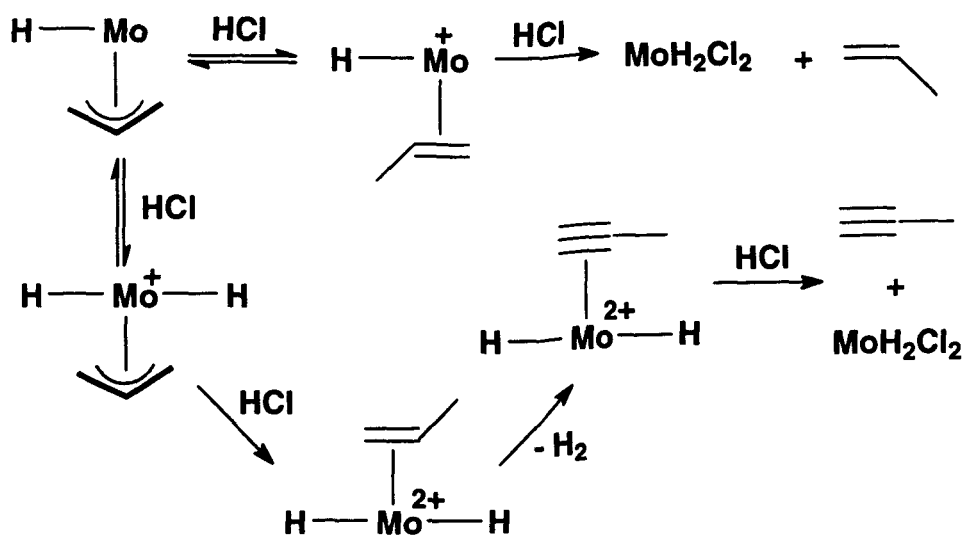


Scheme 6.7. Protonation of $Mo(H)(\eta^3-C_3H_5)(dppe)_2$, dppe = $Ph_2PCH_2CH_2PPh_2$.
Phosphine ligand omitted for clarity.

The protonation of the other $\eta^3$-allyl hydrido complex $(\eta^3$-C$_3$H$_5$)Os(CO)(H)(PR$_3$)$_2$ (R = P$^i$Pr$_3$, PMe$^t$Bu$_2$) with CH$_3$COOH, HBF$_4$ and HCl was studied by Schlünken and Werner.[165b] The results showed the elimination of the propene in all cases, no matter which acid was used for the protonation, and the formation of the hydride complex Os(CO)(H)(PR$_3$)$_2$(CH$_3$CO$_2$) in the case of CH$_3$COOH was employed. This is also in agreement with the result obtained for the protonation of **5.7**.

Fortunately, the propene hydride complexes **6.3** and **6.4** are stable enough for the spectroscopic characterization. The decomposition of these complexes may because of the elimination of the propene, and in the case of no other ligand to occupy the vacancy after the dissociation of propene, the rhenium complex decomposed. The protonation of **5.7** with CF$_3$COOH in acetone-d$_6$ at -78 °C was also conducted in the presence of PMe$_3$, in an attempt to obtain a PMe$_3$ complex Cp*Re(CO)(H)(PMe$_3$)(CF$_3$CO$_2$) to stabilize the species produced from the elimination of propene. But, the product in this reaction was complex **6.3**, instead of the expected compound. The reason for this could be that the added PMe$_3$ was protonated by CF$_3$COOH to form the phosphonium [HPMe$_3$][CF$_3$CO$_2$], and lost the function to be a ligand. PMe$_3$ is a stronger base than PH$_3$, and the protonation of PH$_3$ occurs in the presence of proton source to give phosphonium PH$_4^+$.[166]

## 6.5. Conclusions

The reactions of **5.7** with various unsaturated bonds, such as C=C, C≡C, C≡N and C≡O, were reported in this Chapter. At room temperature, no reaction occurred. The Re-H bond in complex **5.7** does not have the typical metal hydride bond character, and this is in contrast to most transition metal hydride complexes.

The rhenium center in **5.7** is an electron rich metal center. It was easily attacked by strong electrophiles, such as NO$^+$, [N$_2$C$_6$H$_4$OMe]$^+$ and Ph$_3$C$^+$. The attack of the NO$^+$ at complex **5.7** induced a migration of the hydride to the $\eta^3$-allyl to produce propene complex **6.1**. Although many rhenium nitrosyl olefin complexes with a phosphine ligand

were reported by Gladysz's group,[167] the nitrosyl carbonyl olefin complex was not reported previously in the literature. The reaction of **5.7** with $[N_2C_6H_4OMe]^+$ occurred at the metal center also, and the propene diazenido complex **6.2** was produced. The $Ph_3C^+$ abstracted the hydride from **5.7**, to create a coordinately unsaturated intermediate $[Cp*Re(\eta^3-C_3H_5)(CO)]^+$, followed by the coordination of $CH_3CN$, present as the solvent in the reaction, to form complex **2.2**.[168]

Complex **5.7** is unreactive with weak acid such as $CH_3COOH$. But it can be protonated with strong acids, such as $CF_3COOH$, $CF_3SO_3H$ and $HBF_4$. The protonation of **5.7** in different solvents was studied at both low and room temperature. The results suggested that the metal center was protonated, and the dihydride intermediates formed. It is also possible that the protonation of **5.7** involved the $\eta^3$-allyl or the Re-H bond. The products obtained from the protonation of **5.7** with $CF_3CO_2D$ indicated the formation of the dihydride intermediates $[Cp*Re(\eta^3-C_3H_5)(CO)(H)(D)][CF_3CO_2]$ (the two hydrides can be either *cis* or *trans*), which led to the formation of both complexes **6.5** and **6.6**.

The low temperature $^1H$ NMR studies of the protonation of the *exo* isomer of **5.7** with $CF_3SO_3H$ in acetone-$d_6$ suggested that the formation of a dihydride intermediate is the possible first step. Then, following a migration of one hydride to the $\eta^3$-allyl, coordination of the corresponding anion $CF_3SO_3^-$ yields the propene hydride complex **6.4**. The protonation of **5.7** at the metal center can occur between any two ligands of the three ligands in **5.7**, and the coordination of the anion can also choose different sides of the proposed dihydride intermediates. This might lead to the formation of different isomers of complexes **6.3** and **6.4**, as indicated in the low temperature $^1H$ NMR experiments, and shown in Schemes 6.5 and 6.6. The result presented in this Chapter is only one possible structure of these isomers. The determination of the final structure of **6.3** and **6.4** has not been achieved at this stage.

## 6.6. Experimental Section

### 6.6.1. General Procedure

All reactions were carried out under dry nitrogen in Schlenk apparatus. Solvent purification, spectroscopic measurements were carried out as described in Chapter II. All the solvents were degassed before use.

### 6.6.2. Reaction of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7) with Alkene and Alkyne

#### 6.6.2.1. Reaction of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7) with Ethylene

Complex **5.7** (mixture, *endo/exo* ≈ 8/3, 15 mg, 0.038 mmol) was dissolved in 2 mL hexane, CH$_2$=CH$_2$ was bubbled through the solution for 0.5 h. This solution was stirred at room temperature overnight. The IR showed the ν(CO) of **5.7** did not change, and the $^1$H NMR of this sample in C$_6$D$_6$ showed it is pure **5.7**. No reaction occurred.

#### 6.6.2.2. Reaction of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7) with Hexene and Cyclohexene

The unreacted **5.7** from the reaction with ethylene was recovered. The solvent was removed under vacuum, the remaining **5.7** was dissolved in 2 mL hexene, and the solution was stirred at room temperature overnight. Both the IR and the $^1$H NMR spectra showed that no reaction occurred.

Under the same condition, this reaction was repeated with pure cyclohexene, and both the IR and the $^1$H NMR spectra showed that no reaction occurred.

#### 6.6.2.3. Reaction of Cp*Re($\eta^3$-C$_3$H$_5$)(CO)(H) (5.7) with PhC≡CMe and MeC≡CMe

Complex **5.7** (mixture, *endo/exo* ≈ 9/1, 10 mg, 0.026 mmol) was dissolved in 1.5 mL hexane, 10 drops of PhC≡CMe were added to the solution, and stirred at room temperature for 10 h. The IR and the $^1$H NMR spectra showed no reaction occurred.

Under the same condition, this reaction was repeated with pure MeC≡CMe, and both the IR and the ¹H NMR spectra showed that no reaction occurred.

### 6.6.3. Reaction of Cp*Re(η³-C₃H₅)(CO)(H) (5.7) with CO

Complex **5.7** (mixture, *endo/exo* ≈ 8/1, 10 mg, 0.026 mmol) was dissolved in hexane, and CO was bubbled through for 0.5 h, and stirred at room temperature overnight. The reaction was monitored by IR. At the time when the reaction was carried on for 1 h, 2 h, 3 h, 5 h and 10 h, the IR spectra was recorded, and showed the ν(CO) of **5.7** did not change, but the intensity decreased as the time increased. After the reaction was carried on overnight, the IR of the reaction solution showed that the ν(CO) absorption disappeared, and the ¹H NMR of this sample in C₆D₆ showed the disappearance of the Cp* and Re-H resonances, which indicated the decomposition of **5.7** under the conditions employed for the reaction. No new product could be characterized.

### 6.6.4. Reaction of Cp*Re(η³-C₃H₅)(CO)(H) (5.7) with CH₃CN

Complex **5.7** (mixture, *endo/exo* ≈ 9/1, 10 mg, 0.026 mmol) was dissolved in 1 mL freshly distilled CH₃CN, stirred at room temperature overnight. The reaction was monitored by IR, and it showed the ν(CO) of **5.7** did not change. The CH₃CN was removed by vacuum, and the residue was dissolved in C₆D₆ to record the ¹H NMR spectrum, which indicated that the residue is pure **5.7**. No reaction occurred.

### 6.6.5. Reaction of Cp*Re(η³-C₃H₅)(CO)(H) (5.7) with PMe₃

Complex **5.7** (mixture, *endo/exo* ≈ 7/1, 10 mg, 0.026 mmol) was dissolved in 2 mL hexane, 10 drops of PMe₃ were added to this solution, and stirred at room temperature overnight. The IR and the ¹H NMR of this reaction showed that **5.7** did not change, and no reaction occurred.

### 6.6.6. Preparation of [Cp*Re(η²-C₃H₆)(CO)(NO)][BF₄] (6.1)

Complex **5.7** (mixture, *endo/exo* ≈ 4/1, 13 mg, 0.033 mmol) was dissolved in acetone (2 mL). At -78 °C, NOBF₄ (10 mg, 0.086 M in acetone) was added to it, and stirred at -78 °C for 10 min.. By this time, the solution changed color from colorless to yellow, and the temperature increased to -60 °C, which indicated an exothermic reaction. Solvent was pumped off, the residue was dissolved in CH₂Cl₂, then recrystallized from ether/hexane. The pure product was obtained as yellow crystals (16.07 mg, 0.032 mmol, 74%), m. p.: decomposed at 149 °C to give the dark brown solid. IR (CH₂Cl₂, cm⁻¹): $v_{CO}$ = 2047, $v_{NO}$ = 1765. FABMS (m/z): 422 (M⁺, base), 380 (M⁺ - C₃H₆), 350 (M⁺ - C₃H₆ - CO - 2H). ¹H NMR (CDCl₃, δ), isomer **6.1a**: 4.27, (1H, m, H₃), 3.59 (1H, dd, $J_{12}$ = 2.5 Hz, $J_{13}$ = 15.0 Hz, H₁), 3.29 (1H, d, $J_{23}$ = 13.5 Hz, H₂), 2.52 (3H, d, $J$ = 6.5 Hz, CH₃), 2.23 (15H, s, Cp*). Isomer **6.1b**: 3.93, (1H, m, H₃), 3.00 (1H, dd, $J_{12}$ = 2.5 Hz, $J_{13}$ = 9.0 Hz, H₁), 2.78 (1H, d, $J_{23}$ = 9.0 Hz, H₂), 2.22 (15H, s, Cp*), 2.12 (3H, d, $J$ = 6.5 Hz, CH₃). Anal. Calcd for C₁₄H₂₁BF₄NO₂Re: C, 33.08; H, 4.16; N, 2.76. Found: C, 32.85; H, 3.95; N, 3.06.

### 6.6.7. Preparation of [Cp*Re(η²-C₃H₆)(CO)(N₂C₆H₄OCH₃)][BF₄] (6.2)

Complex **5.7** (mixture, *endo/exo* ≈ 8/1, 15 mg, 0.038 mmol) was dissolved in 2 mL acetone. At -78 °C, [N₂C₆H₄OCH₃][BF₄] (10 mg, 0.09 M in 0.5 mL acetone) was added to this solution. The color of the solution changed from colorless to orange right after [N₂C₆H₄OCH₃][BF₄] was added, and the IR showed disappearance of the v(CO) for **5.7**, and a new CO absorption at 1995 cm⁻¹ for **6.2**. Solvent was pumped off, and the residue was recrystallized from CH₂Cl₂/ether to give the pure product as brown solid (12.29 mg, 0.021 mmol, 63%). IR (CH₂Cl₂, cm⁻¹): $v_{CO}$ = 1982, $v_{NN}$ = 1711. ¹H NMR (CDCl₃, δ): 7.04 (4H, m, C₆H₄), 4.10 (1H, m, H₃), 3.87 (3H, s, OCH₃), 3.47 (1H, m, H₂), 3.10 (1H, dd, $J_{13}$ = 13.0 Hz, $J_{21}$ = 2.0 Hz, H₁), 2.17 (15H, s, Cp*), 2.16 (3H, d, $J$ = 3.6 Hz, CH₃). The FABMS and the microanalysis of **6.2** were not obtained. The sample decomposed while it was kept in the refrigerator waiting for the analysis.

### 6.6.8. Preparation of 2.2 by reaction of 5.7 with [Ph₃C][BF₄] in CH₃CN

Complex **5.7** (mixture, *endo/exo* ≈ 7/1, 12 mg, 0.031 mmol) was dissolved in 3 mL freshly distilled CH₃CN. At -35 °C, [Ph₃C][BF₄] (10 mg, 0.11 M in 0.5 mL CH₃CN) was added to this solution, then stirred for 10 min.. The IR showed disappearance of the CO band from **5.7**, and a new $\nu$(CO) at 1971 cm⁻¹ appeared. Solvent was pumped off, and the residue was recrystallized from CH₂Cl₂/ether to give the product as the yellowish solid, which is a mixture of **2.2** and another unidentified complex. IR (CH₃CN, cm⁻¹): $\nu_{CO}$ = 1971. ¹H NMR (CDCl₃, δ) of **2.2**: 4.83, (1H, m, H$_c$), 3.26 (1H, dd, $J_{sc}$ = 6.0 Hz, $J_{ss}$ = 3.5 Hz, H$_s$), 3.11 (1H, dd, $J_{sc}$ = 6.0 Hz, $J_{ss}$ = 3.5 Hz, H$_s$), 2.80, (3H, s, CH₃CN), 2.03 (1H, d, $J_{ac}$ = 11.6 Hz, H$_a$), 1.96 (15H, s, Cp*), 1.32 (1H, d, J$_{ac}$ = 9.0 Hz, H$_a$). Both the IR and the ¹H NMR spectra data verified that the product is complex **2.2**.

¹H NMR (CDCl₃, δ) of unknown complex: 7.12-7.30 (5H, overlapped with CDCl₃, C₆H₅), 3.79, (1H, m), 3.04 (1H, dd), 2.92 (1H, d), 2.68, (3H, s, CH₃CN), 2.45 (3H, d), 2.15 (15H, s, Cp*).

### 6.6.9. Preparation of Cp*Re(η²-C₃H₆)(H)(CO)(CF₃CO₂) (6.3)

Complex **5.7** (mixture, *endo/exo* ≈ 5/1, 20 mg, 0.051 mmol) was dissolved in acetone-d₆. At -78 °C, 5 drops of CF₃COOH was added to the solution, which was then stirred for 1h. The IR showed that the reaction was not finished at this time. Then, the reaction was continued for another hour while the temperature was raised up without adding more dry ice (-60 °C). The IR showed the disappearance of the CO absorption from **5.7**, and appearance of a new CO band at 1962 cm⁻¹ for **6.3**. Solvent was pumped off, the residue was extracted with hexane. This hexane solution was dried for 12 h, the pure product was obtained as the yellowish solid. IR (hex, cm⁻¹): $\nu_{CO}$ = 1981. CIMS (m/z): 506 (M⁺), 505 (M⁺ - H), 465 (M⁺ - C₃H₅), 463 (M⁺ - C₃H₆ - H), 421 (M⁺ - C₃H₅ - CO₂), 391 (M⁺ - CF₃COOH - H, base). ¹H NMR (C₆D₆, δ): 3.22, (1H, m, H₃), 2.60 (1H,

d, $J_{13}$ = 12.0 Hz, H$_1$), 2.36 (3H, d, $J$ = 6.7 Hz, CH$_3$), 2.20 (1H, d, $J_{23}$ = 8.5 Hz, H$_2$), 1.59 (15H, s, Cp*), -9.28 (1H, s, Re-H).

### 6.6.10. Preparation of Cp*Re($\eta^2$-C$_3$H$_6$)(H)(CO)(CF$_3$SO$_3$) (6.4)

Complex **5.7** (mixture, *endo/exo* $\approx$ 5/1, 18 mg, 0.046 mmol) was dissolved in C$_6$D$_6$ (2 mL), at room temperature, CF$_3$SO$_3$H (3 drops) was added to this solution, then stirred for 10 min.. The IR of the solution showed a new $\nu$(CO) band at 1975 cm$^{-1}$ for the product, and the $\nu$(CO) of **5.7** disappeared at this time. Solvent was pumped off, the residue was dried under vacuum for 3 h. The product was obtained as a brownish solid (18.5 mg, 0.034 mmol, 74%). IR (C$_6$D$_6$, cm$^{-1}$): $\nu_{CO}$ = 1975. CIMS (m/z): 542 (M$^+$), 541 (M$^+$ - H), 407 (M$^+$ - CF$_3$SO$_2$ - 2H), 391 (M$^+$ - CF$_3$SO$_3$H - H, base). $^1$H NMR (C$_6$D$_6$, $\delta$): 4.00, (1H, m, H$_3$), 2.63 (1H, d, $J_{13}$ = 12.2 Hz, H$_1$), 2.39 (3H, d, $J$ = 6.0 Hz, CH$_3$), 2.19 (1H, dd, $J_{23}$ = 8.8 Hz, $J_{21}$ = 1.0 Hz, H$_2$), 1.58 (15H, s, Cp*), -9.68 (1H, s, Re-H). There are two minor hydride resonances at $\delta$ -9.51 and $\delta$ -9.33, which may be assigned to the different isomers of **6.4**.

### 6.6.11. Preparation of Cp*Re($\eta^2$-C$_3$H$_5$D)(H)(CO)(CF$_3$CO$_2$) (6.5) and
###        Cp*Re($\eta^2$-C$_3$H$_6$)(D)(CO)(CF$_3$CO$_2$) (6.6)

Complex **5.7** (mixture, *endo/exo* $\approx$ 3/1, 18 mg, 0.046 mmol) was dissolved in 2 mL C$_6$D$_6$ at room temperature, and CF$_3$COOD (5 drops) was added, then stirred for 10 min.. The IR of the solution showed only one new CO band at 1971 cm$^{-1}$. Solvent was pumped off, and the residue was dried for 5 h. The pure product was obtained as the yellowish solid (mixture of **6.5** and **6.6**, **6.5/6.6** = 3/1; 18.92 mg, 0.037 mmol, 81%). IR (C$_6$D$_6$, cm$^{-1}$): $\nu_{CO}$ = 1971. CIMS (m/z): 465 (M$^+$ - C$_3$H$_6$), 463 (M$^+$ - C$_3$H$_6$ - D, base), 394 (M$^+$ - CF$_3$CO$_2$), 393 (M$^+$ - CF$_3$CO$_2$H), 392 (M$^+$ - CF$_3$CO$_2$D). $^1$H NMR (C$_6$D$_6$, $\delta$): 3.20, (1H, m, H$_3$), 2.59 (1H, d, $J_{13}$ = 12.0 Hz, H$_1$), 2.33 (2H, br, CH$_2$D), 2.18 (1H, d, $J_{23}$ = 8.8 Hz, H$_2$), 1.55 (15H, s, Cp*), -9.32 (1H, s, Re-H). $^2$H{$^1$H} NMR (C$_6$D$_6$, $\delta$): 2.24 (s, CH$_2$D), -9.31 (s, Re-D).

## 6.6.12. Preparation of Cp*Re($\eta^2$-C$_3$H$_6$)(H)(CO)(FBF$_3$) (6.7)

Complex **5.7** (mixture, *endo/exo* ≈ 4/1, 15 mg, 0.038 mmol) was dissolved in C$_6$D$_6$ (2 mL). At room temperature, HBF$_4$ (3 drops, 48 % ether solution) was added to this solution, then stirred for 5 min.. The IR of the solution showed a new ν(CO) band at 1971 cm$^{-1}$ for the product, and the ν(CO) of **5.7** disappeared at this time. Solvent was pumped off, and the residue was dried under vacuum for 8 h. The product was obtained as a brownish solid. IR (C$_6$D$_6$, cm$^{-1}$): ν$_{CO}$ = 1971. CIMS (m/z): 393 (M$^+$ - FBF$_3$, base). $^1$H NMR (C$_6$D$_6$, δ): 2.73, (1H, m, H$_3$), 2.69 (1H, d, $J_{13}$ = 13.0 Hz, H$_1$), 2.47 (1H, d, $J_{23}$ = 5.8 Hz, H$_2$), 2.33 (3H, d, $J$ = 6.0 Hz, CH$_3$), 1.60 (15H, s, Cp*), -9.45 (1H, s, Re-H). There are two minor hydride resonances at δ -9.30 and δ -9.26, which may be assigned to the different isomers of **6.7**.

## 6.6.13. Protonation of 5.7 with CF$_3$COOH in CD$_2$Cl$_2$ at Low Temperature

Complex **5.7** (mixture, *endo/exo* ≈ 3/1, 15 mg, 0.038 mmol) was dissolved in 1 mL CD$_2$Cl$_2$ in a $^1$H NMR tube. This NMR tube was then put into a Schlenk tube, degassed three times, cooled to 173 K in a {ethanol & N$_2$(l)} cooling bath, and the $^1$H NMR spectrum of it was recorded at 183 K, which showed a mixture of both the *endo* and *exo* isomers of **5.7** in a ratio of *endo/exo* = 3/1. The sample was removed from the probe, at 173 K, and 5 drops of CF$_3$COOH were added to this solution. The CF$_3$COOH was a solid at this temperature. The NMR tube was placed in the probe, the $^1$H NMR spectrum was recorded 10 min. later, and showed that it was only pure **5.7**. No reaction occurred. It was thought that this may because CF$_3$COOH did not dissolve in CD$_2$Cl$_2$. Therefore, the sample was removed, quickly shaken for 10 seconds to mix the solution and the solid CF$_3$COOH, and replaced in the probe. The $^1$H NMR spectrum was recorded after 5 min., and showed two hydride resonances at δ -9.32 and δ -9.13. The spectrum was measured again 10 min. later, and showed only a slight decrease of the signal at δ -9.13. The temperature was then raised to 203 K, 213 K, 253 K, and 294 K, and the $^1$H NMR spectra

at these temperatures were recorded (Figure 6.5). As the temperature increased, the resonance at δ -9.13 decreased, and the one at δ -9.32 increased. At 294 K, the signal at δ -9.13 disappeared, and the one at δ -9.32 was the only remaining hydride resonance. The resonances of the propene and the allyl protons of the possible isomers were broad and overlapped, which made the assignments of these signals impossible. Only one Cp* resonance was observed in all the temperature range, it was a singlet at δ 2.03. The product resulting from the low temperature protonation was pumped to dryness, and redissolved in $C_6D_6$ (some insoluble impurities remained); the $^1$H NMR spectrum of it in $C_6D_6$ was identical to that of obtained for complex **6.3**.

### 6.6.14. Protonation of 5.7 with CF₃SO₃H in Acetone-d₆ at Low Temperature

Complex **5.7** (pure *exo* isomer, 15 mg, 0.038 mmol) was dissolved in acetone-$d_6$ in a NMR tube (placed in a Schlenk, degassed before the $^1$H NMR spectrum was recorded), and the $^1$H NMR spectrum of it was recorded at 213 K, which showed only one resonance for the *exo* isomer of **5.7** in the hydride region. The sample was then taken out from the probe, and 5 drops of CF₃SO₃H were added to it at 183 K (ethanol in $N_2(l)$) to give a suspension because of the insolubility of the CF₃SO₃H. The sample was replaced in the probe (213 K), and the spectrum was recorded after 5 min. at 213 K, which showed three hydride resonances at δ -9.19, δ -9.30 and δ -9.42. The temperature was then raised in 10 °C Steps till 273 K, and the spectrum was recorded. As the temperature increased, the resonances at δ -9.19 and -9.42 decreased, and the one at δ -9.30 had a complicated change. At 253 K, the $^1$H NMR spectrum gave four resonances at δ -9.16, -9.24, -9.35 and -9.45 respectively. At 273 K, the $^1$H NMR spectrum was recorded twice at different times, and the result indicated that the resonance at δ -9.30 decreased as the time increased, and the one at δ -9.44 increased. At 294 K, the other three resonances disappeared, and the one at δ -9.44 was the only signal in the hydride region (Table 6.2). The resonances of the propene and the allyl protons of the possible isomers were broad and overlapped, which made the assignments of these signals impossible. Several Cp*

resonances were observed in all the temperature range, and they were at $\delta$ 2.0-$\delta$ 2.1. The $^1$H NMR spectrum of the low temperature protonation product was measured in $C_6D_6$ at room temperature, and it was identical to that of obtained for complex **6.4**.

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# Appendix

## Calculation of the Equilibrium Isotope Effect for the Protonation of Complex 5.7

The calculation of the equilibrium isotope effect for the products obtained from the protonation of complex **5.7** with $CF_3COOD$ was conducted. The stretching frequencies of the Re-D, Re-H, C-D and C-H bonds were considered for the calculation, because the other parts of the two molecules are the same (Equation A1).



(Eq. A1)
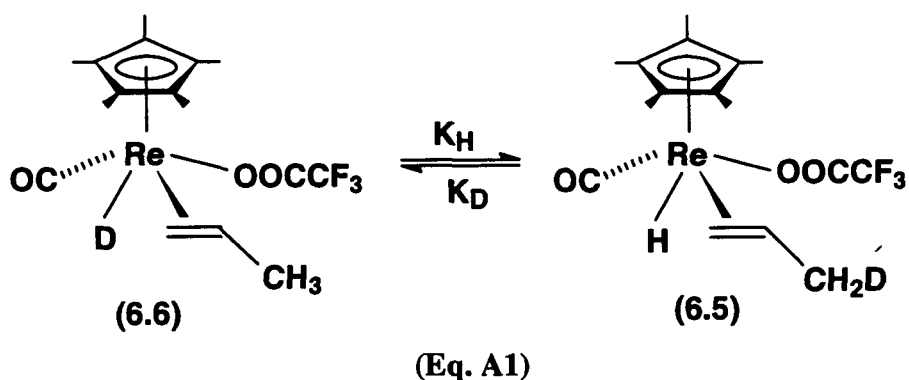
As the IR absorptions of Re-H for both complexes **6.5** and **6.6** were not observed, the selected Re-H stretching frequency for the calculation is 2000 $cm^{-1}$, and this is based on the reported M-H absorptions (the $v_{MH}$ is in the region of 1700-2300 $cm^{-1}$) and the reported data for $Cp_2ReH$ (2037 $cm^{-1}$).[154] The C-H stretching frequency is 3000 $cm^{-1}$.

The formula for the calculation of $K_H / K_D$ is:

$$K_H / K_D = \exp\{(\varepsilon_H - \varepsilon_D) / K_B T\}$$

$$\varepsilon_H - \varepsilon_D = hc/2 \times (1 - 1/1.40) \times (v_{CH} - v_{ReH})^{[169a-e]}$$

When        $h = 6.63 \times 10^{-34}$ js

$c = 3.00 \times 10^{10}$ cm/s

$K_B = 1.38 \times 10^{-23}$ jK$^{-1}$

$T = 293$ K

$v_{ReH} / v_{ReD} = 1.40$

The calculated $K_H / K_D = 2.02$.

This is the estimated equilibrium isotope effect for the distribution of complexes **6.5** and **6.6** based on only the stretching vibrations of Re-H and C-H.