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Activation of Small Molecules by Cationic Rhenium Complexes

by

Catherine Ellen Radzewich

A dissertation submitted in partial fulfillment
of the requirements for the degree of

Doctor of Philosophy

University of Washington

1997

Approved by ___________________________
(Chairperson of Supervisory Committee)

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Abstract

Activation of Small Molecules by Cationic Rhenium Complexes

by Catherine Ellen Radzewich

Chairperson of the Supervisory Committee: Professor Dennis Michael Heinekey
Department of Chemistry

Thermolysis of ReX(CO)₅ (X = CH₃ or H) with PPh₃ and PiPrPh₂ in toluene generates \textit{trans-mer}-Re(X)(PR₃)₂(CO)₃ complexes. Protonation of \textit{trans-mer}-Re(X)(PR₃)₂(CO)₃ with [H(Et₂O)₂]B(Ar')₄ (Ar' = 3,5(CF₃)₂C₆H₃) under an H₂ atmosphere generates stable dihydrogen complexes, [Re(H₂)(PR₃)₂(CO)₃]B(Ar')₄ (PR₃ = PPh₃ (4a), PiPrPh₂ (4b)). The large \textit{J}_{HD} values (4a = 32 Hz, 4b = 30 Hz) and short \textit{T}_{1min} values (4a = 10.3 ms, 4b = 10.5 ms) at 300 MHz are consistent with a dihydrogen formulation. The hydrogen ligand can be removed in solution or the solid state by exposing to vacuum or argon to generate a ligand deficient product, [Re(PR₃)₂(CO)₃]B(Ar')₄ (5). Complexes 4 and 5 react with a variety of small molecules to form [ReL(PR₃)₂(CO)₃]B(Ar')₄ (L = H₂O, NH₃, C₂H₄, N₂, CO, Cl⁻, PPh₃, THF).

[Ph₃C]B(Ar')₄ reacts with Cp₂ReCH₃ and Cp₂ReCH₂CH₃ to abstract an α-hydride from the alkyl ligand to generate carbene complexes, [Cp₂Re=CH₂]B(Ar')₄ (1) and [Cp₂Re=CH(CH₃)]B(Ar')₄ (3). Both complexes 1 and 3 decompose to [Cp₂Re(C₂H₄)]⁺ and [Cp₂Re(NCCD₃)]⁺ in acetonitrile upon addition of BF₄⁻ salts or thermolysis of the solutions at 50 °C for two weeks. [Cp₂Re(CH₃)H]B(Ar')₄ eliminates methane at 0 °C in CH₂Cl₂ to generate [Cp₂Re(CH₂Cl)Cl]B(Ar')₄. Addition of [Me₂O]BF₄ to Cp₂ReR (R = CH₃, CH₂CH₃, CH₂SiMe₃) in acetonitrile forms stable bis-alkyl complexes, [Cp₂Re(CH₃)R]BF₄.
[Cp₂Re=CH₂]B(Ar')₄ (1) reacts with triphenylphosphine and pyridine to generate ylide complexes. Complex 1 reacts with Cl₂, Br₂, I₂ by 1,2-addition across the Re-C double bond to form halomethyl halide complexes. Complex 1 has also been shown to react with oxygen, sulfur and carbene donor reagents to form η²-formaldehyde, η²-thioformaldehyde and η²-olefin complexes.

The addition of Me₂SiCl₂ or (Me₂Si)₂Cl₂ to a THF solution of (η⁵-C₅H₄Li)₂ReCH₃ gives ansa-bridged complexes with a single or double silicon linker. A X-ray diffraction study was undertaken to confirm the structure of (η⁵-C₅H₄-SiMe₂-η⁵-C₅H₄)ReCH₃. Substituted derivatives of Cp₂ReX (X = H, CH₃) have also been synthesized with Me or SiMe₃ groups on each cyclopentadienyl ring. Several methyl hydride rhenocene complexes have been generated by protonation and characterized at low temperature by NMR spectroscopy. Methane elimination from these complexes occurs at ambient temperature, although [(η⁵-C₅H₄-SiMe₂-η⁵-C₅H₄)Re(CH₃)H]B(Ar')₄ has been observed to be more stable at room temperature then analogous complexes.
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ABBREVIATIONS AND SYMBOLS

Å  angstrom
atm  atmosphere
B(Ar')4⁻  B(3,5-(CF3)2C6H3)4⁻
br  broad
Cp  cyclopentadienyl, (η⁵-C₅H₅)-
Cp*  pentamethylcyclopentadienyl, (η⁵-C₅(CH₃)₅)-
Cp'  methylcyclopentadienyl, (η⁵-C₅H₄(CH₃))- 
Cy  cyclohexyl
Cyp  cyclopentyl
d  doublet
δ  chemical shift in ppm (NMR) or bending frequency (IR)
ΔG⁺₉₀₀₀_.rot  free energy of activation of rotation
dcpe  1,2-bis(dicyclohexylphosphino)ethane
dnpe  1,2-bis(dineopentylphosphino)ethane
dppe  1,2-bis(diphenylphosphino)ethane
eq  equation
equiv  equivalents
g  gas
η  hapticity
Hz  hertz
iPr  isopropyl
IR  infrared
J  coupling constant
K

kelvin

L

ligand, neutral 2-electron donor

m

multiplet (NMR) or medium absorbance (IR)

M

molarity or metal atom

Me

methyl

v

linewidth (NMR) or stretching frequency (IR)

NMR

nuclear magnetic resonance

ORTEP

Oak Ridge thermal ellipsoid projection

OTf

trifluoromethanesulfonate (triflate, $SO_3CF_3^-$)

Ph

phenyl

PMDT

$N, N', N'', N'''$-pentamethyldiethylenetriamine

ppm

parts per million

quint

quintet

quart

quartet

R

alkyl

s

singlet (NMR) or strong absorbance (IR)

t

triplet

$t_{1/2}$

half-life

$T_1$

spin-lattice relaxation time

$\tau$

lifetime

$t\text{Bu}$

$tert$-butyl

THF

tetrahydrofuran

TMEDA

tetramethylethylenediamine

TMS

tetramethyldisilane

triphos

$1,1,1$-tris(diphenylphosphino)ethane

vi
vt virtual triplet
w weak spectral intensity
X ligand, anionic 2-electron donor
CHAPTER 1

CATIONIC COMPLEXES OF Rhenium WITH PHOSPHINE AND CARBONYL COLIGANDS

Introduction

Since their initial discovery by Kubas,¹ H₂ complexes of transition metals have been the subject of intensive study by several research groups.² Cationic dihydrogen complexes, conveniently formed by protonation of neutral hydrides or by other routes, are now numerous. Recently, there have been several interesting reports on the synthesis and reactivity of dicationic dihydrogen complexes.³ The effect that a net positive charge has upon the stability of dihydrogen complexes is of interest in their design and predicted reactivity. While there are reported comparisons of dihydrogen complexes within the same transition metal triad,⁴⁵ there are few comparisons of cationic systems to closely related neutral analogs.⁶⁻⁹ Cationic systems require extra considerations. The study of cationic complexes is complicated by the requirement for polar solvents, which can act as ligands to electron deficient metal centers. Anions can also act as potential ligands especially if the hydrogen ligand is labile.

Since there have been numerous studies which describe the synthesis, characterization and reactivity of M(H₂)(PR₃)₂(CO)₃ (M = W, Mo, Cr; PR₃ = PC₃, PIP₃, PCyp₃),¹⁰ the Heinekey group has embarked on a study of related Group 7 cationic analogs. A previous report of [Re(H₂)(PMe₃)₂(CO)₃]BF₄¹¹ describes the low temperature ¹H NMR spectrum of this species, but its thermal instability precluded isolation of the complex. This instability is consistent with the previous observation in our group that [Re(H₂)(PC₃)₂(CO)₃]BF₄¹² also decomposes at low temperatures. We now report that the use of more weakly coordinating anions¹³¹⁴ has enabled us to isolate
and characterize a wide range of cationic complexes of rhenium. Recent work from the Heinekey group has been reported on the synthesis of stable cationic analogs of the Kubas dihydrogen complexes, [trans-mer-Re(H2)(PR3)2(CO)3]B(Ar')4 (PR3 = PCy3, PiPr3).15 The Kubas dihydrogen complexes have been investigated with only a small range of tris-alkyl phosphine coligands. Attempts to synthesize the Group 6 dihydrogen complexes with other phosphines leads to decomposition or coordination of three phosphine ligands and displacement of the dihydrogen ligand. This chapter reports the synthesis of rhenium dihydrogen complexes with a variety of phosphine coligands in order to examine the influence of steric and electronic factors upon dihydrogen binding in this system. Further characterization and reactivity of the PCy3 and PiPr3 analogs will also be presented. The Heinekey group has recently reported on a closely related series of dihydrogen complexes of the form, [Re(H2)(PR3)2(CNtBu)3]+ (PR3 = PCy3, PPh3), in which the carbonyl groups have been substituted by isonitrile coligands.16 The reactivity differences between the carbonyl and isonitrile systems allow for several fruitful comparisons to further understand the binding of dihydrogen.

Results and Discussion

Synthesis of Re(X)(PR3)2(CO)3 (X = CH3 (1), H (2)). In the course of this study, several neutral methyl and hydride complexes of rhenium have been prepared. Compounds 1 and 2 are generated by heating a toluene solution of Re(CH3)(CO)5 or Re(H)(CO)5 with excess phosphine in a thick walled glass vessel.
The solutions are heated at 120 °C for 40-65 hours and degassed every 12 hours. If the CO gas is not removed periodically, the reaction forms unidentified products with continued heating. The progress of the phosphine substitution can be conveniently monitored by $^1$H NMR spectroscopy. The monosubstituted phosphine compounds are typically observed as intermediates in the preparation of the disubstituted compounds. Removal of the solvent in vacuo leaves a sticky yellow residue. After rinsing with several portions of pentane, the yellow color is removed and a white to off-white powder is isolated. The synthesis of compound 1a has been previously investigated and a X-ray diffraction study has been conducted. The experimental section in this chapter provides the conditions of a scaled up reaction and further spectroscopy data on 1a. Compound 2a has been previously prepared by other groups via alternative methods.

The thermal decarbonylation of ReX(CO)$_5$ (X = H, CH$_3$, halides) in the presence of phosphines is an often used synthetic method for generating mixed phosphine-carbonyl complexes of rhenium. These include mono, bis or tris substituted products in various stereoechemical configurations depending upon conditions, phosphine, and X.
group. Previous experiments from this group involved the thermolysis of ReCH₃(CO)₅ with PCy₃ and PPr₃ ligands. The reaction conditions required a higher temperature (130 °C) and longer reaction times (up to 140 hours). The isolated yield of Re(CH₃)(PCy₃)₂(CO)₃ was only 50% and can include up to 50% contamination by ReH(PCy₃)₂(CO)₃, formed as a decomposition product. The yields of 1 and 2 conversely were quite high (> 90%) and the methyl complexes were not observed to decompose to the hydride analogs under the milder reaction conditions. The steric requirement imposed by the bulky phosphines, PPh₃ (145°) to PCy₃ (170°), produced complexes with trans phosphate ligands.

Table 1.1 lists selected ¹H NMR and IR data for complexes 1 and 2. The ¹H NMR spectra of the isolated complexes show a triplet for the rhenium methyl or hydride ligand due to coupling to two equivalent phosphines. The ³¹P ¹H NMR spectra show a single phosphorus signal for each complex. A typical ¹³C ¹H NMR spectrum of the carbonyl region shows two triplets due to coupling to equivalent phosphine ligands. The usual pattern of the carbonyl region in the IR spectra are three bands with weak, strong, and medium intensities as the frequency decreases. All of this data is consistent with the carbonyls arranged in a meridinal configuration and trans phosphate ligands. The stereochemistry of the product was confirmed in one case by a crystal structure of Re(CH₃)(PPh₃)₂(CO)₃ (1a).¹⁷ Although the methyl and carbonyls were disordered, the P-Re-P angle was found to be 177.5°. Complexes 1 and 2 are air stable, although, they are handled exclusively in the drybox due to the sensitivity of subsequent reactions. The methyl complexes are stable in solution while the rhenium hydride complexes form Re(Cl)(PR₃)₂(CO)₃ in CHCl₃ or CH₂Cl₂ over a period of days (PR₃ = PPr₃, PPh₃). The deuteride, Re(D)(PPr₃)₂(CO)₃, can be formed by heating the hydride at 130 °C with several equivalents of D₂O in toluene.
Table 1.1. Selected $^1$H, $^{31}$P($^1$H) NMR and IR Data for Compounds 1 and 2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>1a</th>
<th>1b</th>
<th>2a</th>
<th>2b</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$(M-CH$_3$)$^a$</td>
<td>-1.06</td>
<td>-1.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta$(M-H)$^a$</td>
<td></td>
<td></td>
<td>-5.20</td>
<td>-5.94</td>
</tr>
<tr>
<td>$J_{PH}^b$</td>
<td>6.7</td>
<td>6.6</td>
<td>17.8</td>
<td>18.8</td>
</tr>
<tr>
<td>$\delta$ $^{31}$P$^a$</td>
<td>16.8</td>
<td>19.7</td>
<td>22.8</td>
<td>29.6</td>
</tr>
<tr>
<td>vCO(cm$^{-1})^c$</td>
<td>2018(w),1915(s)</td>
<td>2018(w),1920(s)</td>
<td>2020(w),1925(s)</td>
<td>2020(w),1919(s)</td>
</tr>
<tr>
<td></td>
<td>1878(m)</td>
<td>1871(m)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $^1$H and $^{31}$P($^1$H) NMR chemical shifts in ppm, recorded at 298 K in CDCl$_3$ (1a-b) and C$_6$D$_6$ (2a-b). $^b$ $^{31}$P coupling constant in Hz to the methyl or hydride protons. $^c$ methylene chloride.

Scheme 1.1 is suitable for synthesizing bis phosphine complexes with large cone angles (PPh$_3$ 145$^\circ$ - PCy$_3$ 170$^\circ$). Attempts to form similar complexes with smaller phosphines such as PMe$_3$ were unsuccessful. Addition of excess PMe$_3$ to a toluene solution of Re(CH$_3$)(CO)$_5$, slowly forms cis-Re(CH$_3$)(PMe$_3$)(CO)$_4$. This reaction is complete in 2 days at room temperature with no protection from light. Heating the solution at 60 $^\circ$C over several days shows little further reaction. When heating was continued at 100 $^\circ$C, some Re(CH$_3$)(PMe$_3$)$_2$(CO)$_3$ was formed, but continued heating produced several new unidentified complexes. Due to the small cone angle of PMe$_3$, we predict that complexes with several phosphines and various isomers have been formed.

Recently, cis-fac-Re(CH$_3$)(PPh$_3$)$_2$(CO)$_3$ has been prepared by Bergman and Simpson by another synthetic method. This method allows the addition of a second phosphine at low temperature by replacing a weakly bound CH$_3$CN instead of a more strongly coordinated CO. The synthesis of cis-fac-Re(CH$_3$)(PMe$_3$)$_2$(CO)$_3$ (3a) has been achieved in a similar method as outlined in Scheme 1.2.
\[
\text{Re}(\text{CH}_3)(\text{CO})_5 \xrightarrow{\text{x}_5 \text{PMe}_3} \text{cis-Re}(\text{CH}_3)(\text{PMe}_3)(\text{CO})_4 \xrightarrow{(\text{CH}_3)_2\text{NO}} \text{CH}_3\text{CN}
\]

\[
\text{fac-Re}(\text{CH}_3)(\text{PMe}_3)(\text{CH}_3\text{CN})(\text{CO})_3 \xrightarrow{\text{x}_3 \text{PMe}_3} \text{C}_6\text{H}_6 \quad \text{cis-fac-Re}(\text{CH}_3)(\text{PMe}_3)_2(\text{CO})_3
\]

3a

**Scheme 1.2**

Addition of the first PMe3 to Re(CH3)(CO)5 occurs at room temperature by exposure to room light. One equivalent of trimethylamine N-oxide is added to the monophosphine-substituted complex which undergoes loss of CO2 by nucleophilic attack at a carbonyl ligand. When this reaction is run in CH3CN, the solvent will bind in place of the displaced CO ligand. The acetonitrile ligand is easily displaced upon addition of excess PMe3 in benzene. The cis-fac configuration of the bisphosphine-substituted complex is confirmed by IR vCO bands.

An adaptation of this method has allowed the preparation of complexes with chelating phosphines (Scheme 1.3). Addition of two equivalents of trimethylamine N-oxide to ReCH3(CO)5 in CH3CN produces a new compound after stirring for 24 hours. The IR spectrum of the compound in CH3CN shows three strong bands at 2002, 1893, and 1885 cm\(^{-1}\). This pattern of IR bands is consistent with a facial arrangement of 3 carbonyl ligands, similar to 3a. This intermediate most likely contains two acetonitrile ligands and a methyl group which are facial. The CH3CN solvent is removed in vacuo, followed by the addition of toluene and one equivalent of a chelating phosphine. Stirring overnight affords new compounds with dppe (Ph2PCH2CH2PPh2), dcpe (Cy2PCH2CH2PCy2), and dpe ((tBuCH2)_2PCH2CH2P(CH2tBu)_2) ligands. The IR spectra of all three compounds show 3 strong bands for the carbonyl ligands consistent with a facial arrangement. Table 1.2 lists the CO stretching frequencies for several related compounds.
\[
\text{ReCH}_3(\text{CO})_5 + 2(\text{CH}_3)\text{NO} \rightarrow \text{cis-fac-Re(}\text{CH}_2)(\text{NCCH}_3)_2(\text{CO})_3
\]

Scheme 1.3

| Table 1.2. IR Bond Stretching Frequencies of Related Neutral Carbonyl Complexes. |
|---------------------------------------------------|-----------------|
| Compound                                           | \( \nu_{\text{CO}} \text{(cm}^{-1})^a \) |
| \( \text{cis-ReCH}_3(\text{PMe}_3)(\text{CO})_4 \)   | 2073(w), 1983(s), 1967(vs), 1932(s) |
| \( \text{cis-mer-ReCH}_3(\text{CH}_3\text{CN})_2(\text{CO})_3 \) | 2006(s), 1925(s), 1892(s) |
| \( \text{cis-mer-ReCH}_3(\text{PMe}_3)(\text{CH}_3\text{CN})(\text{CO})_3 \) | 1999(s), 1902(s), 1874(s) |
| \( \text{cis-mer-Re(CH}_3)(\text{PMe}_3)_2(\text{CO})_3 \) (3a) | 2007(s), 1923(s), 1885(s) |
| \( \text{cis-mer-Re(CH}_3)(\text{PPh}_3)_2(\text{CO})_3 \) (THF) | 2005(s), 1922(s), 1885(s) \(^b\) |
| \( \text{cis-mer-Re(CH}_3)(\text{dppe})(\text{CO})_3(\text{C}_7\text{H}_8) \) (3b) | 2006(s), 1925(s), 1892(s) |
| \( \text{cis-mer-Re(CH}_3)(\text{dnpe})(\text{CO})_3(\text{C}_7\text{H}_8) \) (3c) | 2000(s), 1915(s), 1876(s) |
| \( \text{cis-mer-Re(CH}_3)(\text{dcpe})(\text{CO})_3 \) (3d) | 2000(s), 1922(s), 1874(s) |

\(^a\) All IR spectra are recorded in Nujol unless specified otherwise. \(^b\) Reference 20.

It is possible for the complexes with cis monodentate phosphines to isomerize to the thermodynamically preferred trans complexes. It was previously reported that heating \( \text{cis-mer-} \text{ReBr(PMe}_3)_2(\text{CO})_3 \) at 150 °C for 10 hours affords \( \text{trans-mer-} \text{ReBr(PMe}_3)_2(\text{CO})_3 \).\(^{21}\) We have observed that heating \( \text{cis-mer-Re(CH}_3)(\text{PMe}_3)_2(\text{CO})_3 \)
does not show any reaction after several days at 50 °C and further heating to 100 °C leads to decomposition. However, cis-mer-Re(CH₃)(PPh₃)₂(CO)₃ can be cleanly converted to trans-mer-Re(CH₃)(PPh₃)₂(CO)₃ after several days at 50 °C. The lower barrier to isomerization for the PPh₃ complexes is consistent with a dissociative process which is preferred for the bulkier phoshpine. Bergman and Simpson have shown that cis-mer-Re(CH₃)(PPh₃)₂(CO)₃ reacts with phenol and other alcohols by dissociation of a phosphine prior to coordination of the phenol.¹⁰ The cis phosphines are quite labile due to the steric congestion in cis-mer-Re(CH₃)(PPh₃)₂(CO)₃ and consequently we found that the trans isomer shows no reaction with phenol under similar conditions.

Synthesis and Characterization of [Re(H₂)(PR₃)₂(CO)₃]B(Ar')₄

(PR₃ = PPh₃, 4a; PiPrPh₂, 4b). Protonation of complexes 1a,b or 2a,b with [H(Et₂O)]B(Ar')₄ under a hydrogen atmosphere in CH₂Cl₂ affords the corresponding dihydrogen complexes (eq 1). Protonation of the methyl starting complexes, 1a,b, produced methane as evidenced by the ¹H NMR spectra of the reaction mixtures, but otherwise was identical to protonation of 2a,b. A broad resonance at approximately - 4 ppm is observed for the two compounds in the ¹H NMR spectra, with no observable phosphorus coupling. The dihydrogen resonance is observed at 1.5 ppm lower field than the corresponding neutral hydride in CD₂Cl₂.

![Diagram]

X = CH₃ 1a,b; H 2a,b

4a,b
Table 1.3 lists selected $^1$H NMR data for the hydride region as well as data previously collected for the related PCy$_3$ (4c) and PiPr$_3$ (4d) analogs.$^{22}$ All of the dihydrogen complexes are thermally robust and are stable indefinitely in halogenated solvents (CD$_2$Cl$_2$, CDCl$_3$ and 1,2-difluorobenzene) under a partial H$_2$ atmosphere. Complexes 4a and 4b are extremely reactive towards water (vide infra) and could not be cleanly isolated, therefore, we have only characterized them by $^1$H and $^{31}$P($^1$H) NMR spectroscopy. No change is observed for complexes 4a and 4b in the $^1$H or $^{31}$P($^1$H) NMR spectra from 190 K to 300 K, indicating that there is no substantial equilibrium with a dihydride structure, [Re(H)$_2$(PR$_3$)$_2$(CO)$_3$]$^+$. Exposure of solid 4a,b to vacuum or argon atmosphere leads to H$_2$ loss and a corresponding color change from pale yellow to orange (vide infra). This process is completely reversible. Similar reversible H$_2$ loss can be affected in solution by removal of the H$_2$ atmosphere and is accelerated by gently heating. Protonation of ReH(PR$_3$)$_2$(CO)$_3$, 2a and 2b, under vacuum only leads to a mixture of the dihydrogen complexes, 4a and 4b, and the hydrogen loss products. This is consistent with a labile dihydrogen ligand.

When [Re(H$_2$(PR$_3$)$_2$(CO)$_3$]B(Ar')$_4$ (4a,b) is placed under a D$_2$ atmosphere, the intensity of the H$_2$ resonance is decreased as the D$_2$ isotopomer is formed. Isotope exchange for 4a and 4b is slow and signals due to 4a--d$_1$ and 4b--d$_1$ were partially
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$(HH)$^b$</th>
<th>$\delta$(HD)$^b$</th>
<th>J$_{\text{HH}}$$^c$</th>
<th>$\Delta\delta$$^d,e$</th>
<th>$T_{1\text{min}}$$^e,f$</th>
<th>$\Delta v_{1/2}$$^e,l$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Re(H$_2$)(PPh$_3$)$_2$(CO)$_3$]$^+$ (4a)</td>
<td>−3.86</td>
<td>−3.89</td>
<td>32</td>
<td>30</td>
<td>10.3$^i$</td>
<td>54</td>
</tr>
<tr>
<td>[Re(H$_2$)(PrPrPh)$_2$(CO)$_3$]$^+$ (4b)</td>
<td>−4.26</td>
<td>−4.29</td>
<td>30</td>
<td>30</td>
<td>10.5$^i$</td>
<td>52</td>
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<tr>
<td>[Re(H$_2$)(PCy$_3$)$_2$(CO)$_3$]$^+$ (4c)</td>
<td>−4.78</td>
<td>−4.81</td>
<td>32</td>
<td>34</td>
<td>9.38$^e$</td>
<td>49</td>
</tr>
<tr>
<td>[Re(H$_2$)(PrPr)$_3$(CO)$_3$]$^+$ (4d)</td>
<td>−4.97</td>
<td>−5.01</td>
<td>33</td>
<td>37</td>
<td>9.6$^h$</td>
<td>23</td>
</tr>
</tbody>
</table>

$^a$ All measurements recorded at 298 K in CD$_2$Cl$_2$ except where noted. $^b$ Chemical shift in ppm. $^c$ Coupling constant in Hz. $^d$ Isotope shift ($\Delta\delta = \delta$(HH) − $\delta$(HD)) in ppb. $^e$ Recorded in a 500 MHz field. $^f$ $T_{1\text{min}}$ in ms. $^g$ 248 K. $^h$ 232 K. $^i$ 254 K. $^j$ Half-height width in Hz.
obscured by the presence of the residual H$_2$ resonance. An inversion recovery experiment (180°—τ—90°) with τ set to null the signal of the H$_2$ ligand reveals a triplet with a large $J_{\text{HD}}$ coupling due to the HD ligand. The observed $^1$H NMR resonances for the dihydrogen ligand of 4a–d$_1$ and 4b–d$_1$ are slightly upfield of the H$_2$ isotopomers with a chemical shift difference of approximately 30 ppb which is consistent with a typical intrinsic isotope shift.$^{23}$

Relaxation data for 4a,b and the PCy$_3$ (4c) and PiPr$_3$ (4d) analogs were collected at 500 MHz in CD$_2$Cl$_2$ by standard inversion recovery NMR methods. Very short minimum T$_1$ values of 10±1 ms were observed for all four dihydrogen complexes (Table 1.3). In order to gauge the relaxation contribution of the rhenium metal center as well as the phosphine ligands we have also considered the T$_{1\text{min}}$ values for the neutral hydrides, 2a and 2b. Luo and coworkers have previously reported the variable temperature $^1$H NMR T$_1$ data for ReH(PPh$_3$)$_2$(CO)$_3$ (2a).$^{18}$ They have observed the T$_{1\text{min}}$ of 177 ms at 203 K in CD$_2$Cl$_2$ (250 MHz). The T$_{1\text{min}}$ is proportional to the field of the magnet and the value becomes 354 ms at 500 MHz. We have determined the T$_{1\text{min}}$ of ReH(PiPrPh$_2$)$_2$(CO)$_3$ (2b) to be 325 ms at 217 K in CD$_2$Cl$_2$ (500 MHz). The long T$_{1\text{min}}$ values of 2a (325 ms) and 2b (354 ms) are in the expected range of hydride complexes. The data indicates that the rapid relaxation observed for complexes 4a–d is dominated by the dipole–dipole interaction of the η$_2$–H$_2$ ligand and any relaxation contribution from the rhenium metal center or protons of the phosphine ligands is negligible.

The T$_{1\text{min}}$ values for the dihydrogen ligand can be used to calculate the bond distance within the limits of fast and slow rotation (Table 1.4).$^{24}$ An average slow rotation bond length of 0.96 Å is calculated versus the fast rotation bond length of 0.76 Å. Gusev and coworkers have recently discussed the utility of T$_{1\text{min}}$ data in determining the H–H bond distance for dihydrogen complexes.$^{25}$ Specifically, they have addressed
the difficulties in assigning "fast" or "slow" rotation corrections to calculate the H–H bond distances. They have compared several known dihydrogen complexes which have $J_{\text{HD}}$ values greater than 25 Hz as well as reported $T_{1\text{min}}$ data. The calculated H–H bond lengths for this series as well as complexes 4a–d are best approximated by the slow-spinning data. By correcting for a fast-spinning $H_2$ ligand, the H–H bond lengths are on average 0.2 Å shorter and several approach the unreasonable distance of 0.74 Å for free $H_2$.26

<table>
<thead>
<tr>
<th>Compound</th>
<th>H–H (Å) slow rotation</th>
<th>H–H (Å) fast rotation</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Re(H$_2$)(PPh$_3$)$_2$(CO)$_3$]$^+$ (4a)$^{a,b}$</td>
<td>0.95</td>
<td>0.75</td>
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<tr>
<td>[Re(H$_2$)(PiPrPh$_2$)$_2$(CO)$_3$]$^+$ (4b)$^{a,c}$</td>
<td>0.95</td>
<td>0.76</td>
</tr>
<tr>
<td>[Re(H$_2$)(PCy$_3$)$_2$(CO)$_3$]$^+$ (4c)</td>
<td>0.97</td>
<td>0.77</td>
</tr>
<tr>
<td>[Re(H$_2$)(PiPr$_3$)$_2$(CO)$_3$]$^+$ (4d)</td>
<td>0.97</td>
<td>0.77</td>
</tr>
</tbody>
</table>

$^a$ Corrected for neutral hydride relaxation. $^c$ Measurement of the $T_{1\text{min}}$ of Re(H)(PPh$_3$)$_2$(CO)$_3$ was taken from ref. 18 and corrected to a 500 MHz field. $^b$ Measurement of the $T_{1\text{min}}$ of Re(H)(PiPrPh$_2$)$_2$(CO)$_3$ was 325 ms at 217 K in a 500 MHz field (CD$_2$Cl$_2$ solution).

Recent reports from the groups of Heinekey$^{3a}$ and Morris$^{27}$ have correlated the H–H bond distances determined by solid state NMR or neutron diffraction techniques to $J_{\text{HD}}$ values. Theoretical calculations by Hush and coworkers have also revealed a linear relationship between $J_{\text{HD}}$ values and H–H distances.$^{28}$
Figure 1.1. Plot of H–H bond distance (Å) versus $J_{HD}$ (Hz). The solid line results from experimental data tabulated by Heinekey$^{24}$ and Morris$^{27}$ for compounds with known H–H bond distances as determined by solid state NMR or neutron diffraction methods. The dashed line results from calculated bond distances and calculated HD coupling constants as determined by Hush and coworkers$^{28}$ for a series of osmium dihydrogen complexes synthesized by Taube and coworkers.$^{29}$ The symbols represent the H–H bond distances calculated from the $T_{1\text{min}}$ data for complexes 4a–d ($\bullet$ = slow rotation) ($\Delta$ = fast rotation).

The average $J_{HD}$ value of 32 Hz for complexes 4a–d corresponds with an average H–H bond distance of 0.89 Å from the solid line in Figure 1.1. This value is intermediate between those determined for slow and fast rotation from the $T_{1\text{min}}$ data. Surprisingly, 0.89 Å is the H–H distance determined for W(H$_2$)(PiPr$_3$)$_2$(CO)$_3$ ($J_{HD} = 34.0$ Hz) by solid state NMR.$^{10e,30}$ A recent report by Kubas and coworkers has also indicated similar H–H distances for isostructural cationic and neutral dihydrogen complexes. Solid-state NMR was used to calculate an H–H distance of 0.89 Å for
[Mn(H₂)(CO)(dppe)₂]B(Ar')₄ and 0.88 Å for the analogous neutral complex Mo(H₂)(CO)(dppe)₂ (dppe = Ph₂PC₂H₄PPh₂).³⁰

The correlation of H–H bond distances and J_HD values as calculated by Hush deserves some comment. The dashed line depicted in figure 1.1 has a remarkably similar slope compared to the solid line determined from experimental data, but is shifted down indicating that the H–H bond distances are shorter than those determined by solid state NMR and neutron diffraction methods. The complexes which were studied by Hush and coworkers belong to a category of dihydrogen complexes with "stretched" dihydrogen bonds.²⁸ The cationic and dicaticionic Os complexes, [Os(NH₃)₄L(η²-H₂)]²⁺, exhibit strong π-back-bonding which accounts for the long H–H bond lengths and shorter J_HD values.²⁹ If the line for these complexes is extrapolated to the region of 30-35 Hz the corresponding H–H distances would become unreasonably short. Until more experimentally determined H–H bond lengths for the Taube compounds are reported it is unclear if the correlation to J_HD is truly different compared to other dihydrogen complexes. Obviously, one must be careful in applying this correlation to the large number of dihydrogen complexes which have J_HD values between 30 and 35 Hz.

Protonation of Complexes cis-mer-Re(CH₃)P₂(CO)₃ (P₂ = (PMe₃)₂ (3a), dppe (3b), dcppe (3c), dppe (3d)). Addition of [H(Et₂O)₂]B(Ar')₄ to complexes 3a-d under an H₂ atmosphere did not lead to new dihydrogen complexes. The ¹H NMR spectra did not reveal signals for coordinated hydrogen and the ³¹P{¹H} NMR spectra indicated the formation of several complexes which could not be identified. The instability of a dihydrogen complex in this system was puzzling based on the apparent similarities to the complexes with trans phosphines. Unstable dihydrogen complexes without phosphine coligands have been previously observed in related systems. Perutz and coworkers have investigated M(CO)₅(H₂) (M = W, Mo, Cr)
complexes by matrix isolation methods.\textsuperscript{31} Previous attempts have been made in the Heinekey group to synthesize \([\text{Re}(\text{H}_2)(\text{CO})_5]^+\) by low temperature protonation of \(\text{ReH}(\text{CO})_5\).\textsuperscript{32} A dihydrogen complex was never observed by \(^1\text{H}\) NMR spectroscopy. Apparently these dihydrogen complexes are unstable due to the lack of sufficient backbonding from the electron poor metal center to the \(\sigma^*\) orbital of the dihydrogen ligand. In a similar system in which the carbonyl ligands are replaced by more basic isonitrile ligands, \([\text{Re}(\text{H}_2)(\text{CN}^\text{tBu}_3)_5]^+\) was observed at low temperature but was too unstable to isolate.\textsuperscript{16} The greater stability of the \([\text{Re}(\text{H}_2)(\text{CN}^\text{tBu}_3)_5]^+\) complex is consistent with greater backbonding to the \(\sigma^*\) orbital of the dihydrogen ligand compared to the carbonyl complexes, but decomposition likely results by the inability of the \text{CN}^\text{tBu} ligands to provide an agostic interaction upon \(\text{H}_2\) liberation.

Kubas and coworkers have reported several studies upon the rotational barrier of the dihydrogen ligand when coordinated to various Group 6 complexes. The barrier is directly affected by the amount of \(\pi\) donation to the \(\text{H}_2\) ligand rather than the \(\sigma\) bond which is considered more significant in the strength of the M-\(\text{H}_2\) bond. In the most stable configuration for \(\text{W}(\text{P}^\text{iPr}_3)_2(\text{CO})_3(\text{H}_2)\), as evidenced by neutron diffraction, the \(\text{H}_2\) molecule lies along the P-M-P axis. Rotation of the \(\text{H}_2\) ligand by 90° would line the \(\sigma^*\) orbital along the same filled metal d orbital that is backbonding to the CO ligands. The orientation of the \(\text{H}_2\) ligand in the dihydrogen complexes derived from complexes 3a-d, with the phosphine ligands trans to CO ligands, will have less of a preference and possibly become more labile due to insufficient \(\pi\)-back-bonding.

Another factor which may lead to unstable \(\text{H}_2\) complexes is the instability of the complexes upon \(\text{H}_2\) liberation. Complexes 4a-d have been observed to have very labile \(\text{H}_2\) ligands and a stable agostic complex is generated (\textit{vide infra}) upon \(\text{H}_2\) loss. Although complexes of the type \textit{cis-mer-MP}_2(\text{CO})_3^{n+} (n = 0 (Cr, Mo, W); +1 (Mn, Re)) have not been investigated, \([\text{Mn(dppe)}_2(\text{CO})]\text{B(Ar')}_4\) and \([\text{Mn(dppe)}_2(\text{CO})]\text{B(Ar')}_4\) have been characterized
by X-ray crystallography and contain agostic interactions with an ortho-hydrogen of the phosphine ligand. In fact, [Mn(dppe)$_2$(CO)]B(Ar')$_4$ has been observed to have two agostic interactions from mutually trans phosphines, therefore, complexes with a single chelating phosphine ligand should also be capable of forming an agostic interaction.

**Reactivity of [Re(H$_2$)(PCy$_3$)$_2$(CO)$_3$]B(Ar')$_4$ (4c) with Bases.** The dihydrogen ligand of complex 4c is readily deprotonated by several bases. Addition of 1,8-bis(dimethylamino)naphthalene (Proton–Sponge®) or 2,6-di-tert-butyl-4-methylpyridine to a CD$_2$Cl$_2$ solution of the dihydrogen complex leads to immediate formation of the neutral hydride, ReH(PCy$_3$)$_2$(CO)$_3$. The strong base KOrBu will also deprotonate the dihydrogen complex, but only over the course of several days due to its low solubility in CD$_2$Cl$_2$. If the base is not sterically hindered, as is the case with ammonia and aniline, displacement of the H$_2$ ligand and coordination of the base is observed. Two nitrogen bases which do not react with 4c are pentafluoropyridine and 2,6-diisopropylaniline.

**Synthesis of [Re(PR$_3$)$_2$(CO)$_3$]B(Ar')$_4$ (PR$_3$ = PPh$_3$, 5a; PiPrPh$_2$, 5b).** When Re(CH$_3$)(PR$_3$)$_2$(CO)$_3$, 1a,b, is reacted with [H(Et$_2$O)$_2$]B(Ar')$_4$ under vacuum an orange solution results. Rapid methane evolution was observed. The formally ligand deficient product is also produced upon removal of H$_2$ from 4a,b in the solid state or solution (eq 2).
The compounds are thermally stable in solution and do not show any decomposition over several months. Complexes 5a and 5b are extremely reactive towards water and could only be characterized in solution by $^1\text{H}$ and $^{31}\text{P}[^1\text{H}]$ NMR spectroscopy. Previous results from this group have given us a clearer picture of the nature of 5a and 5b by the characterization of the PCy$_3$ (5c) and P$i$Pr$_3$ (5d) analogs. Complexes 5c and 5d have been found to be less reactive towards H$_2$O and have been characterized by elemental analysis to demonstrate that the complexes are ligand deficient. A single crystal X-ray analysis of 5c exhibits a distorted octahedral structure in which the β C-H bond from one of the cyclohexyl rings is interacting with the electron deficient metal center in the solid state.$^{15}$ This structure is very similar to the reported structure of the neutral tungsten analog, W(PCy$_3$)$_2$(CO)$_3$, and is consistent with the observed agostic interaction of W(P$i$Pr$_3$)$_2$(CO)$_3$.$^{10c}$

Since complexes 5a and 5b have not been successfully characterized in the solid state, we were interested in investigating the nature of this agostic complex in solution by NMR spectroscopy methods. Based on our reactivity studies, these complexes have been observed to react with and coordinate a wide variety of small molecules in varying strengths ($\text{vide infra}$). These reactions are conveniently monitored by $^{31}\text{P}[^1\text{H}]$ NMR spectroscopy which shows a single resonance for the agostic species as well as subsequent formation of new complexes. Reaction of the agostic species with small
molecules to give 18 electron complexes is also accompanied by a dramatic color change. The agostic complex in methylene chloride solution is bright orange and forms dark orange crystals in the solid state. All of the 18 electron complexes studied thus far have been observed to be pale yellow or colorless in solution and in the solid state. This is also observed for [Re(PR₃)₂(CNtBu)₃]⁺ and W(PR₃)₂(CO)₃, both are dark purple in solution and as solids, and the 18 electron complexes are yellow or colorless.¹,¹⁶

Complexes 5a and 5b are typically generated in situ for NMR spectroscopy studies by the protonation of ReCH₃(PR₃)₂(CO)₃ with [H(Et₂O)₂]B(Ar⁺)₄ in CD₂Cl₂. We have observed that the agostic complexes will undergo moderate to strong bonding of H₂O and THF and considered that the excess Et₂O in solution could behave as a potential ligand. The Et₂O can be removed from solutions of 5a and 5b by addition of CH₂Cl₂ followed by removal of the volatiles in vacuo. This process is repeated several times and the resulting ¹H NMR spectra indicate the absence of Et₂O in solution. The ³¹P{¹H} NMR of the agostic complexes is invariant in the presence or absence of Et₂O.

Complexes 5a and 5b are soluble and stable in halogenated solvents. The ³¹P{¹H} NMR chemical shifts for these complexes do not show a significant shift upon changing solvent (CD₂Cl₂, CDCl₃ or 1,2-C₆F₂H₄). There have been several recent reports on coordination of methylene chloride as well as complexes which oxidatively add CH₂Cl₂ through a C–Cl bond to give chloro–methyl chloride complexes. There are three reports of isolable methylene chloride complexes which have been structurally characterized,³⁵ as well as others which have been identified only in solution.³⁶ Gladysz and coworkers have shown that an errant peak in the ¹³C{¹H} NMR spectrum of [Cp*Re(NO)(PPh₃)(ClCH₂Cl)]BF₄ is associated with a bound CH₂Cl₂ and can be distinguished from the resonance for free CH₂Cl₂.³⁶a We investigated the low temperature ¹³C{¹H} NMR spectra of [Re(PR₃)₂(CO)₃]B(Ar⁺)₄ in CH₂Cl₂ and did not observe any peaks which could be attributed to bound solvent. We also find that the ¹H
and $^{13}$C NMR resonances due to the B(Ar')$_4$ anion are entirely independent of the nature of the cation present.

Reactivity of Re(X)(PR$_3$)$_2$(CO)$_3$ (X = H, CH$_3$; PR$_3$ = PPh$_3$, P$^1$PrPh$_2$) with [Ph$_3$C]B(Ar')$_4$. We have begun to explore other routes toward the synthesis of complexes 4a,b and 5a,b. These complexes are extremely reactive towards water and the coordination of water is irreversible. In order to prevent the coordination of water in these complexes, we have attempted to scrupulously eliminate all sources of water. The solvents are dried over activated silica gel after pre-drying over P$_2$O$_5$ or Na/K benzophenone. The rhenium methyl and hydride starting materials are dried for several hours under dynamic vacuum and stored in an inert atmosphere drybox. A diethyl ether solution of the precursor for [H(Et$_2$O)$_2$]B(Ar')$_4$ synthesis, NaB(Ar')$_4$, is dried over activated silica gel. These precautions have led to cleaner solutions of 4a,b and 5a,b, but water coordination remains as an impurity in 30% yield as determined by $^{31}$P{$^1$H} NMR spectra. Recent reports from the Brookhart and Schrock groups have also observed difficulties in the attempted synthesis of cationic Et$_2$O complexes by protonation with [H(Et$_2$O)$_2$]B(Ar')$_4$. These complexes are also very sensitive to the presence of water and it appears that [H(Et$_2$O)$_2$]B(Ar')$_4$ is quite hygroscopic and will always be contaminated with water despite attempts to synthesize it under very dry conditions.

In order to synthesize complexes 4a,b and 5a,b by another route we have investigated the reactivity of [Ph$_3$C]B(Ar')$_4$ toward rhenium methyl and hydride complexes. Preliminary results indicate that [Ph$_3$C]$^+$ quickly abstracts CH$_3$- from 1a,b and H$^-$ from 2a,b. The solutions are yellow which is inconsistent with the formation of the corresponding agostic complexes, but the $^{31}$P{$^1$H} NMR spectra each display a single resonance which corresponds with the agostic species and no resonance is observed for the water complex. Addition of one atmosphere of H$_2$ gas to these solutions
results in the slow conversion to the dihydrogen complexes, but does not go to completion as monitored by $^1\text{H}$ and $^{31}\text{P}$$^1\text{H}$ NMR spectroscopy. This seems to indicate that there is a possible interaction between the Ph$_3$CH or Ph$_3$CCH$_3$ that is formed and the five-coordinate cations. Attempts were made to isolate [Re(P$_i$PrPh$_2$)$_2$(CO)$_3$]$^+$ in a scaled up synthesis by recrystallization from CH$_2$Cl$_2$/pentane. After rinsing the product several times with pentane, the solid did become slightly orange and a $^1\text{H}$ NMR spectra of the filtrate indicated the formation of Ph$_3$CH. There is some precedence for coordination of Ph$_3$CH in an $\eta^2$-arene fashion by cationic rhenium complexes.$^{39,40}$ These complexes have been observed to have distinct $^1\text{H}$ NMR resonances for the hydrogens of the coordinated phenyl group. Contrary to this we have not observed any unusual resonances in the $^1\text{H}$ NMR spectra to indicate this type of coordination. Perhaps further investigation with a bulkier trityl reagent$^{41}$ with a $4^\text{th}$butyl substituent in the para position of the phenyl groups would lead to the clean synthesis of the five-coordinate complexes.

**Synthesis and Reactivity of ReCl(PR$_3$)$_2$(CO)$_3$ (PR$_3$ = PPh$_3$, 6a; Pi-PrPh$_2$, 6b; PC$_{3}$, 6c)**. An HCl-Et$_2$O solution was added to Re(CH$_3$)(PR$_3$)$_2$(CO)$_3$ (PR$_3$ = PPh$_3$, PC$_3$) in toluene or CH$_2$Cl$_2$. Bubbles were observed and after stirring approximately one hour the solvent was removed in vacuo and the white solid was rinsed with several portions of pentane and dried in vacuo. For both 6a and 6c a single resonance is observed in the $^{31}\text{P}$$^1\text{H}$ NMR spectra and the typical weak, strong, and medium bands are observed in the IR spectra indicating equivalent phosphines and three carbonyls in a meridinal arrangement. 6a has been synthesized previously by alternate routes and the characterization is consistent with those reports.$^{42}$

A recent publication from our group has reported the novel formation of a dihydrogen complex by the *unaided* displacement of Cl$^-$ from ReCl(PC$_3$)$_2$(CN$_3$Bu)$_3$ by H$_2$. We have conducted preliminary reactivity studies of the corresponding chloride
complexes in the carbonyl system. ReCl(PCy3)2(CO)3 does not react in CD2Cl2 with ligands such as H2 (3 atm) or CO (0.8 atm) and appears to be indefinitely stable in CD2Cl2. ReCl(PCy3)2(CO)3 does react with NaB(Ar')4 and gives quantitative formation of [Re(PCy3)2(CO)3]B(Ar')4 (5c) in 48 hours as well as a white precipitate, presumably NaCl. The corresponding dihydrogen complex is also formed when the reaction is conducted under an H2 atmosphere. Kubas and coworkers have used a similar strategy to synthesize manganese dihydrogen and five coordinate complexes with the B(Ar')4 anion. MnBr(dppe)2CO (dppe = Ph2PCH2CH2PPh2) reacts with NaB(Ar')4 in CH2Cl2 to form the dark blue [Mn(dppe)2(CO)]B(Ar')4 after 30 minutes at room temperature. This reaction is apparently more facile due to the weaker Mn-Br bond.

ReCl(PPh3)2(CO)3 (6a) reacts much slower with NaB(Ar')4 and appears to be dependent upon the presence of water in solution. Initially, 6a was observed to react with NaB(Ar')4 to give a species with coordinated water after 24 hours. When the 6a and NaB(Ar')4 were dried in vacuo at 100 °C prior to reaction, only minor formation of [Re(PPh3)2(CO)3]B(Ar')4 (5a) was observed after 48 hours at room temperature. Heating this reaction caused extensive decomposition. ReCl(PiPrPh2)2(CO)3 (6b) has been observed by 1H and 31P{1H} NMR spectroscopy by reaction of HCl(g) with a CD2Cl2 solution of Re(CH3)(PiPrPh2)2(CO)3 (1b).

Stability of Dihydrogen Complexes: H2 Loss, Homolytic Cleavage, Halogenated Solvents, Anions, and Heterolytic Cleavage. Protonation of neutral hydrides is a common synthetic route to cationic dihydrogen complexes. It has been observed in the [Re(H2)(PR3)2(CO)3]+ system, that the choice of acid to form the dihydrogen complexes is crucial to their stability. The labile dihydrogen ligands in [Re(H2)(PR3)2(CO)3]+ (2) can be easily displaced by anionic ligands such as chloride and triflate.22 Even BF4−, which is often considered an unreactive anion, led to the
decomposition of 4c at low temperature.\textsuperscript{12} The use of the less reactive anion, B(Ar')$_4$-, has allowed the formation of a stable series of dihydrogen complexes,
\[ \text{[Re(H$_2$)(PR$_3$)$_2$(CO)$_3$]B(Ar')$_4$.} \]

The nature of the ligands as well as the charge on the metal complex can be used to predict the expected backbonding to the H$_2$ ligand. Isonitrile ligands are expected to be better donors than carbonyls, and the donation from the alkyl phosphines should be greater than from aryl phosphines. Neutral complexes should also be more electron rich than cationic complexes. Table 1.5 lists the carbonyl stretching frequencies of a series of compounds in order to demonstrate these trends.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$CO (cm$^{-1}$, Nujol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Re(CO)$_4$(PPh$_3$)$_2$]$^+$ (7a)</td>
<td>2002</td>
</tr>
<tr>
<td>[Re(CO)$_4$(PC$_3$)$_2$]$^+$ (7c)</td>
<td>1983</td>
</tr>
<tr>
<td>[Re(CO)(PC$_3$)$_2$(CNBu)$_3$]$^+$</td>
<td>1900</td>
</tr>
<tr>
<td>W(CO)$_4$(PiPr$_3$)$_2$</td>
<td>1870</td>
</tr>
</tbody>
</table>

There is now a large series of closely related cationic rhenium dihydrogen complexes which have been studied by several different research groups.\textsuperscript{44} We have attempted to draw comparisons based on the reactivity of these complexes as summarized in Table 1.6. The stability towards various anions is apparently a function of the electron density at the metal center. When the carbonyl ligands of 4c are replaced by the less $\pi$ acidic isonitrile ligands the reactivity is dramatically different. Not only is [Re(H$_2$)(PC$_3$)$_2$(CNBu)$_3$]$^+$ stable with a wider variety of anions, but the cationic dihydrogen complex can also be formed by chloride displacement from ReCl(PC$_3$)$_2$(CNBu)$_3$ by H$_2$.\textsuperscript{16} Complexes with a higher phosphine to carbonyl ratio such as [(triphos)Re(H$_2$)(CO)$_2$]$^{44c}$ and [ReH$_2$(PR$_3$)$_4$(CO)]$^{44a,b}$ are also stable towards
more nucleophilic anions such as BF$_4^-$ and CF$_3$COO$^-$. Three of the complexes listed in Table 1.6 are reported to be thermally unstable and have only been investigated by low temperature $^1$H NMR spectroscopy. It is likely that the anions used in these complexes contribute to their thermal instability.

The series of rhenium carbonyl complexes, [Re(H$_2$)(PR$_3$)$_2$(CO)$_3$]$^+$, are also surprisingly stable in halogenated solvents such as methylene chloride, chloroform, and Freon-21 (CHFCl$_2$). The analogous Group 6 complexes, M(H$_2$)(PR$_3$)$_2$(CO)$_3$ (M = W, Mo, Cr), must be studied in toluene although it has been shown that W(H$_2$)(P$^{3}$Pr$_3$)$_2$(CO)$_3$ can briefly withstand dissolution in CD$_2$Cl$_2$ at low temperature (< -20 °C).$^{25}$ Even the rhenium isonitrile complexes, [Re(H$_2$)(PC$_3$)$_2$(CNrBu)$_3$]$^+$, are only moderately stable in halogenated solvents.$^{16}$ Both of these systems are more electron rich than the rhenium carbonyl complexes and are presumably more susceptible to oxidation. This is evidenced by the isolation and characterization of a stable Re(II) chloride complex, [ReCl(PC$_3$)$_2$(CNrBu)$_3$]$^+$, which forms by decomposition of [Re(PC$_3$)$_2$(CNrBu)$_3$]$^+$ in chlorinated solvents (CD$_2$Cl$_2$, CDCl$_3$, CDFCl$_2$).$^{16}$ Similarly, W(PC$_3$)$_2$(CO)$_3$ can also be oxidized by one electron to form a neutral 17 electron halide complex, WI(PC$_3$)$_2$(CO)$_3$.$^{10k}$

The electron density at the metal center is not only a factor in the stability of these complexes towards anions and oxidation, but also upon the reactivity of the dihydrogen ligand. Table 1.6 outlines the trends of dihydrogen lability, homolytic cleavage and heterolytic cleavage for several closely related complexes. Greater backbonding from a more electron rich metal center contributes both to a greater tendency to homolytically cleave the H$_2$ bond and to tighter binding to the metal center. The neutral W complexes have been observed to have an equilibrium between bound dihydrogen and dihydride and yet the hydrogen in this system is quite labile. Contrary to this the cationic isonitrile complex of rhenium binds hydrogen more strongly, relative to the agostic CH bond, as
<table>
<thead>
<tr>
<th>Compounds</th>
<th>$H_2$ Lability</th>
<th>Halogenated Solvent</th>
<th>Dihydride Formation</th>
<th>Anions</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W(H_2)(PCy_3)_2(CO)_3$</td>
<td>labile</td>
<td>stable $&lt;-20$ °C</td>
<td>equilibrium</td>
<td>—</td>
<td>Cu alkoxide</td>
</tr>
<tr>
<td>$[\text{Re}(H_2)(PCy_3)_2(CO)_3]^+ \text{(4c)}$</td>
<td>labile</td>
<td>stable</td>
<td>none</td>
<td>$B(Ar')_4^-$</td>
<td>(see text)</td>
</tr>
<tr>
<td>$[\text{Re}(H_2)(PCy_3)_2(CNtBu)_3]^+$</td>
<td>slowly labile</td>
<td>stable for a few days</td>
<td>none</td>
<td>$\text{Cl}^-$, $\text{OTf}^-$, $\text{BF}_4^-$</td>
<td>KOtBu</td>
</tr>
<tr>
<td>(triphos$\text{Re}(H_2)(CO)_2$)$^+^b$</td>
<td>med. labile</td>
<td>stable</td>
<td>none</td>
<td>$\text{BF}_4^-$</td>
<td>NEt$_3$</td>
</tr>
<tr>
<td>$[\text{Re}(H_2)(\text{PMe}_3)_2(CO)_3]^+$</td>
<td>thermally unstable</td>
<td>stable</td>
<td>none</td>
<td>$\text{CF}_3\text{COO}^-$</td>
<td>—</td>
</tr>
<tr>
<td>$[\text{Re}(H_2)(\text{PMe}_3)_3(CO)_2]^+$</td>
<td>thermally unstable</td>
<td>stable</td>
<td>none</td>
<td>$\text{CF}_3\text{COO}^-$</td>
<td>—</td>
</tr>
<tr>
<td>$[\text{Re}(H_2)(\text{PMePh}_2)_3(CO)_2]^{+d}$</td>
<td>thermally unstable</td>
<td>stable</td>
<td>equil/dihydride at higher $T$</td>
<td>$\text{BF}_4^-$</td>
<td>NEt$_3$</td>
</tr>
<tr>
<td>$[\text{Re}_2(\text{PMePh}_2)_4(CO)]^+^{+d}$</td>
<td>no $H_2$ loss</td>
<td>stable</td>
<td>dihydride</td>
<td>$\text{BF}_4^-$</td>
<td>KOH</td>
</tr>
<tr>
<td>$[\text{Re}_2(\text{PMe}_3)_4(CO)]^+$</td>
<td>no $H_2$ loss</td>
<td>stable</td>
<td>equil/dihydride at RT</td>
<td>$\text{CF}_3\text{COO}^-$</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$ Reference 1 and 10. $^b$ Reference 44c. $^c$ Reference 44a. $^d$ Reference 44b. $^e$ Reference 16.
determined by direct competition studies, yet there has been no evidence that oxidative addition to form the dihydride complex occurs.²²,⁴³

Certainly, there are other factors which will also affect the lability and homolytic cleavage of a dihydrogen molecule. Since these systems have been observed to interact with the phosphine through a pendant C–H bond upon loss of the dihydrogen ligand, the strength of the agostic interaction must also be considered. The strength of the agostic bond can only be measured indirectly and is presumed to be approximately 10 ± 6 kcal/mol for W(PCy₃)₂(CO)₃.¹⁰₇ Presumably the strength of the agostic bond for the analogous rhenium complexes would not be significantly different from this. Another factor which will affect the oxidative addition of the dihydrogen ligand to a dihydride structure is a significant rearrangement of the metal center. This transformation results in a formal oxidation of the metal center by two electrons and a structural change from a six-coordinate, octahedral complex to a seven-coordinate complex. How these factors will affect the observed reactivity of the dihydrogen ligand is difficult to ascertain, but it is clear that there is more involved than a simple measure of electron density at the metal center.

We have observed that sterically protected nitrogen compounds which are relatively strong bases, such as 1,8-bis(dimethylamino)napthalene and 2,6-di-tert-butyl-4-methyl pyridine, will easily deprotonate [Re(H₂)(PCy₃)₂(CO)₃]⁺ (4c). This reactivity is similar to that observed for related rhenium dihydrogen complexes with phosphine and carbonyl coligands. Both [triphosRe(H₂)(CO)₂]⁺ and [Re(H₂)(PMePh₂)₃(CO)₂]⁺ are deprotonated by NEt₃. Upon substituting a carbonyl ligand in the latter complex with a more donating phosphine ligand, the structure becomes a dihydride and consequently can only be deprotonated by a stronger base such as KOH. Both W(H₂)(PCy₃)₂(CO)₃ and [Re(H₂)(PCy₃)₂(CN¹Bu)₃]⁺ are only weakly acidic and strong bases such as a copper alkoxide¹⁰m and KO'Bu¹⁶, respectively, are used to deprotonate the dihydrogen
complexes. The lower acidity of the Kubas dihydrogen complex compared to $4c$ is not surprising upon changing from a cationic dihydrogen complex to a neutral complex even though they are believed to have similar HH bond distances according to $T_{1\text{min}}$ data and $J_{\text{HD}}$ values. The nature of the ligands also has a dramatic affect upon the acidity of the dihydrogen complex since $[\text{Re(H}_2\text{)(PCy}_3\text{)}_2\text{(CNiBu)}_3]^{\text{+}}$ does not react with 1,8-bis(dimethylamino)napthalene and is deprotonated only using a large excess of KO$_2$Bu. However, these results are consistent with the lower stretching frequencies of the corresponding carbonyl complexes listed in Table 1.5. Complex $4c$ is proposed to be less electron donating to the dihydrogen ligand which would account for the greater acidity. The infrared stretching frequencies of CO, N$_2$ or SO$_2$ complexes as a relative gauge of the electron richness of dihydrogen complexes is more useful in distinguishing properties such as acidity compared to using HH bond distances as derived from $T_{1\text{min}}$ data or $J_{\text{HD}}$ values.

Reactivity of $[\text{Re(PR}_3\text{)}_2\text{(CO)}_3]\text{B(Ar')}_4$ ($5a,b,c$) with O$_2$ and CO: Formation of $[\text{Re(PR}_3\text{)}_2\text{(CO)}_4]\text{B(Ar')}_4$ ($PR_3 = \text{PPh}_3$, $7a$; $Pi-\text{PrPh}_2$, $7b$; PCy$_3$, $7c$). Exposure of solutions of the agostic complexes, $5a,b,c$, to air results in immediate loss of the characteristic orange color to give colorless solutions. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra indicate the formation of several species, including peaks that correspond to the water complexes. In a scaled up reaction, a solution of $[\text{Re(PPh}_3\text{)}_2\text{(CO)}_3]\text{B(Ar')}_4$ in CH$_2$Cl$_2$ was exposed to an atmosphere of dry O$_2$ at $-78$ °C and the solution turned brown when warmed to room temperature. Large colorless crystals were grown from benzene in approximately 60% yield. A single resonance at 3.7 ppm was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. This same resonance has been observed repeatedly as a minor impurity in many reactions and had been attributed to decomposition with O$_2$. The IR spectrum shows a single strong band for a carbonyl stretch at 2002 cm$^{-1}$. In the
$^{13}$C{H} NMR spectrum a triplet is observed at 185 ppm with a 7.4 Hz coupling to phosphorus. All of this data suggests that the carbonyl ligands in this molecule are equivalent and this is consistent with a formulation of trans-[Re(PPh$_3$)$_2$(CO)$_4$]B(Ar')$_4$. No other products are ever observed in the reaction with O$_2$, but presumably the CO comes from the release of CO from the decomposition and a minimum of 25% of the rhenium containing products are unobserved by $^1$H or $^{31}$P{H} NMR spectroscopy. Addition of excess PCy$_3$ to the crude reaction material generates OPCy$_3$ as well as other oxidized products indicating that the unaccounted for rhenium products are likely to be paramagnetic oxide complexes. Kubas and coworkers have noted that W(PR$_3$)$_2$(CO)$_4$ often forms from disproportionation of W(PCy$_3$)$_2$(CO)$_3$ in solution or upon exposure to O$_2$.$^{10}$

Authentic samples of the tetracarbonyl species have been generated by reaction of CO with [Re(PR$_3$)$_2$(CO)$_3$]B(Ar')$_4$ (PR$_3$ = PPh$_3$, PiPrPh$_2$, PCy$_3$). Each reaction gives a colorless solution with a single $^{31}$P{H} NMR resonance which is identical to the product observed with O$_2$. [Re(PCy$_3$)$_2$(CO)$_3$]B(Ar')$_4$ also reacts in the solid state with CO to give immediate color change from orange to white. The solid was then placed under dynamic vacuum for one hour and no reversibility is observed. $^{31}$P{H} NMR and IR spectra indicate the quantitative formation of [Re(PCy$_3$)$_2$(CO)$_4$]B(Ar')$_4$ with no residual agostic species. Contrary to this, [Re(PCy$_3$)$_2$(CO)$_3$]B(Ar')$_4$ does not appear to react in the solid state with O$_2$. Exposure of the solid to an atmosphere of dry O$_2$ shows no color change over the course of one hour. A subsequent $^{31}$P{H} NMR spectrum of the dissolved product indicates mainly [Re(PCy$_3$)$_2$(CO)$_3$]B(Ar')$_4$ with only a minor amount of [Re(PCy$_3$)$_2$(CO)$_4$]B(Ar')$_4$.

Synthesis of [Re(OH$_2$)(PR$_3$)$_2$(CO)$_3$]B(Ar')$_4$ (PR$_3$ = PPh$_3$, 8a; Pi–PrPh$_2$, 8b). Excess H$_2$O was added to a CH$_2$Cl$_2$ solution of [Re(Pi–PrPh$_2$, 8b). Excess H$_2$O was added to a CH$_2$Cl$_2$ solution of [Re(Pi–
PrPh₂₂(CO)₃B(Ar')₄ to form a golden yellow solid upon removing the solvent in vacuo. The solid was exposed to dynamic vacuum for 2 hours during which there was no observable color change. ¹H and ³¹P{¹H} NMR spectra of the dissolved solid indicate the formation of a single new species. A broad singlet at 0.39 ppm in the ¹H NMR spectra integrates for two protons for 8b. When 8a is generated with less than an equivalent of H₂O, a triplet at 1.45 ppm is observed for the bound H₂O with a 1.4 Hz coupling to the phosphines. Low temperature ¹H and ³¹P{¹H} NMR spectral features do not decoalesce at lower temperatures (down to 205 K); therefore, providing no evidence for a hydroxy–hydride structure. The IR also provides good evidence for bound H₂O with an ν(OH) at 3562 (w) cm⁻¹ and δ(HOH) at 1608 (m) cm⁻¹. 8b does not react in CD₂Cl₂ with a full atmosphere of H₂, but does react with CO to give [Re(Pi-PrPh₂₂(CO)₄)B(Ar')₄ and free H₂O. The aquo complexes are oxygen sensitive in solution and [Re(PR₃)₂(CO)₄]B(Ar')₄ is the main decomposition product.

[Re(OH₂)(PR₃)₂(CO)₃]B(Ar')₄ (PR₃ = PCy₃, PiPr₃) have been previously characterized by ¹H, ³¹P{¹H}, and ¹³C{¹H} NMR.⁴⁵ The coordinated water in these complexes is much more labile compared to complexes 8a and 8b and can be partially displaced by H₂ to form the dihydrogen complexes and free water.

Synthesis of [Re(NH₃)(PCy₃)₂(CO)₃]B(Ar')₄ (9c). Both [Re(H₂)(PCy₃)₂(CO)₃]⁺ (4c) and [Re(PCy₃)₂(CO)₃]⁺ (5c) will react with NH₃ in the solid state or in solution. The addition of NH₃ (200 Torr) to 5c in the solid state results in an immediate color change from orange to white. Placing the solid under dynamic vacuum for one hour does not convert 9c to 5c and ¹H and ³¹P{¹H} NMR spectra indicate the clean formation of a new complex. The resonance for bound NH₃ was not located in the ¹H NMR spectrum and is presumably obscured by the cyclohexyl resonances. The ²H NMR spectrum of Re(ND₃)(PCy₃)₂(CO)₃]B(Ar')₄ in CH₂Cl₂
shows a broad resonance at 2.03 ppm. An IR spectrum of 9c as a Nujol mull shows three bands at 2047(w), 1942(s) and 1934(m) for the carbonyl ligands and bands for the NH3 ligand for $\nu$(NH) at 3375(w) and 3300(w) cm$^{-1}$ and a bending band, $\delta$(NH3), at 1612(m) cm$^{-1}$. When a solution of 9c in CD$_2$Cl$_2$ is pressurized with H$_2$ (1 atm), the dihydrogen complex is not detected. When a solution of 4c is pressurized with approximately 0.5 equivalents of NH$_3$, H$_2$ is displaced until all of the NH$_3$ is coordinated and no deprotonation to the neutral ReH(PCy$_3$)$_2$(CO)$_3$ is observed.

**Reactivity of [Re(PCy$_3$)$_2$(CO)$_3$]B(Ar')$_4$ (5c) with C$_2$H$_4$.** When ethylene (300 torr) was added to a CD$_2$Cl$_2$ solution of 5c, the color changed from a bright orange to pale orange. The $^{31}$P$\{^1$H$\}$NMR spectrum at room temperature indicated a broad resonance for 5c (33%) along with a sharp resonance at 1.84 ppm (66%). The new species is presumably the ethylene adduct, [Re(C$_2$H$_4$)(PCy$_3$)$_2$(CO)$_3$]B(Ar')$_4$ (10c). By cooling the sample to 10 °C only the $^{31}$P$\{^1$H$\}$ NMR resonance for 10c remained. Warming to room temperature regenerated the agostic complex, 5c. The $^1$H NMR spectrum shows a broad resonance at 3.3 ppm in addition to free ethylene, the cyclohexyl, and anion resonances. The $^2$H NMR spectrum of [Re(C$_2$D$_4$)(PCy$_3$)$_2$(CO)$_3$]B(Ar')$_4$ (10c–d$_4$) in CH$_2$Cl$_2$ show resonances for both free C$_2$D$_4$ as well as bound ethylene–d$_4$.

**Reactivity of [Re(PCy$_3$)$_2$(CO)$_3$]B(Ar')$_4$ with THF.** When Re(CH$_3$)(PCy$_3$)$_2$(CO)$_3$ is reacted with [H(Et$_2$O)$_2$]B(Ar')$_4$ in THF, a pale yellow solution results. A yellow solid is recovered upon precipitation with pentane. An IR spectrum of the compound in Nujol shows 3 bands at 2043(w), 1937(s) and 1913(m) cm$^{-1}$. The $^{31}$P$\{^1$H$\}$ NMR spectrum of the compound in CD$_2$Cl$_2$ does not show any resonances and presumably the resonance is exchange broadened due to the labile THF. When
[Re(THF)(PCy3)2(CO)3]B(Ar')4 (11c) is placed under a H2 atmosphere in CD2Cl2, 4c
is generated quantitatively. Complex 11c reacts in THF–d8 to form
[Re(PCy3)2(CO)4]B(Ar')4 (7c) when pressurized with 400 torr of CO. Heating the solid
11c at 100 °C for 2 days under dynamic vacuum or recrystallization from
CH2Cl2/pentane removes the bound THF and a subsequent 31P{1H} NMR spectrum
shows only 5c.

Reactivity of [Re(PPh3)2(CO)3]B(Ar')4 (5a) with PPh3. 5a reacts
with excess PPh3 to generate [mer–Re(PPh3)3(CO)3]B(Ar')4 (12a). The 31P{1H} NMR
spectrum shows a triplet at 0.2 ppm which integrates as one phosphine and a doublet at
3.8 ppm which integrates as two phosphines. The Jpp = 18.5 Hz is consistent with a cis
phosphorus coupling.

Conclusions

The thermolysis of toluene solutions of ReX(CO)5 (X = CH3 or H) in the
presence of PPh3 or P3PrPh2 generates trans-mer-Re(X)(PR3)2(CO)3 complexes.
Protonation of the neutral methyl or hydride complexes with [H(Et2O)]B(Ar')4 under an
H2 atmosphere generates stable dihydrogen complexes, [Re(H2)(PR3)2(CO)3]B(Ar')4,
which have been characterized by 1H NMR spectroscopy. Large HD coupling constants
and short $T_{1\text{min}}$ values are consistent with a dihydrogen formulation. These dihydrogen complexes are similar to their PCy$_3$ and P$i$Pr$_3$ analogs and there is no evidence that changing the steric or electronics of the phosphine ligands has had an effect upon the dihydrogen ligand. The hydrogen ligand is labile and can be removed in solution or the solid state by exposing the dihydrogen complexes to vacuum or argon. The formally ligand-deficient products, [Re(PR$_3$)$_2$(CO)$_3$]B(Ar')$_4$, are proposed to form a weak interaction with a CH bond of the phosphine ligand by analogy with structurally characterized complexes, [Re(PCy$_3$)$_2$(CO)$_3$]B(Ar')$_4$ and W(PR$_3$)$_2$(CO)$_3$ (PR$_3$ = P$i$Pr$_3$, PCy$_3$). The dihydrogen ligand or agostic bond is easily displaced in the presence of small molecules to form [ReL(PR$_3$)$_2$(CO)$_3$]$^+$ (L = H$_2$O, NH$_3$, C$_2$H$_4$, N$_2$, CO, Cl$^-$, PPh$_3$, THF).

Experimental Section

**General Considerations.** Due to the extreme air- and moisture-sensitivity of some of the organometallic products, manipulations were conducted with rigorous exclusion of air and water. Solid samples were handled and stored under argon in Vacuum Atmosphere or Braun inert-atmosphere boxes. Solution samples were handled using standard vacuum line or schlenk techniques. Chlorinated solvents were predried by distillation from P$_2$O$_5$ under argon (99.995%), and stored under vacuum over activated silica gel (activated by heating at 320 °C under dynamic vacuum for 4 hours) in glass vessels equipped with a Teflon needle valve. Hydrocarbon solvents were predried by distillation from Na/K alloy/benzophenone under argon, and stored under vacuum over activated silica gel in glass vessels equipped with a Teflon needle valve. Deuterated solvents (Cambridge Isotope Labs) were dried and stored in a manner similar to their
protio analogs. All solvents were subject to three freeze-pump-thaw cycles and vacuum-transferred immediately prior to use.

Reagent grade chemicals were used as received unless stated otherwise. Re(CH₃)(CO)₅ and ReH(CO)₅ were prepared from Re₂(CO)₁₀ (Strem) using literature methods.⁴⁶,⁴⁷ PCy₃ (Strem) was recrystallized from ethanol, Pi-PrPh₂ (Aldrich) and PPh₃ (Aldrich) were used as received, and Pi-Pr₃ and PMe₃ (Strem) were degassed and stored under argon. [H(Et₂O)₂]B(Ar')₄ (Ar' = 3.5-(CF₃)₂C₆H₃) was prepared by the method of Brookhart.¹³ Hydrogen (Airco, 99.999%), deuterium (Cambridge, 99.8%), carbon monoxide (Airco, 99.99%), ammonia (Aldrich, 99.99+%), ammonia-d₃ (Cambridge, 99%), ethylene (Airco, 99.9%), ethylene-d₄ (Cambridge, 98%), hydrogen chloride (Airco, 99%), and nitrogen (Airco, 99.999%) were used as received; and oxygen (General Welding Supply, 99.9%) was flushed through a cold trap (-78 °C) immediately prior to use.

¹H, ²H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on Bruker AC-200 (200.133 MHz ¹H, 30.7 MHz ²H, 81.015 MHz ³¹P), AF-300 (300.117 MHz ¹H, 75.465 MHz ¹³C) and WM-500 (500.136 MHz ¹H) spectrometers equipped with B-VT 1000 temperature controller modules with copper-constantan thermocouples. Temperature calibration was accomplished following the Van Geet methanol calibration method.⁴⁸ ¹H and ¹³C NMR chemical shifts (δ) are referenced to the internal residual proton or natural abundance ¹³C resonances of the deuterated solvent relative to TMS. ³¹P{¹H} NMR chemical shifts (δ) are reported in parts per million relative to 85% H₃PO₄ (external standard). All NMR tube reactions were conducted in flame sealed tubes or J. Young® screw-cap tubes. T₁min measurements were performed on a Bruker WM-500 spectrometer equipped with an Aspect 3000 cpu, using a standard 180°-τ-90° inversion-recovery pulse sequence.
The $^1$H and $^{13}$C($^1$H) resonances for B(Ar')$_4$ are identical with those reported for complex 2a and have been omitted from subsequent complexes.

Infrared spectra were recorded on a Perkin Elmer 1600 series FT spectrophotometer as Nujol mulls or in solution. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN and Canadian Microanalytical Service Ltd., Delta B.C.

Synthesis of Complexes.

Trans-mer-Re(CH$_3$)(PPh$_3$)$_2$(CO)$_3$ (1a). A thick walled glass vessel, equipped with a Kontes valve, was charged with Re(CH$_3$)(CO)$_5$ (502 mg, 1.46 mmol) and PPh$_3$ (1.15 g, 4.38 mmol). Toluene (20 mL) was added, the solution was cooled to -78 °C and evacuated, warmed to room temperature, and repeated twice. The solution was heated at 130 °C for 61 hours and evacuated every 12 hours to remove CO gas generated during the reaction. The toluene was removed in vacuo and the yellow solid was washed with pentane until all the yellow impurities were removed. The resulting white solid was isolated in 89.6% yield. $^1$H NMR (CDCl$_3$): -1.06 (t, $^3$J$_{PH}$ = 6.7 Hz, 3H, Re-CH$_3$); 7.29 (m, 18H, PPh$_3$ meta and para); 7.49 (m, 12H, PPh$_3$ ortho).

$^{13}$C($^1$H) NMR (CDCl$_3$): -22.3 (t, $^2$J$_{PC}$ = 6.3 Hz, Re-CH$_3$); 128.0 (vt, J$_{PC}$ = 4.5 Hz, PPh$_3$ ortho or meta); 129.6 (s, PPh$_3$ para); 133.6 (vt, J$_{PC}$ = 5.6 Hz, PPh$_3$ ortho or meta); 135.3 (t, AXX', J$_{PC}$ + J$_{PC}$ = 23.2 Hz, PPh$_3$ ipso); 195.4 (br, CO trans to CH$_3$); 199.0 (t, $^2$J$_{PC}$ = 9.3 Hz, CO cis to CH$_3$). $^{31}$P($^1$H) NMR (CDCl$_3$): 16.8 (s). IR (cm$^{-1}$, CH$_2$Cl$_2$, νCO): 2023(w), 1916(s), 1872(m).

Trans-mer-Re(CH$_3$)(Pi-PrPh$_2$)$_2$(CO)$_3$ (1b). A thick walled glass vessel, equipped with a Kontes valve, was charged with Re(CH$_3$)(CO)$_5$ (498 mg, 1.46 mmol) and Pi-PrPh$_2$ (1.00 g, 4.38 mmol). Toluene (20 mL) was added, the solution was
cooled to -78 °C and evacuated, warmed to room temperature, and repeated twice. The solution was heated at 130 °C for 40 hours and evacuated every 12 hours to eliminate CO gas generated during the reaction. The toluene was removed in vacuo and the yellow solid was washed with pentane until all the yellow impurities were removed. The resulting white solid was isolated in 53.3% yield. $^1$H NMR (CDCl$_3$): -1.12 (t, $^3$J$_{PH}$ = 6.6 Hz, 3H, ReCH$_3$); 1.11 (dd, $^3$J$_{PH}$ = 14.9 Hz, $^3$J$_{HH}$ = 7.0 Hz, 12H, P(CH(CH$_3$_2)Ph$_2$); 2.91 (sept, $^3$J$_{HH}$ = 7.0 Hz, 2H, P(CH(CH$_3$_2)Ph$_2$); 7.38 (m, 12H, Pi-PrPh$_2$ meta and para); 7.51 (m, 8H, Pi-PrPh$_2$ ortho). $^{13}$C($^1$H) NMR (CDCl$_3$): -25.7 (t, $^2$J$_{PC}$ = 6.6 Hz, ReCH$_3$); 19.5 (s, P(CH(CH$_3$_2)Ph$_2$); 28.9 (t, AX', $^3$J$_{PC}$ + $^3$J$_{PC}$ = 14.0 Hz, P(CH(CH$_3$_2)Ph$_2$); 129.0 (vt, $^3$J$_{PC}$ = 4.3 Hz, Pi-PrPh$_2$ ortho or meta); 130.6 (Pi-PrPh$_2$ para); 134.4 (t, AX''), $^3$J$_{PC}$ + $^3$J$_{PC}$ = 20.9 Hz, Pi-PrPh$_2$ ipso); 134.7 (vt, $^3$J$_{PC}$ = 4.8 Hz, Pi-PrPh$_2$ ortho or meta); 197.1 (t, $^2$J$_{PC}$ = 6.7 Hz, CO trans to CH$_3$); 200.4 (t, $^2$J$_{PC}$ = 9.0 Hz, CO cis to CH$_3$). $^{31}$P($^1$H) NMR (CDCl$_3$): 19.7 (s). IR (cm$^{-1}$, CH$_2$Cl$_2$, εCO): 2023(w), 1916(s), 1872(m).

**mer-trans-Re(CH$_3$)(PCyPh$_2$)$_2$(CO)$_3$ (1c).** A thick walled glass vessel, equipped with a Kontes valve was charged with Re(CH$_3$)(CO)$_5$ (212mg, 0.621mmol) and PCyPh$_2$ (500mg, 1.86mmol). Toluene (20mL) was added, the solution was cooled to -78°C and evacuated, warmed to room temperature, and repeated twice. The solution was heated at 130°C for 58 hours and evacuated every 12 hours to remove CO gas generated during the reaction. The toluene was removed in vacuo and the yellow solid was washed with pentane until all the yellow impurities were removed. $^1$H NMR(CDCl$_3$): -1.20 (t, $^3$J$_{HP}$ = 6.6Hz, Re-CH$_3$); 0 to 2.6 (m, RePCyPh$_2$); 7.2 to 7.9 (m, RePCyPh$_2$). $^{31}$P($^1$H) NMR(CDCl$_3$): 17.9 (PCyPh$_2$). Approx. 67% pure.

**trans-mer-Re(H)(PPh$_3$)$_2$(CO)$_3$ (2a).** A thick walled glass vessel, equipped with a Kontes valve was charged with PPh$_3$ (1.00 g, 4.38 mmol) and toluene
(10 mL). Under an argon flow, Re(H)(CO)$_5$ (0.2 mL, 1.40 mmol) was added via syringe. The solution was cooled to -78 °C and evacuated, warmed to room temperature, and repeated twice. The solution was heated for at 130 °C for 83 hours and evacuated every 12 hours to remove CO gas generated during the reaction. The toluene was removed in vacuo and the yellow solid was washed with pentane until all the yellow impurities were removed. The resulting white solid was isolated in 77% yield. $^1$H NMR (C$_6$D$_6$): -4.45 (t, $^2$J$_{PH}$ = 17.8 Hz, Re-H); 7.03 (m, PPh$_3$ meta and para); 7.84 (m, PPh$_3$ ortho). $^{31}$P($^1$H) NMR (C$_6$D$_6$): 22.8 (s). IR (cm$^{-1}$, CH$_2$Cl$_2$, v$_{CO}$): 2020(w), 1925(s).

**trans-mer-Re(H)(Pi-PrPh$_2$)$_2$(CO)$_3$ (2b).** A thick walled glass vessel, equipped with a Kontes valve was charged with Pi-PrPh$_2$ (1.11 g, 4.23 mmol) and toluene (10 mL). Under an argon flow, ReH(CO)$_5$ (0.2 mL, 1.40 mmol) was added via syringe. The solution was cooled to -78 °C and evacuated, warmed to room temperature, and repeated twice. The solution was heated at 130 °C for 53 hours and evacuated every 12 hours to remove CO gas generated during the reaction. The toluene was removed in vacuo and the yellow solid was washed with pentane until all the yellow impurities were removed. The resulting white solid was isolated in 75% yield. $^1$H NMR (C$_6$D$_6$): -5.55 (t, $^2$J$_{HP}$ = 18.8 Hz, Re-H); 1.08 (dd, $^3$J$_{PH}$ = 16.2 Hz, $^3$J$_{HH}$ = 6.9 Hz, P(CH(CH$_3$)$_2$)Ph$_2$); 2.61 (m, P(CH(CH$_3$)$_2$)Ph$_2$); 6.94 (m, PiPrPh$_2$ meta and para); 7.74 (m, PiPrPh$_2$ ortho). $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$): 18.6 (s, P(CH(CH$_3$)$_2$)Ph$_2$); 29.4 (t, AXX', J$_{PC}$ + J$_{PC}$ = 15.6 Hz, P(CH(CH$_3$)$_2$)Ph$_2$); 128.2 (s, PiPrPh$_2$ ortho or meta); 129.7 (s, PiPrPh$_2$ para); 133.3 (s, PiPrPh$_2$ ortho or meta); 137.0 (t, AXX', J$_{PC}$ + J$_{PC}$ = 20.8 Hz, PiPrPh$_2$ ipso); 177.8 (m, CO trans to H); 179.1 (m, CO cis to H). $^{31}$P($^1$H) NMR (C$_6$D$_6$): 29.6 (s). IR (cm$^{-1}$, CH$_2$Cl$_2$, v$_{CO}$): 2020(w), 1919(s).

**mer-trans-Re(D)(PiPrPh$_2$)$_2$(CO)$_3$ (2b-d$_1$).** A thick walled glass vessel, equipped with a Kontes valve was charged with Re(H)(PiPrPh$_2$)$_2$(CO)$_3$ (100mg,
0.137 mmol) and 10 mL of toluene. Under an argon flow, D₂O (0.25 mL, 13.90 mmol) was added via syringe. The solution was heated for two weeks at 120°C. An aliquot of the solution was removed for ¹H and ³¹P{¹H} NMR. The ¹H NMR did show some evidence of decomposition, but there were no peaks in the hydride region. ³¹P{¹H} NMR (CDCl₃): 28.9 (ΠPrPPh₂) and a small peak at 1.54.

**Reaction of Re(CH₃)(CO)₅ with PMe₃.** A screw cap NMR tube was charged with Re(CH₃)(CO)₅ (19.2 mg, 0.06 mmol) and 0.5 mL C₇D₈ was vacuum transferred to the tube. Under an argon flow a septum was placed on the tube and PMe₃ (15 μL, 0.17 mmol) was transferred to the solution via syringe. The sample was degassed via three freeze-pump-thaw cycles. The reaction was monitored for several days by ¹H and ³¹P{¹H} NMR. Re(CH₃)(PMe₃)(CO)₄ is formed after two days without protection from light. No further reaction was observed until the sample was heated at 100°C. Initial product formation suggested conversion of the mono-phospine product to the bis-phosphine product. Upon continued heating several new products appeared.

**cis-Re(CH₃)(PMe₃)(CO)₄.** A thick walled glass vessel, equipped with a Kontes valve was charged with Re(CH₃)(CO)₅ (501 mg, 1.46 mmol) and toluene (15 mL). Under an argon flow PMe₃ (0.25 mL, 2.78 mmol) was added via syringe and the solution was degassed by two freeze-pump-thaw cycles. The solution was allowed to stir for 2 days without protection from light. Toluene was removed in vacuo from the light yellow solution to give an oily yellow solid. All attempts at recrystallization were unsuccessful due to the high solubility of this compound. ¹H NMR (C₇D₈): -0.28 (d, ³JPH = 9.1 Hz, ReCH₃); 0.90 (d, ²JPH = 8.8 Hz, RePMe₃). ³¹P{¹H} NMR (C₇D₈): -46.4 (RePMe₃). IR (nujol mull): νCO 2073(w), 1983(s), 1967(vs), 1932(s) cm⁻¹.
**fac-**Re(CH$_3$)(PM$_3$)(CH$_3$CN)(CO)$_3$. A small glass vessel, equipped with a Kontes valve was charged with Re(CH$_3$)(PM$_3$)(CO)$_4$ (290mg, 0.745mmol). Acetonitrile (10mL) was vacuum transferred to the vessel and degassed by one freeze-pump-thaw cycle. Acetonitrile (3mL) was vacuum transferred to another small glass vessel, equipped with a Kontes, containing (CH$_3$)$_2$NO (58mg, 0.772mmol) and degassed with one freeze-pump-thaw cycle. Under an argon flow the solution of (CH$_3$)$_2$NO was transferred via cannula to the solution of Re(CH$_3$)(PM$_3$)(CO)$_4$. The solution was allowed to stir overnight under an argon flow to facilitate the removal of (CH$_3$)$_2$N gas produced during the reaction. An aliquot of this solution was used for IR, $^1$H, and $^{31}$P($^1$H) NMR. $^1$H NMR(CDCl$_3$): -0.56 (d, $^3$J$_{HP} = 9.9$ Hz, 3H, ReCH$_3$); 1.47 (d, $^2$J$_{HP} = 8.4$ Hz, 9H, RePM$_3$); 2.34 (d, $^5$J$_{HP} = 1.6$ Hz, 3H, ReNCCH$_3$). $^{31}$P($^1$H) NMR(CDCl$_3$): -34.6 (PM$_3$). IR (CH$_2$Cl$_2$): $\nu$CO 1999(s), 1902(s), 1874(s) cm$^{-1}$.

**fac-cis-**Re(CH$_3$)(PM$_3$)$_2$(CO)$_3$ (3a). The CH$_3$CN was removed in vacuo from the solution of Re(CH$_3$)(PM$_3$)(CH$_3$CN)(CO)$_3$ and 10 mL of C$_6$H$_6$ was vacuum transferred to the flask and degassed by three freeze-pump-thaw cycles. Under an argon flow PM$_3$ (0.14mL, 2.16mmol) was syringed to the solution. The flask was closed and allowed to stir overnight. The solvent was removed in vacuo. $^1$H NMR(CDCl$_3$): -0.82 (t, $^3$J$_{PH} = 10.0$ Hz, ReCH$_3$), 1.40 (vt, $^3$J$_{PH} = 7.6$ Hz, RePM$_3$). $^{31}$P($^1$H) NMR(CDCl$_3$): -45.7 (PM$_3$). IR (nujol mull): $\nu$CO 2007(s), 1923(s), 1885(s) cm$^{-1}$.

[**trans-mer-**Re(H$_2$)(PPh$_3$)$_2$(CO)$_3$]B(Ar')$_4$ (4a). A screw cap NMR tube was charged with Re(CH$_3$)(PPh$_3$)$_2$(CO)$_3$ (10 mg, 0.013 mmol) and [H(Et$_2$O)$_2$]B(Ar')$_4$ (13 mg, 0.013 mmol). CD$_2$Cl$_2$ (0.5 mL) was vacuum transferred to the tube. The solution was frozen and evacuated, an atmosphere of H$_2$ was added to the tube and
thawed. $^1$H NMR (CD$_2$Cl$_2$): -3.8 (br s, ReH$_2$); 6.7 to 8.0 (m, PPh$_3$ and B(Ar')$_4$).
$^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$): 8.1 (s).

$[\text{trans-mer-Re(H}_2\text{)(Pi-PrPh}_2\text{)}_2\text{(CO)}_3\text{)]B(Ar')}_4$ (4b). A screw cap NMR tube was charged with Re(CH$_3$)(Pi-PrPh$_2$)(CO)$_3$ (10 mg, 0.013 mmol) and [H(Et$_2$O)$_2$]B(Ar')$_4$ (13 mg, 0.013 mmol). CD$_2$Cl$_2$ (0.5 mL) was vacuum transferred to the tube. The solution was frozen and evacuated, an atmosphere of H$_2$ was added to the tube and thawed. $^1$H NMR (CD$_2$Cl$_2$): -4.26 (ReH$_2$); 1.17 (m, P(CH(CH$_3$)$_2$)Ph$_2$); 3.04 (m, P(CH(CH$_3$)$_2$)Ph$_2$); 7.55 and 7.73 (m, PiPrPh$_2$ and B(Ar')$_4$). $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$): 14.7 (s).

Reactivity of $[\text{Re(H}_2\text{)(PCy}_3\text{)}_2\text{(CO)}_3\text{)]B(Ar')}_4$ (4c) with Base:
Formation of ReH(PCy$_3$)$_2$(CO)$_3$. In a typical reaction, 4c (10 mg, 0.006 mmol) with 2,6-Di-tert-butyl-4-methylpyridine (2 mg, 0.010 mmol) was added to a sealable NMR tube attached to a 4 mm Kontes valve. Methylene chloride-$d_2$ (0.5 mL) was vacuum transferred to the tube and placed under H$_2$ (400 torr) before sealing. The solution immediately turned colorless. $^1$H and $^{31}$P{$^1$H} NMR indicate clean formation of ReH(PCy$_3$)$_2$(CO)$_3$ in addition to the appropriate resonances due to protonated base. $^1$H NMR (CD$_2$Cl$_2$): -6.66 (t, $J_{PH} = 20.5$ Hz, 2H); 1.1-2.1 (br, 66H). $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$): 30.6 (s).

$[\text{trans-mer-Re(PPh}_3\text{)}_2\text{(CO)}_3\text{)]B(Ar')}_4$ (5a). A sealable NMR tube was charged with Re(CH$_3$)(PPh$_3$)$_2$(CO)$_3$ (15 mg, 0.018 mmol) and [H(Et$_2$O)$_2$]B(Ar')$_4$ (19 mg, 0.019 mmol). A 1 mL portion of CH$_2$Cl$_2$ was vacuum transferred to the tube and removed in vacuo to remove excess ether from the solution and repeated. A 0.5 mL portion of CD$_2$Cl$_2$ was vacuum transferred to the tube. The sample was degassed by
three freeze-pump-thaw cycles before sealing the tube. \(^1\)H NMR (CD\(_2\)Cl\(_2\)): 6.7 to 8.0 (m, PPh\(_3\) and B(Ar')\(_4\)). \(^{31}\)P\{\(^1\)H\} NMR (CD\(_2\)Cl\(_2\)): 14.6 (s).

\[\text{[trans-mer-Re(Pi-PrPh\(_2\)\(_2\))(CO)\(_3\)]B(Ar')\(_4\)}\] (5b). A sealable NMR tube was charged with Re(CH\(_3\))(Pi-PrPh\(_2\)\(_2\))(CO)\(_3\) (15 mg, 0.020 mmol) and [H(Et\(_2\)O)\(_2\)]B(Ar')\(_4\) (20 mg, 0.020 mmol). A 1 mL portion of CH\(_2\)Cl\(_2\) was vacuum transferred to the tube and removed \textit{in vacuo} to remove excess ether from the solution and repeated. A 0.5 mL portion of CD\(_2\)Cl\(_2\) was vacuum transferred to the tube. The sample was degassed by three freeze-pump-thaw cycles before sealing the tube. \(^1\)H NMR (CD\(_2\)Cl\(_2\)): 1.17 (m, P(CH(CH\(_3\))\(_2\))Ph\(_2\)); 3.04 (m, P(CH(CH\(_3\))\(_2\))Ph\(_2\)); 7.55 and 7.73 (m, PiPrPh\(_2\) and B(Ar')\(_4\)). \(^{31}\)P\{\(^1\)H\} NMR (CD\(_2\)Cl\(_2\)): 20.9 (s).

\textbf{Reaction of Re(CH\(_3\))(PCyPh\(_2\)\(_2\))(CO)\(_3\) with HB(Ar')\(_4\)} A sealable NMR tube was charged with Re(CH\(_3\))(PCyPh\(_2\)\(_2\))(CO)\(_3\) (15 mg, 0.018 mmol) and HB(Ar')\(_4\) (19 mg, 0.019 mmol). A 1 mL portion of CH\(_2\)Cl\(_2\) was vacuum transferred to the tube and removed \textit{in vacuo} to remove excess ether from the solution and repeated. A 0.5 mL portion of CD\(_2\)Cl\(_2\) was vacuum transferred to the tube. The sample was degassed by three freeze-pump-thaw cycles before sealing the tube. \(^1\)H NMR(CD\(_2\)Cl\(_2\)): 0.08 to 2.72 (m, PCyPh\(_2\)); 7.53 and 7.73 (m, PCyPh\(_2\) and B(Ar')\(_4\)). \(^{31}\)P\{\(^1\)H\} NMR(CD\(_2\)Cl\(_2\)): 19.0 (PCyPh\(_2\)). Approx. 44% pure.

\textbf{Reaction of Re(CH\(_3\))(PMe\(_3\)\(_2\))(CO)\(_3\) with HB(Ar')\(_4\)} A screw cap NMR tube was charged with Re(CH\(_3\))(PMe\(_3\)\(_2\))(CO)\(_3\) (6 mg, 0.014 mmol) and HB(Ar')\(_4\) (14 mg, 0.014 mmol). A 0.5 mL portion of CDCl\(_3\) was vacuum transferred to the tube. The sample was degassed by three freeze-pump-thaw cycles before sealing the tube. \(^1\)H NMR(CDCl\(_3\)): 1.6 (m, PMe\(_3\)); 7.5 (m, p-B(Ar')\(_4\)); 7.7 (m, o-B(Ar')\(_4\)). \(^{31}\)P\{\(^1\)H\}
NMR(CDCl3): -38.1; -35.8; -32.0; -31.0. After 1 day at room temperature the $^{31}$P{$^1$H} NMR spectra shows one peak at -35.8.

**trans-mer-ReCl(PPh$_3$)$_2$(CO)$_3$ (6a).** A schlenk flask was charged with Re(CH$_3$)(PPh$_3$)$_2$(CO)$_3$ (200 mg, 0.247 mmol) and 10 mL of methylene chloride. Under an argon flow excess HCl (1 M in Et$_2$O, 0.5 mL) was added via syringe and the solution was stirred for an hour. The solvent was removed in vacuo and the solid was rinsed with two 5 mL portions of pentane. The white solid was recovered in 93% yield (190 mg). $^1$H NMR (CD$_2$Cl$_2$): 7.35 (m, 18H, PPh$_3$ meta and para); 7.58 (m, 12H, PPh$_3$ ortho). $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$): 9.7 (s). IR (cm$^{-1}$, Nujol, v$_{CO}$): 2045 (w), 1940 (s), 1892 (m).

**trans-mer-ReCl(Pi-PrPh$_2$)$_2$(CO)$_3$ (6b).** A screw cap NMR tube was charged with Re(CH$_3$)(Pi-PrPh$_2$)$_2$(CO)$_3$ (10 mg, 0.013 mmol) and 0.5 mL of CD$_2$Cl$_2$. The solution was degassed with one freeze-pump-thaw cycle. A glass vessel (2.81 mL), equipped with a Kontes valve was pressurized with 100 torr of HCl gas (0.015 mmol) which was vacuum transferred to the NMR tube at -196 °C. $^1$H NMR (CD$_2$Cl$_2$): 1.10 (dd, $^3$J$_{PH}$ = 15.5 Hz, $^3$J$_{HH}$ = 7.0 Hz, 12H, P(CH(CH$_3$)$_2$)Ph$_2$); 3.27 (sept of trip, AX$'X'$, $^3$J$_{PH}$ + $^3$J$_{H' H}$ = 2.4 Hz, $^3$J$_{HH}$ = 7.0 Hz, 2H, P(CH(CH$_3$)$_2$)Ph$_2$); 7.43 (m, 12H, Pi-PrPh$_2$ meta and para); 7.65 (m, 8H, Pi-PrPh$_2$ ortho). $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$): 16.4 (s).

**trans-mer-ReCl(PCy$_3$)$_2$(CO)$_3$ (6c).** A small glass vessel with an 8 mm Kontes tap was charged with Re(CH$_3$)(PCy$_3$)$_2$(CO)$_3$ (100 mg, 0.118 mmol) and 15 mL of toluene was vacuum transferred to the flask. Under an argon flow excess HCl (1 M in Et$_2$O, 0.5 mL) was added via syringe and the solutions was stirred for an hour. The solvent was removed in vacuo and the solid was rinsed with two 5 mL portions of
pentane. The white solid was recovered in 88% yield (90 mg). \(^{1}\text{H} \) NMR (CD\(_2\)Cl\(_2\)): 0.9 to 2.5 (m, RePC\(_{3}\)). \(^{13}\text{C} \{^{1}\text{H} \} \) NMR (CD\(_2\)Cl\(_2\)): 29.59 (P-\(\gamma\)-C); 30.86 (t, J\(_{PC} = 3\) Hz, P-\(\beta\)-C) 32.68 (P-\(\delta\)-C); 38.82 (t, J\(_{PC} = 11.2\) Hz, P-\(\alpha\)-C); 196.9 (br, CO); 200.8 (t, J\(_{PC} = 9.2\) Hz, CO). \(^{31}\text{P} \{^{1}\text{H} \} \) NMR (CD\(_2\)Cl\(_2\)): 13.87 (s). IR (cm\(^{-1}\), Nujol, v\(_{CO}\)): 2025 (w), 1914 (s), 1869 (m).

\textit{[trans-Re(PPPh\(_3\))\(_2\)(CO)\(_4\)]B(Ar')\(_4\)} (7a). A screw cap NMR tube was charged with Re(CH\(_3\))(PPPh\(_3\))\(_2\)(CO)\(_3\) (10 mg, 0.012 mmol) and [H(Et\(_2\)O)\(_2\)]B(Ar')\(_4\) (14 mg, 0.014 mmol). CDCl\(_3\) (0.5 mL) was vacuum transferred to the tube and the solution was degassed by three freeze-pump-thaw cycles. The NMR tube was exposed to 760 torr of CO gas to give a colorless solution. \(^{1}\text{H} \) NMR (CDCl\(_3\)): 7.20 and 7.44 (m, B(Ar')\(_4\) and PPh\(_3\)). \(^{31}\text{P} \{^{1}\text{H} \} \) NMR (CDCl\(_3\)): 3.7 (s). IR (cm\(^{-1}\), CH\(_2\)Cl\(_2\), v\(_{CO}\)): 2003.

Reaction of Re(CH\(_3\))(PPPh\(_3\))\(_2\)(CO)\(_3\) with HB(Ar')\(_4\) under O\(_2\)(g). A glass vessel, equipped with a Kontes valve was charged with Re(CH\(_3\))(CO)\(_3\)(PPPh\(_3\))\(_2\) (100 mg, 0.123 mmol) and [H(Et\(_2\)O)\(_2\)]B(Ar')\(_4\) (125 mg, 0.123 mmol). At -78 °C, 5 mL of CH\(_2\)Cl\(_2\) was vacuum transferred to the flask. An atmosphere of oxygen gas was added to the flask and the solution was allowed to slowly warm to room temperature while stirring. The solution turned a dark red-brown and was allowed to stir for an hour before the solvent was removed in vacuo. Colorless crystals were grown from benzene. \(^{1}\text{H} \) NMR (CDCl\(_3\)): 7.48 and 7.70 (m, B(Ar')\(_4\) and PPh\(_3\)). \(^{13}\text{C} \{^{1}\text{H} \} \) NMR (CDCl\(_3\)): 129.6 (vt, J\(_{PC} = 5.3\) Hz, PPh\(_3\) ortho or meta); 131.5 (t, AXX', J\(_{PC} + J_{P'C} = 26.9\) Hz, PPh\(_3\) ipso); 132.4 (vt, J\(_{PC} = 6.1\) Hz, PPh\(_3\) ortho or meta); 185.5 (t, J\(_{2P'C} = 7.4\) Hz, Re-CO). \(^{31}\text{P} \{^{1}\text{H} \} \) NMR (CDCl\(_3\)): 3.7 (s). IR (cm\(^{-1}\), CH\(_2\)Cl\(_2\), v\(_{CO}\)): 2002 (s).

\textit{[trans-Re(Pi-PrPh\(_2\))\(_2\)(CO)\(_4\)]B(Ar')\(_4\)} (7b). A screw cap NMR tube was charged with Re(H)(Pi-PrPh\(_2\))\(_2\)(CO)\(_3\) (10 mg, 0.014 mmol) and [H(Et\(_2\)O)\(_2\)]B(Ar')\(_4\) (14
mg, 0.014 mmol). CDCl₃ (0.5 mL) was vacuum transferred to the tube and the solution was degassed by three freeze-pump-thaw cycles. The NMR tube was exposed to 760 torr of CO gas to give a colorless solution. ¹H NMR (CDCl₃): 0.93 (dd, 3JHP = 17.3 Hz, 3JHH = 6.9 Hz, P(CH(CH₃)₂Ph₂); 7.35 and 7.57 (m, B(Ar')₄ and Pi-PrPh₂).

³¹P{¹H} NMR (CDCl₃): 9.1 (s).

[trans-Re(PCy₃)₂(CO)₄]B(Ar')₄ (7c). A small glass vessel, equipped with an 8 mm Kontes valve was charged with 5c (15 mg, 0.009 mmol). The orange solid was exposed to 300 torr of CO and immediately turned white. The solid was placed under dynamic vacuum for 2 hours and no color change was observed. ¹H NMR (CD₂Cl₂): 1.3-2.0 (br, 60H); 2.2 (br, 6H). ³¹P{¹H} NMR (CD₂Cl₂): 17.9 (s). IR (cm⁻¹, Nujol, vCO): 1983 (s).

[trans-mer-Re(OH₂)(Pi-PrPh₂)₂(CO)₃]B(Ar')₄ (8b). A small glass vessel, equipped with an 8 mm Kontes valve was charged with Re(CH₃)(Pi-PrPh₂)₂(CO)₃ (101 mg, 0.136 mmol) and [H(Et₂O)₂]B(Ar')₄ (138 mg, 0.136 mmol). Methylene chloride (5 mL) was vacuum transferred and under an argon flow at -78 °C, 20 µL of H₂O was added via syringe. The solution was allowed to warm to room temperature to give a golden yellow solution. The solvent was removed in vacuo and the light yellow solid was exposed to full vacuum for 2 hours and isolated in 80% yield. ¹H NMR (CD₂Cl₂): 0.39 (br, ReOH₂); 1.21 (dd, 3JHP = 16.5Hz, 3JHH = 7.08Hz, P(CH(CH₃)₂Ph₂)); 3.05 (quint, 3JHH = 6.9Hz, P(CH(CH₃)₂Ph₂)); 7.46 and 7.70 (br m, B(Ar')₄ and Pi-PrPh₂). ¹³C{¹H} NMR (CD₂Cl₂): 18.2 (s, P(CH(CH₃)₂Ph₂)); 30.0 (t, AXX', JPC + JPC = 15.3 Hz, P(CH(CH₃)₂Ph₂)); 127.4 (t, AXX', JPC + JPC = 22.2Hz, Pi-PrPh₂ ipso); 130.0 (vt, JPC = 4.6 Hz, Pi-PrPh₂ ortho or meta); 132.4 (s, Pi-PrPh₂ para); 133.6 (vt, JPC = 4.7Hz, Pi-PrPh₂ ortho or meta); 193.4 (t, 2JPC = 8.2Hz, CO cis to CH₃); 194.5 (t, 2JPC = 6.7Hz, CO trans to CH₃). ³¹P{¹H} NMR (CD₂Cl₂):
27.7 (s). IR (cm\(^{-1}\), Nujol): \(\nu\text{(CO)}\) 1972(s), 1921(m); \(\nu\text{(OH)}\) 3562(w); \(\delta\text{(HOH)}\) 1608(m).

**[trans-mer-Re(NH\(_3\))(PCy\(_3\))\(_2\)(CO)\(_3\)]B(\text{Ar}^+)_4\** (9c). A small glass vessel, equipped with an 8 mm Kontes valve was charged with 5c (15 mg, 0.009 mmol). The orange solid was exposed to 600 torr of NH\(_3\) and slowly turned white. The solid was placed under dynamic vacuum for 1 hour and no color change was observed. \(^1\text{H}\) NMR (CD\(_2\)Cl\(_2\)): 1.3-2.0 (br, 60H); 2.2 (br, 6H). \(^{31}\text{P}\{^1\text{H}\}\) NMR (CD\(_2\)Cl\(_2\)): 13.6 (s). IR (cm\(^{-1}\), Nujol): \(\nu\text{(CO)}\) 2047 (w), 1942(s), 1934(m); \(\nu\text{(NH)}\) 3375 (w), 3300 (w); \(\delta\text{(NH\(_3\))}\) 1612 (m).

**[trans-mer-Re(ND\(_3\))(PCy\(_3\))\(_2\)(CO)\(_3\)]B(\text{Ar}^+)_4\** (9c-d3). An NMR tube affixed to a 4 mm Kontes valve was charged with 5c (6 mg, 0.0035 mmol). The solid was exposed to 600 torr of ND\(_3\) until the solid was colorless and then placed under dynamic vacuum. 0.5 mL of CH\(_2\)Cl\(_2\) was added by vacuum transferred and the tube was sealed. \(^2\text{H}\) NMR (CH\(_2\)Cl\(_2\)): 2.03 (s, ND\(_3\)).

**[trans-mer-Re(C\(_2\)H\(_4\))(PCy\(_3\))\(_2\)(CO)\(_3\)]B(\text{Ar}^+)_4\** (10c). An NMR tube affixed to a 4 mm Kontes valve was charged with 5c (6 mg, 0.0035 mmol). CD\(_2\)Cl\(_2\) (0.5 mL) was vacuum transferred to the tube and pressurized with 300 torr C\(_2\)H\(_4\). The tube was sealed at -196 °C. The solution was pale orange at room temperature and turned colorless at -78 °C. This color change was completely reversible. \(^1\text{H}\) NMR (CD\(_2\)Cl\(_2\)): 1.2-2.0 (br, 60H); 2.3 (br, 6H); 3.29 (br, 4H, C\(_2\)H\(_4\)). \(^{31}\text{P}\{^1\text{H}\}\) NMR (CD\(_2\)Cl\(_2\)): 1.8 (s).

**[trans-mer-Re(C\(_2\)D\(_4\))(PCy\(_3\))\(_2\)(CO)\(_3\)]B(\text{Ar}^+)_4\** (10c-d3). An NMR tube affixed to a 4 mm Kontes valve was charged with 3b (6 mg, 0.0035 mmol). CH\(_2\)Cl\(_2\)
(0.5 mL) was vacuum transferred to the tube and pressurized with 300 torr C\textsubscript{2}D\textsubscript{4} and sealed. \(^2\)H NMR (CH\textsubscript{2}Cl\textsubscript{2}): 3.29 (br, C\textsubscript{2}D\textsubscript{4}).

[Re(N\textsubscript{2})(PC\textsubscript{y}3\textsubscript{3})(CO)\textsubscript{3}]B(Ar')\textsubscript{4}. A screw cap NMR tube was charged with 5c (8 mg, 0.0047 mmol). CD\textsubscript{2}Cl\textsubscript{2} was vacuum transferred to the tube and place under N\textsubscript{2} (760 torr). The solution turned colorless at low temperature. \(^1\)H NMR (190 K, CD\textsubscript{2}Cl\textsubscript{2}): 1.2-2.0 (br, 60H); 2.4 (br, 6H). \(^{31}\)P\{\(^1\)H\} NMR (190 K, CD\textsubscript{2}Cl\textsubscript{2}): 17.1 (s).

[Re(N\textsubscript{2})(Pi-Pr\textsubscript{3})\textsubscript{2}(CO)\textsubscript{3}]B(Ar')\textsubscript{4}. A screw cap NMR tube was charged with 5d (7 mg, 0.0048 mmol). CD\textsubscript{2}Cl\textsubscript{2} was vacuum transferred to the tube and place under N\textsubscript{2} (760 torr). The solution turned colorless at low temperature. \(^1\)H NMR (240 K, CD\textsubscript{2}Cl\textsubscript{2}): 1.3 (m, 36H, P(CH(CH\textsubscript{3})\textsubscript{2})\textsubscript{2}); 2.7 (m, 6H, P(CH(CH\textsubscript{3})\textsubscript{2})\textsubscript{2}). \(^{31}\)P\{\(^1\)H\} NMR (240 K, CD\textsubscript{2}Cl\textsubscript{2}): 25.0 (s).

[trans-mer-Re(THF)(PC\textsubscript{y}3\textsubscript{3})(CO)\textsubscript{3}]B(Ar')\textsubscript{4} (11c). A 10 mL round bottom flask was charged with trans-mer-Re(CH\textsubscript{3})(PC\textsubscript{y}3\textsubscript{3})(CO)\textsubscript{3} (50 mg, 0.059 mmol), [H(ET\textsubscript{2}O)\textsubscript{2}]B(Ar')\textsubscript{4} (60 mg, 0.059 mmol) and attached to a swivel frit apparatus. The swivel frit was attached to a vacuum line and 3 mL of THF was vacuum transferred at -78 °C. The pale yellow solution was warmed to room temperature and stirred for 10 minutes. The solvent volume was reduced to 1 mL in vacuo and 3 mL of pentane was vacuum transferred to the solution. A yellow solid precipitated upon mixing and the solution was filtered followed by washing with pentane. The solid was collected in 89% yield (93 mg). IR (cm\textsuperscript{-1}, Nujol, v\textsubscript{CO}): 2043(w), 1937(s), 1913(m).

[mer-Re(PPh\textsubscript{3})\textsubscript{3}(CO)\textsubscript{3}]B(Ar')\textsubscript{4} (12a). A screw cap NMR tube was charged with PPh\textsubscript{3} (5 mg, 0.019 mmol), ReCH\textsubscript{3}(PPh\textsubscript{3})\textsubscript{2}(CO)\textsubscript{3} (10 mg, 0.012 mmol), and [H(ET\textsubscript{2}O)\textsubscript{2}]B(Ar')\textsubscript{4} (13 mg, 0.013 mmol). CDCl\textsubscript{3} (0.5 mL) was vacuum transferred and the solution was degassed by three freeze-pump-thaw cycles. \(^1\)H NMR (CDCl\textsubscript{3}):
6.6 to 7.8 (m, B(Ar')₄ and PPh₃). $^{31}$P{¹H} NMR (CDCl₃): 0.2 (t, $^{2}$J_{pp} = 18.3 Hz, PPh₃ trans to CO); 3.8 (d, $^{2}$J_{pp} = 18.7 Hz, PPh₃ cis to CO).
Notes to Chapter 1.

(1) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. 

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1137–1138. (d) Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T. M.; Morris, 
Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; 
(6) \([\text{Mn(H}_2)(\text{CO})(\text{dppe})_2]B(\text{Ar})_4 (\text{dppe} = \text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)\) (King, W. A.; Luo, X.-L.; Scott, B. L.; Kubas, G. J.; Zilm, K. W. J. Am. Chem. Soc. 1996, 118, 6782–6783.)


(8) \(\text{MnH(H}_2)(\text{R}_2\text{PC}_2\text{H}_4\text{PR}_2)_2\) (R = Me, Et) (Perthuisot, C.; Fan, M.; Jones, W. D. Organometallics 1992, 11, 3622–3629.)


(22) Heinekey, D. M.; Radzewich, C. E.; Voges, M. H.; Schomber, B. M., submitted for publication.


(41) [(p-^1^BuC_6H_5)3C]B(Ar')_4 has been synthesized by the reaction of [H(Et_2O)_2]B(Ar')_4 with (p-^1^BuC_6H_5)3COH. Hodenland, C.; Radzwich, C. E., unpublished results, 1993.


CHAPTER 2

REACTIVITY OF (η⁵-C₅H₅)₂Re-X WITH ELECTROPHILIC REAGENTS

Introduction

The study of biscyclopentadienyl transition metal complexes has been a principal area of organometallic chemistry for over 40 years. Since the "sandwich" type structure of ferrocene was reported in the early 1950's, metalloocene structures have been discovered for all metals in the titanium through iron triads.¹ The first metalloocene complex of rhenium, Cp₂ReH, was initially reported by Wilkinson and Birmingham in 1955.² During initial reactivity studies it was reported that Cp₂ReH reacts with acids to form [Cp₂ReH₂]⁺ without loss of hydrogen.²,³ The study of rhenocene complexes has received relatively little attention compared to other metalloocene complexes. Complexes of the type Cp₂ReX (X = H, alkyl, Cl), are electron rich and previous investigations have documented the reactivity of rhenocene complexes with H⁺, Me⁺, Ph₃C⁺, and Ag⁺ reagents.⁴⁻¹⁴ In some cases, these reactions have led to formation of cationic rhenocene complexes with interesting chemistry and these routes are also useful towards the synthesis of new starting materials in this system.

Rhenocene chemistry has been relatively underexplored compared to the group 6 metalloocene complexes of molybdenum and tungsten. Several authors have alluded to the lack of research of rhenocene complexes due to the difficulties in the synthesis of Cp₂ReH.¹⁵⁻¹⁷ The synthesis of Cp₂ReH reported by Wilkinson and Birmingham is accomplished by the reduction of ReCl₅ with excess NaCp in THF followed by the addition of NaBH₄.² The reported yield of 40% is difficult to reproduce and although some improvements have been made to the original preparation, which allows for a more
dependable synthesis, the yields are still low.\textsuperscript{12,13} Recovery of pure material is facilitated by sublimation of the Cp\textsubscript{2}ReH directly from the reaction mixture. The conversion of Cp\textsubscript{2}ReH to simple derivatives, such as a variety of alkyl complexes and Cp\textsubscript{2}ReCl, has also proven to be difficult. Initial attempts to synthesize Cp\textsubscript{2}ReR (R = CH\textsubscript{3}, CH\textsubscript{2}CH\textsubscript{3}, CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}, CH\textsubscript{2}CH=CH\textsubscript{2}) by alkylation of Cp\textsubscript{2}ReLi\textsuperscript{+}PMDT with RX (X = Cl, Br) in hydrocarbon solvents led to samples contaminated with Cp\textsubscript{2}ReH.\textsuperscript{18} The target alkyl complexes are difficult to separate from Cp\textsubscript{2}ReH since both are soluble in hydrocarbon solvents and both are easily sublimed at moderate temperatures. Mink and Stucky have described attempts to purify these air-sensitive complexes by column chromatography which led to decomposition, although fractional crystallization in pentane did lead to higher purity alkyl complexes.\textsuperscript{18} Mink and Stucky also observed that the use of alkyl bromide reagents in the synthesis of Cp\textsubscript{2}Re(CH\textsubscript{2}CH=CH\textsubscript{2}) and Cp\textsubscript{2}ReCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3} significantly reduced the amount of Cp\textsubscript{2}ReH.\textsuperscript{18} The explanation for this observation was that the alkyl chlorides are likely to have more acidic protons and will then protonate Cp\textsubscript{2}ReLi. Gould and Heinekey have proposed that the alkyl bromide and iodide reagents are more potent alkylating agents and can lead to formation of cationic dialkyl complexes such as Cp\textsubscript{2}Re(CH\textsubscript{3})\textsubscript{2}\textsuperscript{+} which could then protonate any Cp\textsubscript{2}ReLi in solution.\textsuperscript{12,19}

The synthesis of pure alkyl complexes has been described in detail by Gould and Heinekey.\textsuperscript{12} Cp\textsubscript{2}ReLi is generated by addition of a slight excess of nBuLi to Cp\textsubscript{2}ReH in THF at -78 °C. Addition of excess CH\textsubscript{3}Cl by vacuum transfer followed by slowly warming the solution to room temperature generates Cp\textsubscript{2}ReCH\textsubscript{3}. Their procedure leads to alkyl complexes which are free from Cp\textsubscript{2}ReH and the yields are very reproducible (> 90% for Cp\textsubscript{2}ReCH\textsubscript{3}). The significant improvements in the synthesis of these materials opened the study of biscyclopentadienyl complexes of rhenium to further exploration.

Although the reactivity of Cp\textsubscript{2}ReX with electrophilic reagents has been explored in the past, the lack of pure rhenocene starting materials and other factors have limited the
success of these investigations. Welter and Stucky have reported the reactivity of [Ph₃C]BF₄ with Cp₂ReCH₃ and Cp₂ReCH₂CH₃.⁶,¹⁴ The reaction of Cp₂ReCH₃ is presumed to proceed through an α-hydride abstraction from the methyl group which leads to an unstable carbene complex. ^1H NMR resonances for this unstable complex were observed, but were quickly replaced by resonances for the ethylene complex, [Cp₂Re(C₂H₄)]⁺. The proposed mechanism for this reaction is shown in Scheme 2.1.¹⁴

Scheme 2.1
The other required product, \([\text{Cp}_2\text{Re}]^+\), was not observed and presumably it decomposed to several different products. The reaction of \(\text{Cp}_2\text{ReCH}_2\text{CH}_3\) with \([\text{Ph}_3\text{C}]\text{BF}_4\) also results in the production of \(\text{Cp}_2\text{Re(C}_2\text{H}_4)^+\), but was proposed to be generated by a \(\beta\)-hydride abstraction from the ethyl group.\(^{14}\)

Due to the contamination of the alkyl complexes by \(\text{Cp}_2\text{ReH}\), the reactivity of this complex with \([\text{Ph}_3\text{C}]\text{BF}_4\) was also investigated.\(^{14}\) Welter and Stucky claim to have isolated a complex formulated as \(\text{Cp}_2\text{ReBF}_4\) from reaction of \(\text{Cp}_2\text{ReH}\) with \([\text{Ph}_3\text{C}]\text{BF}_4\). While a structure for the complex was not proposed, a lack of an IR band for Re-H and elemental analysis was used to rule out the formation of \([\text{Cp}_2\text{ReH}_2]\text{BF}_4\). The \(^1\text{H}\) NMR spectrum of \(\text{Cp}_2\text{ReBF}_4\), when dissolved in acetone, indicated the formation \([\text{Cp}_2\text{ReH}_2]\text{BF}_4\). A related complex was reported by the reaction of \(\text{Cp}_2\text{ReH}\) with \(\text{CuCl}_2\) to form \([\text{Cp}_2\text{Re}]\text{CuCl}_2\) and includes a crystal structure with the cyclopentadienyl rings in a \textit{bent} conformation.\(^9\) The addition of \([\text{Cp}_2\text{Re}]\text{CuCl}_2\) to \(\text{CCl}_4\) produces \(\text{CHCl}_3\) which is a typical test for the existence of a metal hydride complex. These reports have led us to take a closer look at the reactivity of \(\text{Cp}_2\text{ReH}\) with potential oxidizing reagents such as \([\text{Ph}_3\text{C}]^+\) and \([\text{Cp}_2\text{Fe}]^+\).

Welter and Stucky have also investigated the reactivity of the alkyl complexes, \(\text{Cp}_2\text{ReCH}_3\) and \(\text{Cp}_2\text{ReCH}_2\text{CH}_3\), with \([\text{H(Et}_2\text{O}]\text{BF}_4\).\(^{14}\) Analysis of the products by gas chromatography after the reaction indicate the formation of \(\text{CH}_4\) and \(\text{C}_2\text{H}_6\) respectively. A careful study of these reactions was carried out by Gould and Heinekey.\(^5,12\) The observation and characterization of thermally labile alkyl hydride complexes has been reported as well as a thorough analysis of the mechanism of alkane elimination from these complexes.

Baudry and Ephritikhine have reported the synthesis of \(\text{Cp}_2\text{ReCl}\) by reaction of \(\text{Cp}_2\text{ReH}\) with halogenated solvents such as chloroform although this results in very poor yields.\(^7\) \(\text{Cp}_2\text{ReCl}\) is reported to react with donor ligands such as \(\text{PPh}_3\) and pyridine in
the presence of silver salts to form \([\text{Cp}_2\text{ReL}]^+\) (\(L = \text{PPPh}_3, \text{NC}_3\text{H}_5\)) complexes. We have observed that \(\text{Cp}_2\text{ReH}\) is easily oxidized by chlorinated solvents to form \([\text{Cp}_2\text{ReH}_2]\text{Cl}\) as a major product which may account for the low yields of \(\text{Cp}_2\text{ReCl}\). We report a scaled up synthesis of analytically pure \(\text{Cp}_2\text{ReCl}\) in nearly quantitative yield as well as subsequent reactivity with various reagents.

Cationic transition metal complexes which are electron and/or ligand deficient are prone toward attack by the counteranion, which has led to increased interest in non-coordinating anions.\(^{20}\) The report of a convenient preparation of sodium (3,5-trifluoromethyl)tetraphenylborate ([\(\text{Na}\)B(\(\text{Ar}'\))\(_4\), \(\text{Ar}' = 3,5(\text{CF}_3)\_2\text{C}_6\text{H}_3\)]) has been useful in organometallic chemistry.\(^{21}\) The trifluoro groups increase the solubility of these complexes in common solvents such as CH\(_2\)Cl\(_2\) and disperse the anionic charge throughout the anion volume rendering it non-nucleophilic. Several convenient reagents of \(\text{B(\text{Ar}')}_4^-\) have been reported by various groups: \([\text{Na}]\text{B(\text{Ar}')}_4\) and \([\text{H(Et}_2\text{O})_2]\text{B(\text{Ar}')}_4\) have been reported by Brookhart and coworkers, Boudjok and Bahr have reported the synthesis of \([\text{Ph}_3\text{C}]\text{B(\text{Ar}')}_4\),\(^{22}\) Golden and coworkers have reported \([\text{Li(H}_2\text{O})_4]\text{B(\text{Ar}')}_4\) and \([\text{Ag(Et}_2\text{O})_2]\text{B(\text{Ar}')}_4\),\(^{23}\) Hughes and coworkers have developed a synthesis for \([\text{Tl}]\text{B(\text{Ar}')}_4\),\(^{24}\) and the synthesis of \([\text{Cp}_2\text{Fe}]\text{B(\text{Ar}')}_4\) is reported in this chapter.

Results and Discussion

Preparation and Characterization of \([\text{Cp}_2\text{Re}=\text{CH}_2]^+\) (1–\(\text{B(\text{Ar}')}_4\); 1–\(\text{BPh}_4\)). A solution of \(\text{Cp}_2\text{ReCH}_3\) in methylene chloride reacts rapidly with \([\text{Ph}_3\text{C}]\text{B(\text{Ar}')}_4\) to form \([\text{Cp}_2\text{Re}=\text{CH}_2]\text{B(\text{Ar}')}_4\) (1) and \(\text{Ph}_3\text{CH}\) (eq 2.1).
Complex 1 is precipitated from solution by addition of pentane and isolated by filtration. The solid is rinsed several times with pentane and dried in vacuo; the pink solid is isolated in 97% yield. Complex 1 has been characterized by $^1$H and $^{13}$C NMR spectroscopy as well as by elemental analysis. The downfield resonances observed in the $^1$H and $^{13}$C NMR spectra are indicative of the formation of a transition metal carbene complex. The $^1$H NMR spectrum of 1 in CD$_2$Cl$_2$ shows two resonances for the cation, a singlet for the ten equivalent cyclopentadienyl protons at 5.60 ppm and a singlet for the two protons of the carbene ligand at 13.19 ppm. The $^{13}$C NMR spectrum of the cyclopentadienyl region shows a doublet of quintets with an average one bond CH coupling constant of 188 Hz, and an average two and three bond CH coupling constant of 7 Hz to give the quintet pattern. This coupling pattern of the cyclopentadienyl region is simpler than expected by virtue of the averaging of the CH coupling constants, but is consistent with what has been observed for several different complexes which have been investigated in this study. The carbon resonance of the carbene ligand appears at 247.7 ppm as a triplet due to coupling of the two equivalent protons with a one bond CH coupling constant of 152 Hz.

While the Cp$_2$ReX (X = H, alkyl, OCH$_3$) complexes are air sensitive, decomposing rapidly upon exposure to air in the solid state or solution, complex 1 is air stable in the solid state and in solution showing no decoloration over several days. Contrary to previous reports of 1-BF$_4$, 1-B(Ar')$_4$ appears to be indefinitely stable as a solid at ambient temperature and has not appeared to decompose over two years in
CD₂Cl₂ when stored at -28 °C. Complex 1 can also be formed as a tetraphenylborate salt upon reaction of Cp₂ReCH₃ with [Ph₃C]BPh₄ in CH₂Cl₂. Complex 1-BPh₄ is also isolated as a pink solid and the ¹H NMR data for the cation is similar to that observed for 1-B(Ar')₄. Complex 1-BPh₄ is thermally stable but the low solubility in CH₂Cl₂ makes it inconvenient for synthesis of further derivatives. It was hoped that 1-BPh₄ would provide suitable crystals for analysis by X-ray diffraction techniques, but several attempts led to crystals which were too small and often appeared as flat plates. Large crystals of 1-B(Ar')₄ can be grown from concentrated Et₂O or CH₂Cl₂ solutions which are layered with pentane. Unfortunately, repeated attempts at analysis by X-ray diffraction techniques lead to a data set which could not be indexed.

This reactivity is also general for derivatives of Cp₂ReCH₃. The reaction of Me₂SiCp₂ReCH₃ with [Ph₃C]B(Ar')₄ in CH₂Cl₂ immediately forms [Me₂SiCp₂Re=CH₂]B(Ar')₄ (2) and Ph₃CH (eq 2.2).

The pale orange solid is isolated in 77% yield upon precipitation with pentane. The spectroscopic data for the methylene ligand of complex 2 is similar to that of the parent complex, 1. A singlet is observed in the ¹H NMR spectrum at 12.76 ppm for the Re=CH₂ protons and two pseudotriplet resonances (JCH = 1.8 Hz) are observed for the cycopentadienyl protons (δ 6.02 and 5.87). The AA'BB' pattern for the cyclopentadienyl protons is consistent with the formulation as a monomeric ansa-bridged complex (see Chapter 4). The ¹³C NMR resonance for Re=CH₂ (δ 246.1) is a triplet with JCH = 150
Hz. Large orange crystals of 2 can be grown by the slow diffusion of pentane into a concentrated CH₂Cl₂ solution. Unfortunately, attempts to characterize this complex by X-ray diffraction techniques results in two unique structures with differing bond lengths.

**Preparation and Characterization of [Cp₂Re=CH(CH₃)]B(Ar')₄ (3).**

Cp₂ReCH₂CH₃ reacts rapidly with [Ph₃C]B(Ar')₄ in methylene chloride to form [Cp₂Re=CH(CH₃)]B(Ar')₄ (3) and Ph₃CH (eq 2.3).

\[
\text{Re=CH₂CH₃} \xrightarrow{[\text{Ph₃C}]B(\text{Ar'})₄} \text{Re=CH(CH₃)} + \text{Ph₃CH} \quad (2.3)
\]

Complex 3 is isolated by precipitation with pentane followed by filtration to give a pale orange solid in 94% yield. ¹H and ¹³C NMR spectra indicate the formation of an ethylidene complex and surprisingly no isomerization to the ethylene complex was observed at room temperature. The ¹H NMR spectrum of 2 in CD₂Cl₂ shows a doublet at 1.53 ppm for the methyl group of the ethylidene group and a quartet at 13.82 ppm for the carbene proton (JHH = 8 Hz). Two singlets are observed for the cyclopentadienyl resonances (δ 5.56 and 5.51). The carbene carbon is located as a doublet at 266.0 ppm and shows a one bond CH coupling constant of 143 Hz in the ¹³C NMR spectrum. A quartet is observed for the methyl carbon of the ethylidene ligand at 45.0 ppm with a one bond CH coupling constant of 128 Hz. Two separate patterns are observed for the cyclopentadienyl carbons, both appear as doublet of quintets and are centered at 86.0 and 85.6 ppm.
A minor amount of \([\text{Cp}_2\text{Re}(\text{C}_2\text{H}_4)]\text{B}(\text{Ar}^\prime)_4\) (δ 5.2, Cp and 2.23, \(\text{C}_2\text{H}_4\)) is observed to form initially. This indicates that while the reaction of \(\text{Cp}_2\text{ReCH}_2\text{CH}_3\) with \(\text{Ph}_3\text{C}^+\) proceeds primarily by α-hydride abstraction, a small amount of product is formed due to β-hydride abstraction. The ethylene complex is not formed by a 1,2-hydride migration since the initial product ratio (> 95/5) remains constant at ambient temperature. Similar observations have been reported by Gladysz and coworkers. The reaction of \([\text{Ph}_3\text{C}]\text{BF}_4\) with \(\text{Cp}\text{Re(NO)(PPh}_3\text{)R}\) (\(\text{R} = \text{CH}_2\text{CH}_3\), \(\text{CH}_2\text{CH}_2\text{CH}_3\)) was initially reported to proceed exclusively by α-hydride abstraction. Subsequent investigations showed that β-hydride abstraction did occur to form the olefin complexes in 5% yield for the ethyl complex and 13% yield for the n-propyl complex.

The observation of two inequivalent cyclopentadienyl resonances in the \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra for \([\text{Cp}_2\text{Re=CH(CH}_3\text{)]B}(\text{Ar}^\prime)_4\) indicates that the methyl group is aligned with one Cp while the hydrogen of the carbene ligand is aligned with the other Cp as indicated in structure A (see scheme 2.2).

![Scheme 2.2](image)

The rotation of the carbene ligand must be slow on the NMR timescale in order to observe this inequivalence. A sample of \([\text{Cp}_2\text{Re=CH(CH}_3\text{)]B}(\text{Ar}^\prime)_4\) in \(\text{CD}_3\text{NO}_2\) was heated to 63 °C at 200 MHz. No coalescence of the cyclopentadienyl resonances was observed and
the resonances remain quite sharp at this temperature. A minimum barrier for the rotation about the rhenium carbon double bond is calculated as $\Delta G^\ddagger_{\text{rot}} \geq 17.7$ kcal/mol. This large barrier to rotation is a reflection of the difference in energy between conformers A and B and not directly related to the strength of the $\pi$ bond.\textsuperscript{25}

This alignment of the carbene ligand is not what would be predicted by steric, although it seems unlikely that a small substituent such as a methyl group would be in close contact with the Cp ligand. Molecular orbital arguments can be used to predict that structure A is highly favored over a conformation in which the carbene substituents lie within the plane between the two Cp ligands (Structure B). Structure A is also the preferred conformer for neutral analogs of 3. Caulton and coworkers have synthesized $\text{Cp}_2\text{W}=\text{CH(CH}_3)$ which also shows inequivelant cyclopentadienyl rings by $^1\text{H NMR}$ spectroscopy and have confirmed this arrangement with a crystal structure of $\text{Cp}_2\text{W}=\text{CH(Ph)}$.\textsuperscript{26}

The carbene ligand in this system will be considered a neutral 2 electron donor and a $\pi$ acceptor.\textsuperscript{27,28} This bonding scheme will be used due to the demonstrated electrophilic behavior of this carbene ligand as described in Chapter 3. Figure 2.2 shows the interaction of the carbene ligand with the 3 orbitals which are available for bonding in a bent metalloocene complex.\textsuperscript{29} The $\pi$ interaction of the filled $b_2$ metal orbital with the empty $p_z$ orbital of the carbene ligand dictates the orientation of the carbene substituents.
Figure 2.1. Molecular orbital interaction diagram between valence orbitals of the 16 electron fragment, "Cp₂Re⁺", and a carbene fragment, :CHR. Adapted from references 28 and 29.
Thermolysis of 1-B(\(\text{Ar'}\)\(\text{Ar}^+\))\(_4\) and 3-B(\(\text{Ar'}\)\(\text{Ar}^+\))\(_4\). The carbone complexes were heated in CD\(_2\)Cl\(_2\) at 40 °C and monitored periodically by \(^1\text{H}\) NMR spectroscopy. The reaction was very slow and the complexes gradually disappeared over the course of a couple of weeks. Several products were observed to form which could not be identified. The thermolysis of 1-B(\(\text{Ar'}\)\(\text{Ar}^+\))\(_4\) and 3-B(\(\text{Ar'}\)\(\text{Ar}^+\))\(_4\) in CD\(_3\)CN led to cleaner reactions. The carbenes completely disappeared in 2 weeks when heated to 55 °C in an oil bath. The two main products identified by their \(^1\text{H}\) NMR chemical shifts were [\(\text{Cp}_2\text{Re(C}_2\text{H}_4)\)]B(\(\text{Ar'}\)\(\text{Ar}^+\))\(_4\)\(^6\) and [\(\text{Cp}_2\text{Re(NCCD}_3)\)]B(\(\text{Ar'}\)\(\text{Ar}^+\))\(_4\)\(^13\) (eq 2.4). Other minor products were also formed which could not be identified.

\[
\begin{align*}
\text{Re}\equiv\text{CHR} & \xrightarrow{\Delta} \text{CD}_3\text{CN} \quad \text{Re}^- \quad + \quad \text{R = H or CH}_3 \\
\end{align*}
\]

Reactions of \(\text{Cp}_2\text{ReCH}_3\) and \(\text{Cp}_2\text{ReCH}_2\text{CH}_3\) with \([\text{Ph}_3\text{C}]\text{BF}_4\). Welter and Stucky have previously described the reactivity of \(\text{Cp}_2\text{ReCH}_3\) and \(\text{Cp}_2\text{ReCH}_2\text{CH}_3\) with \([\text{Ph}_3\text{C}]\text{BF}_4\).\(^6,14\) They report that a thermally unstable methylene complex is formed by \(\alpha\)-hydride abstraction from \(\text{Cp}_2\text{ReCH}_3\) and a stable ethylene complex is formed by \(\beta\)-hydride abstraction from \(\text{Cp}_2\text{ReCH}_2\text{CH}_3\). The results that we have obtained with \([\text{Ph}_3\text{C}]\text{B(\(\text{Ar'}\)\(\text{Ar}^+\))}\) contrast with these observations and so we have reinvestigated the reactions with \([\text{Ph}_3\text{C}]\text{BF}_4\). The reaction of \(\text{Cp}_2\text{ReCH}_3\) with \([\text{Ph}_3\text{C}]\text{BF}_4\) in CD\(_2\)Cl\(_2\) forms several unidentifiable products and no evidence for the carbene complex was observed. The reaction is much cleaner in CD\(_3\)CN and shows almost exclusive formation of [\(\text{Cp}_2\text{Re=CH}_2\)]\text{BF}_4 as well as a small amount of [\(\text{Cp}_2\text{Re(NCCD}_3)\)]\text{BF}_4.\(^30\) The carbene complex is reasonably stable and decomposes
after 24 hours at room temperature. The two major products indicated by $^1$H NMR spectroscopy are \([\text{Cp}_2\text{Re}((C_2H_4))]\text{BF}_4\) and \([\text{Cp}_2\text{Re}((\text{NCCD}_3))]\text{BF}_4\). Several other minor products are formed as well.

The reaction of \(\text{Cp}_2\text{ReCH}_2\text{CH}_3\) with \([\text{Ph}_3\text{C}]\text{BF}_4\) gives \([\text{Cp}_2\text{Re}((C_2H_4))]^+\) immediately when the reaction proceeds in either CD$_2$Cl$_2$ or CD$_3$CN. A minor formation of the carbene complex, 3, is observed in the initial $^1$H NMR spectrum. The reaction in CD$_3$CN leads to fewer side products and \([\text{Cp}_2\text{Re}((\text{NCCD}_3))]^+\) is also formed as a major product. Gould has observed that \([\text{Cp}_2\text{Re}=\text{CH}(\text{CH}_3)]\text{BF}_4\) is formed when the reaction is monitored at low temperature, but the complex is unstable and isomerizes to the ethylene complex at room temperature.$^{31}$

**Reactivity of \([\text{Cp}_2\text{Re}=\text{CH}_2]B(\text{Ar'}_4)\) (1) and \([\text{Cp}_2\text{Re}=\text{CH}(\text{CH}_3)]\)**

\(B(\text{Ar'}_4)\) (3) with BF$_4^-$ and PF$_6^-$. Addition of BF$_4^-$ salts to CD$_3$CN solutions of 1–B(\text{Ar'}_4) and 3–B(\text{Ar'}_4) does slowly lead to decomposition which is similar to the [\(\text{Ph}_3\text{C}\)]BF$_4$ reactions. Complex 1 was allowed to react with either excess \([\text{NH}_4]\text{BF}_4\), \([\text{NH}_4]\text{PF}_6\), or NaBF$_4$ in CD$_3$CN. The reactions with the ammonium salts were much quicker presumably due to greater solubility in CD$_3$CN. The reactions proceeded to give very clean formation of \([\text{Cp}_2\text{Re}((C_2H_4))]\text{BF}_4\) and \([\text{Cp}_2\text{Re}((\text{NCCD}_3))]\text{BF}_4\) as well as a small amount of free ethylene (δ 5.4). The reaction with \([\text{NH}_4]\text{BF}_4\) produced the two rhenium containing products in a 50/50 ratio, while the NaBF$_4$ reaction gave 33/66 respectively. The difference in product ratios is unclear. The reaction of complex 3 with NaBF$_4$ appeared to be somewhat different. There were many minor products formed during the reaction and the reaction was much slower than for complex 1. The acetonitrile and ethylene complexes were only formed as minor products. There was no evidence of coupling to form 2-butene as a product.
The instability of the carbene complexes appears to be directly related to the nature of the anion. This is unusual for two reasons. First, the decomposition of \([\text{Cp}_2\text{Re}=\text{CH}_2]^+\) and \([\text{Cp}_2\text{Re}=\text{CH}(\text{CH}_3)]^+\) presumably proceeds to \([\text{Cp}_2\text{Re}(\text{C}_2\text{H}_4)]^+\) by different mechanisms. Complexes of the type \(\text{LnM}=\text{CH}_2\) have often been observed to form the corresponding ethylene complexes in 50% yield with the other 50% of the metal complex decomposing or forming a solvent stabilized complex.\(^{32}\) The mechanism of this reaction has been studied by Gladysz and coworkers for \([\text{CpRe(NO)(PPh}_3](=\text{CH}_2)]\text{BF}_4\) and was shown to proceed through a bimolecular coupling,\(^{32}\) similar to the intermediate previously depicted in Scheme 2.1. Consistent with this reactivity they have observed that the bulkier complex, \([\text{Cp}^*\text{Re(NO)(PPh}_3](=\text{CH}_2)]\text{BF}_4\), is considerably more stable than the parent complex.\(^{33}\) Probably the best evidence for this type of decomposition pathway is the reported isolation of a 1,3-dimetallacyclobutane complex by Grubbs and Ott, from a reaction which is thought to produce "\(\text{Cp}_2\text{Ti}=\text{CH}_2\)" (eq 2.5).\(^{34}\)

\[
\begin{align*}
\text{[Diagram]} & \\
\text{[Equation 2.5]} & \quad (2.5)
\end{align*}
\]

Several complexes of the form \(\text{LnM}=\text{CH}(\text{CH}_3)\) have also been observed to form corresponding ethylene complexes upon decomposition. This reaction has been proposed to proceed via a [1,2]hydrogen shift. A bimolecular coupling reaction similar to those observed from methylene complexes would produce 2-butene. Gladysz and coworkers have explored the conversion of \([\text{CpRe(NO)(PPh}_3](=\text{CHR})]\text{BF}_4\) complexes to the corresponding olefin complexes.\(^{35}\) In this case a solvent coordinated species would not be expected to form. The [1,2]hydrogen shift for alkylidene complexes is affected by the electrophlicity of the \(\alpha\) carbon. Therefore, the higher alkylidene complexes tend to be
less stable then the ethylidene complexes due to a greater δ+ on the α carbon. Also transition metal complexes with more donating ligands such as alkyl phosphines or cyclopentadienyl ligands tend to stabilize the alkylidene by lowering the electrophilicity of the α carbon.

Addition of a catalytic amount of 1,8-bis(dimethylamino)naphthalene (Proton-Sponge®) to [Cp2Re=CH(CH3)]B(Ar')4 did not promote isomerization to the ethylene complex. Schrock and Casey have both reported the rearrangement of neutral ethylidene complexes to ethylene complexes is catalyzed by the addition of acid.36,37 The reverse reaction has also been observed by Schrock and coworkers who reported that a catalytic amount of an acidic phosphine (PPh2) caused the isomerization of a low valent, neutral ethylene complex, [N3N]Ta(C2H4) (N3N3+ = (Me3SiNCH2CH2)3N3-), to the more stable ethylidene complex, [N3N]Ta=CH(CH3).38 Gladysz and coworkers have proposed that similar mechanisms are unlikely to proceed for electrophilic carbene complexes of high valent metal centers.32 [CpRe(NO)(PPh3)(=CHCH2R)]PF6 complexes are observed to have acidic β hydrogens and can be deprotonated to form neutral vinyl complexes by DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) or KOtBu.39

The other unusual factor about the anion dependence on the stability of complexes 1 and 3 is that while the less nucleophilic B(Ar')4- has been observed to be less reactive towards electrophilic transition metal complexes (see Chapter 1) the reactivity with BF4- usually leads to decomposition. Both complexes 1 and 3 appear to undergo relatively clean conversion to new products without loss to side reactions by decomposition with BF4-, as compared to the intensity of the B(Ar')4- resonances in the 1H NMR spectra. How BF4- promotes the isomerization of 3 to the ethylene complex and the bimolecular coupling of complex 1 is currently unknown.
Reactivity of Cp$_2$ReCH$_3$ and Cp$_2$ReCH$_2$CH$_3$ with [Cp$_2$Fe]B(Ar')$_4$. Hydride abstraction by Ph$_3$C$^+$ reagents has been proposed in some systems to proceed by an initial electron transfer from the metal alkyl complex followed by a hydrogen atom transfer.$^{40,41}$ Scheme 2.3 depicts the mechanism of hydride abstraction by oxidation as applied to Cp$_2$ReCH$_3$.

![Scheme 2.3](image)

Cooper and Gladysz have both proposed an electron transfer mechanism for their studies of the reactivity of transition metal alkyl complexes with trityl cation. To date, Cooper has provided the best evidence for this mechanism by the isolation and characterization of stable radical cations, [Cp$_2$W(CH$_3$)(C$_2$H$_5$)]$^{++}$, which react with Ph$_3$C$^+$ by hydrogen atom abstraction. The first requirement which is met by our system is that the metal complexes must be electron rich. The second requirement is that the cationic radical complex which is formed is stable enough to then transfer a hydrogen atom.$^{42}$

In order to more closely investigate the possibility of an initial electron transfer we wanted to look at the reactivity of Cp$_2$ReR complexes with an oxidizing reagent (i.e. a
reagent which will initially react by electron transfer) such as \( \text{Cp}_2\text{Fe}^+ \).\(^{43}\) Based on the results of the \( \text{Ph}_3\text{C}^+ \) reactions, the stability of the carbene complexes generated would be sensitive to the anion. [\( \text{Cp}_2\text{Fe} \)]B(Ar')\(_4\) was prepared by a similar method to that reported for [\( \text{Cp}_2\text{Fe} \)]BPh\(_4\) by Jordan and coworkers.\(^{44}\) NaB(Ar')\(_4\) is added to an aqueous solution of [\( \text{Cp}_2\text{Fe} \)]\(_2\)SO\(_4\)\(^{45}\) and precipitation of [\( \text{Cp}_2\text{Fe} \)]B(Ar')\(_4\) occurs after stirring overnight (eq 2.6).

\[
\text{Cp}_2\text{Fe} + \text{H}_2\text{SO}_4 \rightarrow [\text{Cp}_2\text{Fe}]_2\text{SO}_4 + \text{NaB(Ar')}_4 \xrightarrow{\text{H}_2\text{O}} [\text{Cp}_2\text{Fe}]\text{B(Ar')}_4 \quad (2.6)
\]

The reactivity of \( \text{Cp}_2\text{ReCH}_3 \) and \( \text{Cp}_2\text{ReCH}_2\text{CH}_3 \) with [\( \text{Cp}_2\text{Fe} \)]B(Ar')\(_4\) in CD\(_2\)Cl\(_2\) led to many different products which could not be identified. In CD\(_3\)CN, [\( \text{Cp}_2\text{Fe} \)]B(Ar')\(_4\) reacts with \( \text{Cp}_2\text{ReCH}_3 \) to give [\( \text{Cp}_2\text{Re(\text{NCCD}_3)} \)]\(^+\) and [\( \text{Cp}_2\text{Re=CH}_2 \)]B(Ar')\(_4\). [\( \text{Cp}_2\text{Re(\text{NCCD}_3)} \)]\(^+\) is proposed to be formed from an intermediate methyl hydride complex which loses methane and coordinates acetonitrile (Scheme 2.4).\(^{46}\) The reaction of [\( \text{Cp}_2\text{Fe} \)]B(Ar')\(_4\) and \( \text{Cp}_2\text{ReCH}_2\text{CH}_3 \) affords [\( \text{Cp}_2\text{Re(\text{NCCD}_3)} \)]\(^+\) and the ethylene complex with no evidence of the ethylidene complex.
Recent work by Tilset and coworkers has shown that oxidation of metal hydride complexes can generate acidic radical cation species which can then react by proton transfer with a neutral hydride complex and form a dihydride or dihydrogen product. It is unknown if a similar radical cationic alkyl complex is capable of proton transfer. When the reaction of [Cp$_2$Fe]$^+$ with Cp$_2$ReCH$_2$CH$_3$ is conducted with 2 equivalents of proton sponge, the acetonitrile complex is still generated and no change in product formation is observed. Investigation of this reaction by $^1$H NMR spectroscopy at lower
temperatures might confirm the presence of the unstable alkyl hydride complex which reacts further to generate the acetonitrile complex. The [Cp₂Fe]⁺ experiments seem to confirm that the carbene complexes can be formed via an electron transfer mechanism.

Reactions of [Ph₃C]B(Ar⁺)₄ with other Cp₂ReR Compounds. The isolation of two new carbene complexes in this system, led us to further investigate the reactivity of [Ph₃C]⁺ with known alkyl complexes of rhenocene. Unfortunately, this series is currently limited to complexes where R = CH₂CH₂CH₃, CH₂CH=CH₂, CH₂SiMe₃, and CH₂Ph.⁴⁸ We were intrigued by the findings of Gladysz and coworkers regarding the identity of the alkyl complexes affecting whether hydride abstraction occurs at the α or β position leading to the isolation of a carbene complex or an olefin complex.³²,⁴⁹ According to their findings, straight chain alkyl groups will preferably undergo α-hydride abstraction as observed for the ethyl and propyl complexes in their system. The benzyl complex also undergoes α-hydride abstraction due to the lack of a β-hydrogen. When the alkyl complexes are bulkier, such as i-propyl, a mixture of α and β-hydride abstraction occurs and other alkyls only give β-hydride abstraction products. Two alkyls in the rhenocene system which would provide interesting subjects are Cp₂ReCH₂CH=CH₂ and Cp₂ReCH₂SiMe₃.

The reaction of Cp₂Re(CH₂CH=CH₂) with [Ph₃C]B(Ar⁺)₄ in CH₂Cl₂ gives a brown solution. A brown oil separates from the solution upon the addition of pentane and further attempts at crystallization of this complex failed. The ¹H NMR spectrum of the crude reaction mixture indicated two cyclopentadienyl resonances of equal intensity and several doublet of doublet resonances between 1.5 and 4 ppm. No downfield resonances were observed which would indicate the formation of a carbene complex. The reaction was also monitored at -80 °C by ¹H NMR spectroscopy and the product was formed immediately, suggesting that there was no rearrangement from another complex at
low temperature. Scheme 2.5 shows the possible reaction pathways for the reaction of Cp₂ReCH₂CH=CH₂ with [Ph₃C⁺]. The first two possibilities are simply hydride abstraction from either the α or the β carbon. The last reaction is electrophilic attack of the Ph₃C⁺ at the γ carbon of the allyl ligand.

Scheme 2.5

The lack of any carbene resonances rules out the first reaction by α-hydride abstraction. The inequivalent cyclopentadienyl resonances and several inequivalent proton resonances seems inconsistent with the allene structure which would be formed by β-hydride abstraction. Fortunately, the complex was finally isolated by anion exchange with NaI and [Cp₂Re(η²-CH₂CHCH₂CPh₃)]I (4) was precipitated from acetone. The
$^1$H NMR spectrum of the isolated product confirmed that electrophilic attack at the $\gamma$-carbon had occurred. The $^1$H NMR spectrum indicated 5 separate resonances for the protons of the propene-substituted ligand which have all been assigned based on coupling constants and decoupling studies (Scheme 2.6, Table 2.1).

\[ + \text{I}^- \]

![Scheme 2.6](image)

**Table 2.1. Chemical Shifts and Coupling Constants for Complex 4.**

<table>
<thead>
<tr>
<th>Proton</th>
<th>Chemical Shift (ppm)</th>
<th>Coupling Constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.77</td>
<td>C (13.7) &amp; B (1)</td>
</tr>
<tr>
<td>B</td>
<td>2.72</td>
<td>multiplet</td>
</tr>
<tr>
<td>C</td>
<td>2.34</td>
<td>A (13.7) &amp; B (9.1)</td>
</tr>
<tr>
<td>D</td>
<td>2.01</td>
<td>B (9.4) &amp; E (5.0)</td>
</tr>
<tr>
<td>E</td>
<td>1.72</td>
<td>B (13.2) &amp; D (5.0)</td>
</tr>
</tbody>
</table>

Electrophilic attack on the $\gamma$-carbon of $\eta^1$-allyl complexes is well precededted and has been reviewed by Rosenblum.\textsuperscript{50} The only known reactivity of \textit{Cp}_2Re(\textit{CH}_2\textit{CH}=\textit{CH}_2) is the protonation with [H(\textit{Et}_2\textit{O})]BF\textsubscript{4} reported by Gould.\textsuperscript{13} At low temperatures a cationic allyl hydride complex is formed although it was observed that even at -70 °C it was slowly isomerizing to an $\eta^2$-propene structure which has been
previously synthesized. The mechanism of this transformation is not known. The allyl hydride complex could be in equilibrium with an $\eta^1$-propene $\sigma$-complex which then undergoes a hydride shift or a rearrangement to the $\eta^2$ structure. Reductive elimination of propene followed by attachment in the $\eta^2$ configuration could occur assuming that "Cp$_2$Re$\pi$" is trapped quickly to prevent products resulting from reaction with the solvent. In another mechanism the allyl hydride could be in rapid equilibrium with the neutral allyl complex and at higher temperatures the site of attack would be the $\gamma$-C of the allyl ligand. The bulky electrophile, [Ph$_3$C]$\pi$, would likely attack only at the $\gamma$-C. The $\eta^2$-propene complex has been observed to have only one cyclopentadienyl resonance in the $^1$H NMR suggesting that the olefin is spinning rapidly on the NMR timescale or a coincidental chemical shift for the two Cp ligands. [Cp$_2$Re($\eta^2$-CH$_2$CH=CH$_2$CPh$_3$)]$\pi$I has inequivalent cyclopentadienyl ligands presumably due to the steric of the CPh$_3$ group which hinders the rotation. High temperature $^1$H NMR spectrum have not been investigated to observe the coalescence of these resonances. Presumably other olefin complexes of this type could be synthesized by addition of various electrophiles ([Me$_3$O]BF$_4$, SiMe$_3$OTf) to Cp$_2$ReCH$_2$CH=CH$_2$.

The addition of [Ph$_3$C]B(Ar')$_4$ to Cp$_2$ReCH$_2$SiMe$_3$ in CD$_2$Cl$_2$ results in decomposition and the only identifiable species in solution is [Cp$_2$ReH$_2$]B(Ar')$_4$. Gladysz and coworkers have investigated the reaction of [Ph$_3$C]BF$_4$ with CpRe(NO)(PPh$_3$)(CH$_2$CMe$_3$) and could not identify any organometallic products. The trimethylsilylmethyl and neopentyl ligands lack $\beta$-hydrides, but the steric bulk of the alkyl ligands should discourage $\alpha$-hydride abstraction based on the trends reported by Gladysz and coworkers.

**Reactivity of Cp$_2$ReCH$_3$ with [H(Et$_2$O)$_2$]B(Ar')$_4$ and HCl.** Previous investigations from this group have reported the protonation of Cp$_2$ReCH$_3$ to generate
Re(V) alkyl hydride complexes of the form, [Cp₂Re(CH₃)H]⁺. These complexes are thermally unstable and eliminate methane below room temperature. The rate of methane elimination is unaffected by the identity of the anion, although the final product depends upon whether the anion or solvent is strongly coordinating. Therefore, Cp₂ReCl is formed from [Cp₂Re(CH₃)H]Cl while methane elimination from [Cp₂Re(CH₃)H]BF₄ results in decomposition. The protonation of Cp₂ReCH₃ with [H(Et₂O)₂]B(Ar')₄ results in the formation of [Cp₂Re(CH₃)H]B(Ar')₄ at low temperature (see Chapter 4). Upon methane elimination only a single product results which has been identified as resulting from the oxidative addition of methylene chloride by "Cp₂Re⁺" (eq 2.7).

\[
\begin{array}{c}
\text{Cp}_2\text{Re-CH}_3 \\
\text{HB(Ar')}_4 \\
\text{CH}_2\text{Cl}_2
\end{array} \xrightarrow{} \begin{array}{c}
\text{Cp}_2\text{Re-H} \\
\text{CH}_3
\end{array}
\]

(2.7)

There was no evidence for the intermediacy of an \(\eta^1\)-CH₂Cl₂ type complex which has been observed in some systems either as an intermediate prior to oxidative addition⁵¹,⁵² or as a stable complex⁵³,⁵⁴. Confirmation of the structure of 5, depicted above, was obtained by \(^1\)H and \(^{13}\)C NMR spectroscopy. The \(^1\)H NMR spectrum of 5 shows a single Cp resonance at 6.02 ppm and a resonance at 4.40 ppm which integrates for 2
protons. The $^{13}$C NMR resonance for Re–CH$_2$Cl appears as a triplet at $\delta$ 11.5 ($J_{CH} = 163$ Hz). Complex 5 can also be formed by the reaction of [Cp$_2$Re=CH$_2$]B(Ar')$_4$ (1) with Cl$_2$ in CH$_2$Cl$_2$ (see Chapter 3).

A synthetic prep for Cp$_2$ReCl in good yield and purity has remained elusive. Cp$_2$ReCl can be prepared directly from ReCl$_5$ with KCp (4 equiv.) in 10% yield and has been structurally characterized.$^{55}$ The preparation of Cp$_2$ReCl from Cp$_2$ReH has been previously reported by two groups.$^{4,6}$ Baudry and Ephritikine reported that Cp$_2$ReCl is formed by addition of CCl$_4$ to an acetone solution of Cp$_2$ReH. In a similar preparation, Mink and Stucky isolate Cp$_2$ReCl by refluxing Cp$_2$ReH in CHCl$_3$. Both reported yields are quite low although possible side reactions are not investigated. We have observed that Cp$_2$ReH reacts in CDCl$_3$ at room temperature to readily form [Cp$_2$ReH$_2$]Cl. This product presumably forms from the oxidation of Cp$_2$ReH which will be discussed later. The $^1$H NMR investigations of [Cp$_2$Re(CH$_3$)$_2$H]$^+$ by Gould has found that when the anion is chloride, Cp$_2$ReCl will be formed quantitatively upon methane elimination.$^5$ The protonation of Cp$_2$ReCH$_3$ with HCl followed by stirring in CH$_2$Cl$_2$ gives a dark orange solution with brown precipitate. The solvent was removed in vacuo and Cp$_2$ReCl was isolated in 91% yield as an analytically pure solid with a single resonance in the $^1$H NMR spectrum in CD$_2$Cl$_2$ ($\delta$ 4.54). Although this route involves the added step of preparing Cp$_2$ReCH$_3$, the benefits of isolating a clean product in near quantitative yield outweigh the drawbacks.

**Synthesis of Cp$_2$Re(R)CH$_3$$^+$.** The synthesis of the dialkyl, [Cp$_2$Re(CH$_3$)$_2$]PF$_6$, has been previously reported by the reaction of Cp$_2$ReH with excess methyl iodide in the presence of base. We have found that a series of dialkyl complexes can be synthesized by reacting Cp$_2$ReR (R = CH$_3$, CH$_2$CH$_3$, CH$_2$SiMe$_3$) compounds with [Me$_3$O]BF$_4$ in CH$_3$CN (eq 2.8).
The spectroscopic data for complex 6 was identical to that previously reported. The reactions can be run in CD$_2$Cl$_2$ or CD$_3$CN, but are much cleaner in the latter. This reaction doesn't provide an improved route to the dimethyl complex, but is useful for the generation of mixed alkyl complexes. Gould has previously investigated the thermolysis of [Cp$_2$ReH$_2$]$^+$ and [Cp$_2$Re(CH$_3$)$_2$]$^+$ in CD$_3$CN at 90 °C. The dihydride showed no reaction after 5 days while the dimethyl complex showed 50% decomposition to unidentifiable products. We surmised that the thermolysis of complex 7 might show more reactivity due to the presence of $\beta$ hydrogens of the ethyl group. Reductive elimination of methane from complex 7 might provide a facile route to the ethylene complex, [Cp$_2$Re(C$_2$H$_4$)]BF$_4$. Complex 7 was observed to decompose after heating in CD$_3$CN at 70 °C for several days with no evidence for formation of the ethylene or the acetonitrile complexes. The lack of clean methane elimination from this complex is not surprising considering that transfer of a $\beta$ hydrogen would most likely occur to the metal center which for this complex is already electronically saturated.

**Reactivity of Cp$_2$ReH with Electrophiles.** Sweet has reported extensive studies of CpRe(NO)(CO)H with trityl cation in which a hydride is abstracted and Ph$_3$CH is generated. When these reactions are conducted in the presence of donor solvents such as CH$_3$CN, THF, or acetone, products of the type [CpRe(NO)(CO)L]$^+$ (L =
solvent) are generated. In a less coordinating solvent such as methylene chloride the unsaturated metal complex undergoes a novel coordination of η²-\text{Ph₃CH} in which a fluxional process interconverts diastereomers. Gladysz and coworkers have demonstrated in a similar system that \text{CpRe(NO)(PPh₃)H} reacts with [\text{Ph₃C}]PF₆ to generate \text{Ph₃CH} and [\text{CpRe(NO)(PPh₃)L}]⁺ in the presence of THF or diethyl ether.⁵⁷

Mink and Stucky have previously reported that \text{Cp₂ReH} reacts with [\text{Ph₃C}]BF₄ to generate "\text{Cp₂ReBF₄}". It was not reported whether the species is an unsaturated cationic species or if BF₄⁻ is coordinated to the metal center. We have observed that \text{Cp₂ReH} reacts with [\text{Ph₃C}]B(\text{Ar'})₄ in CD₂Cl₂ to generate two species at -78 °C. The first complex has been identified as [\text{Cp₂ReH₂}]B(\text{Ar'})₄ by comparison to the \text{¹H NMR} spectrum of an authentic sample. The second complex exhibits a cyclopentadienyl resonance of equal intensity to [\text{Cp₂ReH₂}]⁺ but no other \text{¹H NMR} resonances could be attributed to this complex. This complex is thermally unstable and quickly decomposes as the temperature is raised above -78 °C. In order to account for the appearance of [\text{Cp₂ReH₂}]⁺ we began to speculate upon the mechanism of this reaction in order to identify the unknown species (Scheme 2.7).
Attempts were made to trap the unknown species with H₂, CH₄, C₂H₄, and PPh₃ to give previously characterized compounds, but none of these compounds were identified in the ¹H NMR spectra. When the reaction between Cp₂ReH and [Ph₃C]B(Ar')₄ was carried out in CD₃CN, [Cp₂Re(NCCD₃)]⁺ was generated as a major product in addition to the
dihydride but a significant amount of decomposition products were also present. It seemed unlikely that \([\text{Cp}_2\text{Re}]^+\) was generated based on the previous result that \([\text{Cp}_2\text{Re}(\text{CH}_3\text{H})]^+\) cleanly reacted with \(\text{CH}_2\text{Cl}_2\) upon methane elimination to form \([\text{Cp}_2\text{Re}(\text{CH}_2\text{Cl}\text{Cl})]^+\).

The synthesis of \([\text{Cp}_2\text{Re}]_2\) has been previously reported by Pasman and Snel and subsequent investigations of its thermal and photochemical reactivity.\(^{58}\) The reactivity of this complex with electrophilic complexes had not been previously investigated. In our hands, reactions of \([\text{Cp}_2\text{Re}]_2\) with \([\text{Ph}_3\text{C}]\text{B}(\text{Ar}^\prime)_4\), \([\text{Cp}_2\text{Fe}]\text{B}(\text{Ar}^\prime)_4\) and \([\text{H(ET}_2\text{O})_2]\text{B}(\text{Ar}^\prime)_4\) failed to provide any clean products even at low temperature.

Although we could not conclusively identify the second product of the reaction of \(\text{Cp}_2\text{ReH}\) with \([\text{Ph}_3\text{C}]\text{B}(\text{Ar}^\prime)_4\), it is clear that \(\text{Cp}_2\text{ReH}\) does not react by a simple hydride abstraction mechanism as described for \(\text{CpRe(NO)(CO)}\text{H}\) and \(\text{CpRe(NO)(PPh}_3\text{)}\text{H}\). \(\text{Cp}_2\text{ReH}\) is more electron rich than either of these complexes and is oxidized by \([\text{Ph}_3\text{C}]^+\). The previous reports of \(\text{Cp}_2\text{ReBF}_4\)\(^{14}\) and \([\text{Cp}_2\text{Re}]\text{CuCl}_2\)\(^{11}\) are more likely to be characterized as \([\text{Cp}_2\text{ReH}_2]^+\) based on the reactivity reported here as well as the suspect characterization of these complexes.

The synthesis of \([\text{Cp}_2\text{ReH}_2]^+\) has been reported by several groups with a variety of anions by the direct protonation of \(\text{Cp}_2\text{ReH}\).\(^{2,3,4,6,13}\) We have prepared \([\text{Cp}_2\text{ReH}_2]\text{B}(\text{Ar}^\prime)_4\) by the reaction of \(\text{Cp}_2\text{ReH}\) with \([\text{H(ET}_2\text{O})_2]\text{B}(\text{Ar}^\prime)_4\) in \(\text{Et}_2\text{O}\). The dihydride was isolated as a white solid in 95 % yield. The \(^1\text{H}\) NMR resonances for the cyclopentadienyl and hydride ligands have been found to vary considerably within the same solvent depending upon the identity of the anion. \([\text{Cp}_2\text{ReH}_2]\text{B}(\text{Ar}^\prime)_4\) has resonances at \(\delta\) 5.30 (Cp) and - 13.83 (H) while the resonances for \([\text{Cp}_2\text{ReH}_2]\text{Cl}\) are observed at \(\delta\) 5.68 (Cp) and - 14.04 (H).
Due to the recent interest in synthesizing dicationic dihydrogen complexes we prepared and isolated [Cp₂ReH₂]OTf. Attempts to react this complex with a large excess of triflic acid did not produce any observable change in the ¹H NMR spectrum.

Reactivity of Cp₂ReCl with Electrophiles. As described above, Cp₂ReCl can now be synthesized in excellent yield and purity. It was anticipated that this compound would be a useful starting material for preparation of a variety of new compounds. [H(Et₂O)₂]B(Ar')₄ reacts cleanly with Cp₂ReCl in CD₂Cl₂ to form [Cp₂Re(H)Cl]B(Ar')₄ (9). A single Cp resonance is observed in the ¹H NMR spectrum at 5.87 ppm with a hydride resonance at -11.84 ppm. Complex 9 reacts with LiNHP* (Ph* = 2,6-diisopropylphenyl) to regenerate Cp₂ReCl and NH₂Ph*.

Attempts to react Cp₂ReCl with halide abstraction reagents such as AgOTf and AgBF₄ led to several products even when conducted in CD₃CN. Complex 9 was often the major product which could be identified from these reactions which is formed by the oxidation of Cp₂ReCl. Thallium reagents are considered to be useful for halide abstraction reagents and are less oxidizing than silver reagents. Tl(B(Ar')₄ was synthesized by addition of TIOEt to an ether solution of [H(Et₂O)₂]B(Ar')₄ and isolated as a white solid.¹⁴ The addition of Tl(B(Ar')₄ to Cp₂ReCl again lead to oxidized products including [Cp₂ReH(Cl)]⁺ as the major product. The reaction of [Me₃O]BF₄ with Cp₂ReCl also produced 9 and the thermolysis of Cp₂ReCl with LiNHP* or KOH in THF failed to produce any reaction.

Reactivity of Cp₂ReOCH₃ with Electrophiles. The synthesis of Cp₂ReOCH₃ from Cp₂ReCH₃ and CH₃OH was reported by Gould.¹³ The reaction was proposed to proceed by protonation to [Cp₂Re(CH₃)H]OCH₃ followed by reductive elimination of methane and coordination of OCH₃⁻. The reactivity of this complex has
not been previously explored. Initial interest in this compound was as a synthetic precursor to a cationic formaldehyde complex which could be generated by hydride abstraction from the methoxide ligand. Reactivity of $\text{Cp}_2\text{ReOCH}_3$ with $[\text{Ph}_3\text{C}]\text{B}(\text{Ar'})_4$ in $\text{CD}_2\text{Cl}_2$ led to many products. The only product which was identified from the mixture was $\text{Ph}_3\text{COCH}_3$, indicating that some of the methoxide complex had reacted by abstraction of $\text{OCH}_3^-$ rather than hydride abstraction. The formaldehyde complex has been formed by an alternate route and is a stable complex under the reaction conditions (see Chapter 3).

Reaction of $[\text{H(Et}_2\text{O})_2]\text{B}(\text{Ar'})_4$ with $\text{Cp}_2\text{ReOCH}_3$ in $\text{CD}_2\text{Cl}_2$ led to clean formation of $\text{CH}_3\text{OH}$ and $[\text{Cp}_2\text{Re(}\text{CD}_2\text{Cl})\text{Cl}]\text{B}(\text{Ar'})_4$. Similarly, $[\text{Me}_3\text{O}]\text{BF}_4$ was observed to react with $\text{Cp}_2\text{ReOCH}_3$ in $\text{CD}_3\text{CN}$ to cleanly form $(\text{CH}_3)_2\text{O}$ and $\text{Cp}_2\text{ReNCCD}_3^+$. 

![Scheme 2.8](image_url)

These reactions were closely monitored by low temperature $^1\text{H}$ NMR spectroscopy and only starting materials were observed at the lowest temperatures. As the temperature was raised to 0 °C resonances for the final products were observed. There was no evidence of
intermediate methoxide-hydride or methoxide-methyl complexes or coordination of methanol or dimethyl ether for these complexes. This indicates that electrophilic attack by Me⁺ and H⁺ most likely occurs directly at the lone pair of the oxygen rather than at the metal. Similar reactivity has been observed by Bryndza and coworkers for the reaction of MeI with (dppe)Pt(CH₃)(OCH₃).⁵⁹ Apparently coordinated alcohols or ethers are unstable in the presence of coordinating solvents such as CD₂Cl₂ and CD₃CN.

Conclusions

This chapter details the reactivity of electron rich Cp₂ReX (X = H, alkyl, Cl, OCH₃) complexes with electrophilic reagents (H⁺, Me⁺, Ph₃C⁺, Cp₂Fe⁺). [Ph₃C]B(Ar')₄ reacts with Cp₂ReCH₃ and Cp₂ReCH₂CH₃ to abstract an α-hydride from the alkyl ligand to generate carbene complexes, [Cp₂Re=CH₂]B(Ar')₄ (1) and [Cp₂Re=CH(CH₃)]B(Ar')₄ (3). The thermal stability of these complexes is dependent upon the anion and a more reactive anion such as BF₄⁻ leads to unstable carbene complexes either by reaction of Cp₂Re(alkyl) with [Ph₃C]BF₄ or by addition of BF₄⁻ salts to solutions of 1 and 3. Both complexes 1 and 3 decompose to [Cp₂Re(C₂H₄)]⁺ and [Cp₂Re(NCCD₃)]⁺ in acetonitrile upon addition of BF₄⁻ salts or thermolysis of solutions. The hydride abstraction from Cp₂Re(alkyl) is proposed to occur via an initial oxidation of the neutral complex followed by hydrogen atom transfer based on reactivity with an oxidizing reagent, [Cp₂Fe]B(Ar')₄.

Addition of [H(∑₂O)₂]B(Ar')₄ to Cp₂ReCH₃ in CH₂Cl₂ forms a thermally unstable alkyl hydride complex, [Cp₂Re(CH₃)H]B(Ar')₄. Methane elimination occurs at 0 °C followed by reaction with the solvent to form a stable chloromethyl chloride complex, [Cp₂Re(CH₂Cl)Cl]B(Ar')₄. Addition of [Me₃O]BF₄ to Cp₂ReR (R = CH₃, CH₂CH₃, CH₂SiMe₃) in acetonitrile forms stable bis-alkyl complexes, [Cp₂Re(CH₃)R]BF₄.

Cp\textsubscript{2}ReH reacts with acids such as [H(Et\textsubscript{2}O)\textsubscript{2}]B(Ar')\textsubscript{4} and HOTf to form the stable dihydride cation, [Cp\textsubscript{2}ReH\textsubscript{2}]\textsuperscript{+}. [Cp\textsubscript{2}ReH\textsubscript{2}]\textsuperscript{+} is formed by reaction of Cp\textsubscript{2}ReH with oxidizing reagents, [Ph\textsubscript{3}C]B(Ar')\textsubscript{4}, [Cp\textsubscript{2}Fe]B(Ar')\textsubscript{4} and [Me\textsubscript{3}O]BF\textsubscript{4}.

**Experimental Section**

**General Considerations.** General experimental techniques have been described in Chapter 1. Several of the starting materials (Cp\textsubscript{2}ReH and Cp\textsubscript{2}Re-alkyl) react rapidly with oxygen and rigorous Schlenk, glove-box, and vac-line procedures were followed. Cp\textsubscript{2}ReH\textsuperscript{12}, Cp\textsubscript{2}ReCH\textsubscript{3}\textsuperscript{12}, Cp\textsubscript{2}ReOCH\textsubscript{3}\textsuperscript{13}, Cp\textsubscript{2}ReCH\textsubscript{2}CH\textsubscript{3}\textsuperscript{12}, Cp\textsubscript{2}ReCH\textsubscript{2}SiMe\textsubscript{3}\textsuperscript{12}, Cp\textsubscript{2}ReCH\textsubscript{2}CH=CH\textsubscript{2}\textsuperscript{12}, [Cp\textsubscript{2}Re]\textsubscript{2}\textsuperscript{58}, Me\textsubscript{2}SiCp\textsubscript{2}ReCH\textsubscript{3}\textsuperscript{60}, [Ph\textsubscript{3}C]BPh\textsubscript{4}\textsuperscript{61}, [Ph\textsubscript{3}C]B(Ar')\textsubscript{4}\textsuperscript{22}, NaB(Ar')\textsubscript{4}\textsuperscript{21} and [H(Et\textsubscript{2}O)\textsubscript{2}]B(Ar')\textsubscript{4}\textsuperscript{21} were all prepared by reported procedures. All other reagents were purchased from Aldrich. The \textsuperscript{1}H and \textsuperscript{13}C resonances for B(Ar')\textsubscript{4} are identical with those reported for complex 1-B(Ar')\textsubscript{4} and have been omitted from subsequent complexes.

**Synthesis of Complexes.**

[(\textsuperscript{5}C\textsubscript{5}H\textsubscript{5})\textsubscript{2}Re=CH\textsubscript{2}]B(Ar')\textsubscript{4} (1-B(Ar')\textsubscript{4}). A 20 mL round bottom flask was charged with (\textsuperscript{5}C\textsubscript{5}H\textsubscript{5})\textsubscript{2}ReCH\textsubscript{3} (250 mg, 0.754 mmol), [Ph\textsubscript{3}C]B(Ar')\textsubscript{4} (835 mg, 0.754 mmol) and attached to a swivel frit apparatus. The swivel frit was attached to a vacuum line and 15 mL of CH\textsubscript{2}Cl\textsubscript{2} was vacuum transferred at -78 °C. The reddish solution was warmed to room temperature and stirred for a few minutes. The solvent volume was reduced in vacuo to 4 mL. Pentane (10 - 15 mL) was vacuum transferred to the solution to give a pink solid with a yellow solution. The solid was collected on the frit and rinsed by condensation of the filtrate solvent which was repeated 5 times. The
pink, air stable solid was collected in 97% yield (870 mg). $^1$H NMR (CD$_2$Cl$_2$): 13.19 (s, 2 H, Re-CH$_2$); 7.74 (m, 8 H, o-B(Ar')$_4$); 7.58 (m, 4 H, p-B(Ar')$_4$); 5.60 (s, 10 H, $\eta^5$-C$_5$H$_5$). $^{13}$C NMR (CD$_2$Cl$_2$): 247.7 (t, J$_{CH}$ = 152 Hz, Re-CH$_2$); 162.2 (quart, $^1$J$_{CB}$ = 49.8 Hz, B(Ar')$_4$ ipso); 135.2 (d, $^1$J$_{CH}$ = 158.9 Hz, o-B(Ar')$_4$); 129.3 (quart, $^2$J$_{CF}$ = 30.1 Hz, m -B(Ar')$_4$); 125.0 (quart, $^1$J$_{CF}$ = 272.3 Hz, B(Ar')$_4$ CF$_3$); 117.9 (d of t, $^1$J$_{CH}$ = 165.9 Hz, $^3$J$_{CF}$ = 3.6 Hz, p-B(Ar')$_4$); 86.4 (d of quint, $^1$J$_{CH}$ = 188 Hz, J$_{CH}$ = 7 Hz, $\eta^5$-C$_5$H$_5$). Anal. Calcd for C$_{43}$H$_{24}$BF$_{24}$Re: C, 43.27; H, 2.03. Found: C, 43.19; H, 2.06.

$[(\eta^5$-C$_5$H$_5$)$_2$Re=CH$_2$]BPh$_4$ (1-BPh$_4$). A 20 mL round bottom flask was charged with ($\eta^5$-C$_5$H$_5$)$_2$ReCH$_3$ (76.5 mg, 0.231 mmol), [Ph$_3$C]BPh$_4$ (130 mg, 0.231 mmol) and attached to a swivel frit apparatus. The swivel frit was attached to a vacuum line and 5 mL of CH$_2$Cl$_2$ was vacuum transferred at -78 °C. The reddish solution was warmed to room temperature and stirred for a few minutes. Pentane (2 mL) was vacuum transferred to the solution to give a pink solid with a yellow solution. The solid was collected on the frit and rinsed by condensation of the filtrate solvent which was repeated 5 times. The pink solid was collected in 80% yield (120 mg). $^1$H NMR (CD$_2$Cl$_2$): 12.95 (s, 2 H, Re-CH$_2$); 7.4 - 6.8 (m, BPh$_4$); 5.29 (s, 10 H, $\eta^5$-C$_5$H$_5$).

$[(\eta^5$-C$_5$H$_4$-Si(CH$_3$)$_2$-$\eta^5$-C$_5$H$_4$)Re=CH$_2$]B(Ar')$_4$ (2). A 20 mL round bottom flask was charged with ($\eta^5$-C$_5$H$_4$-Si(CH$_3$)$_2$-$\eta^5$-C$_5$H$_4$)ReCH$_3$ (75 mg, 0.193 mmol), [Ph$_3$C]B(Ar')$_4$ (214 mg, 0.193 mmol) and attached to a swivel frit apparatus. The swivel frit was attached to a vacuum line and 10 mL of CH$_2$Cl$_2$ was vacuum transferred at -78 °C. The orange solution was warmed to room temperature and stirred for a few minutes. The solvent volume was reduced in vacuo to 2 mL. Pentane (10 - 15 mL) was vacuum transferred to the solution to give an orange solid with a yellow
solution. The solid was collected on the frit and rinsed by condensation of the filtrate solvent which was repeated 5 times. The pale orange solid was collected in 77% yield (185 mg). 

$^1$H NMR (CD$_2$Cl$_2$): 12.76 (s, 2 H, Re=CH$_2$); 6.02 (t, 4H, J$_{HH}$ = 1.8 Hz, $\eta^5$-C$_5$H$_4$); 5.87 (t, 4 H, J$_{HH}$ = 1.8 Hz, $\eta^5$-C$_5$H$_4$); 0.34 (s, 6 H, Si(CH$_3$)$_2$). $^{13}$C NMR (CD$_2$Cl$_2$): 246.1 (t, J$_{CH}$ = 150 Hz, Re=CH$_2$); 101.4 (d of quart, J$_{CH}$ = 186 Hz, J$_{CH}$ = 6 Hz, $\eta^5$-C$_5$H$_4$); 86.6 (d of quart, J$_{CH}$ = 189 Hz, J$_{CH}$ = 7 Hz, $\eta^5$-C$_5$H$_4$); -6.5 (quart, J$_{CH}$ = 123 Hz, Si(CH$_3$)$_2$). Anal. Calcld for C$_{45}$H$_{28}$BF$_{24}$ReSi: C, 43.25; H, 2.26. Found: C, 42.85; H, 2.25.

[($\eta^5$-C$_5$H$_5$)$_2$Re=CH(CH$_3$)]B(Ar')$_4$ (3). A 20 mL round bottom flask was charged with ($\eta^5$-C$_5$H$_5$)$_2$ReCH$_2$CH$_3$ (50 mg, 0.145 mmol), [Ph$_3$C]B(Ar')$_4$ (160 mg, 0.145 mmol) and attached to a swivel frit apparatus. The swivel frit was attached to a vacuum line and 10 mL of CH$_2$Cl$_2$ was vacuum transferred at -78 °C. The orange solution was warmed to room temperature and stirred for a few minutes. The solvent volume was reduced in vacuo to 2 mL. Pentane (10 - 15 mL) was vacuum transferred to the solution to give a orange solid with a yellow solution. The solid was collected on the frit and rinsed by condensation of the filtrate solvent which was repeated 5 times. The pale orange solid was collected in 94% yield (164 mg). 

$^1$H NMR (CD$_2$Cl$_2$): 13.82 (quart, 1 H, J$_{HH}$ = 7.9 Hz, Re=CH(CH$_3$)); 5.56 (s, 5 H, $\eta^5$-C$_5$H$_5$); 5.51 (s, 5 H, $\eta^5$-C$_5$H$_5$); 1.53 (d, 3 H, J$_{HH}$ = 8.1 Hz, Re=CH(CH$_3$)). $^{13}$C NMR (CD$_2$Cl$_2$): 266.0 (d, J$_{CH}$ = 143 Hz, Re=CH(CH$_3$)); 86.0 (d of quint, J$_{CH}$ = 187 Hz, J$_{CH}$ = 6 Hz, $\eta^5$-C$_5$H$_5$); 85.6 (d of quint, J$_{CH}$ = 187 Hz, J$_{CH}$ = 6 Hz, $\eta^5$-C$_5$H$_5$); 45.0 (quart, J$_{CH}$ = 128 Hz, Re=CH(CH$_3$)). Anal. Calcld for C$_{44}$H$_{26}$BF$_{24}$Re: C, 43.76; H, 2.17. Found: C, 43.70; H, 2.16.
[(η⁵-C₅H₅)₂Re(η²-H₂C=CHCHCPh₃)]I (4). A 20 mL round bottom flask was charged with (η⁵-C₅H₅)₂Re(CH₂CH=CH₂) (74.5 mg, 0.21 mmol), [Ph₃C]B(Ar')₄ (231 mg, 0.21 mmol) and attached to a swivel frit apparatus. The swivel frit was attached to a vacuum line and 10 mL of CH₂Cl₂ was vacuum transferred at -78 °C. The brown solution was warmed to room temperature and stirred for a few minutes. The solvent volume was reduced in vacuo to 2 mL. Pentane (10 - 15 mL) was vacuum transferred to give a brown oil which separated from the solvent. Removing the solvent in vacuo left a brown powder. Attempts to recrystallize from CHCl₃/pentane also failed. The solid was dissolved in 10 mL of acetone in a small glass vessel with an 8 mm Kontes valve. Excess NaI (approx. 5 equivalents) was added to the solution which was allowed to stir for 10 days. A yellow precipitate formed from the brown solution and was separated by filtration and washed with a small portion of Et₂O. ¹H NMR (CD₂Cl₂): 7.4 to 7.2 (m, CPh₃); 5.43 (s, η⁵-C₅H₅); 5.11 (s, η⁵-C₅H₅); 3.77 (d of d, J₉₈ = 13.72 and 1 Hz, η²-CH₂=CHCH₂CPh₃); 2.72 (m, η²-CH₂=CHCH₂CPh₃); 2.34 (d of d, J₉₉ = 13.65 and 9.08 Hz, η²-CH₂=CHCH₂CPh₃); 2.01 (d of d, J₉₈ = 9.42 and 5.05 Hz, η²-CH₂=CHCH₂CPh₃); 1.72 (d of d, J₉₉ = 13.22 and 5.06 Hz, η²-CH₂=CHCH₂CPh₃).

[(η⁵-C₅H₅)₂Fe]B(Ar')₄ Ferrocene (0.625 g, 3.36 mmol) was placed in a small beaker followed by 12.5 mL of H₂SO₄. The dark blue solution was stirred for two hours then added to 185 mL of H₂O and filtered. The solution was sparged with Ar in a large Schlenk flask and NaB(Ar')₄ (1g, 1.13 mmol) was added. After stirring for 24 hours a light blue precipitate forms. The solid is collected by filtration, rinsed with H₂O, and dried overnight under dynamic vacuum. Yield 0.892 g (76 %). ¹H NMR (acetone-d₆): 28 (s, 10H, Cp₂Fe⁺); 7.8 (s, 4H, p-B(Ar')₄); 7.7 (s, 8H, o-B(Ar')₄).
[(η⁵-C₅H₅)₂Re(CH₂Cl)Cl]B(Ar')₄ (5). A small glass vessel with an 8 mm Kontes valve was charged with (η⁵-C₅H₅)₂ReCH₃ (50 mg, 0.151 mmol) and [H(Et₂O)₂]B(Ar')₄ (153 mg, 0.151 mmol). Methylene chloride (10 mL) is vacuum transferred to the flask and the solution is stirred at room temperature for 30 minutes. The red solution is reduced in volume to 3 mL and pentane (10 mL) is vacuum transferred to the flask. An oil separates from the solvent, but after stirring for 30 minutes at 0 °C a precipitate forms. The solvent is decanted away and the peach colored solid is dried under dynamic vacuum. Yield 180 mg (94%). ¹H NMR (CD₂Cl₂): 6.02 (s, 10 H, η⁵-C₅H₅); 4.40 (s, 2 H, Re-CH₂Cl). ¹³C NMR (CD₂Cl₂): 98.6 (d of quint, JCH = 191.4 Hz, JCH = 6.3 Hz, η⁵-C₅H₅); 11.5 (t, JCH = 163.1 Hz, Re-CH₂Cl). Anal. Calcd for C₄₃H₂₄BCl₂F₂₄Re: C, 40.84; H, 1.91. Found: C, 40.65; H, 2.02.

(η⁵-C₅H₅)₂ReCl A small glass vessel with an 8 mm Kontes valve was charged with (η⁵-C₅H₅)₂ReCH₃ (176 mg, 0.53 mmol). Diethyl ether (10 mL) was vacuum transferred to the flask and at -78 °C the solution was exposed to an atmosphere of anhydrous HCl. The orange solution slowly precipitated a white solid and was stirred until the solution was colorless. The solvent was removed in vacuo, while cold, and 5 mL of CH₂Cl₂ was added by vacuum transfer at -78 °C. The solution was warmed to room temperature and stirred for 30 minutes. The solution becomes dark orange and a brown solid precipitates. The solvent was removed in vacuo and the orange/brown solid was collected in 91% yield (170 mg). ¹H NMR (CD₂Cl₂): 4.54 (s, η⁵-C₅H₅). Anal. Calcd for C₁₀H₁₀ClRe: C, 34.14; H, 2.86. Found: C, 33.71; H, 3.06.

[(η⁵-C₅H₅)₂Re(CH₃)₂]BF₄ (6). A NMR tube was charged with (η⁵-C₅H₅)₂ReCH₃ (4 mg, 0.012 mmol) and [Me₃O]BF₄ (1.8 mg, 0.012 mmol).
Acetonitrile-$d_3$ (0.5 mL) was vacuum transferred to the tube and flame sealed. $^1$H NMR (CD$_3$CN): 5.38 (s, 10 H, $\eta^5$-C$_5$H$_5$); 0.97 (s, 6 H, Re-CH$_3$).

$$[(\eta^5$-C$_5$H$_5$)$_2$Re(CH$_3$)CH$_2$CH$_3)]BF_4$$ (7). A NMR tube was charged with ($\eta^5$-C$_5$H$_5$)$_2$ReCH$_2$CH$_3$ (2 mg, 0.006 mmol) and [Me$_3$O]BF$_4$ (1 mg 0.007 mg). Acetonitrile-$d_3$ (0.5 mL) was vacuum transferred to the tube and flame sealed. $^1$H NMR (CD$_3$CN): 5.37 (s, 10 H, $\eta^5$-C$_5$H$_5$); 1.69 to 1.46 (m, 5 H, Re-CH$_2$CH$_3$); 0.81 (s, 3 H, Re-CH$_3$).

$$[(\eta^5$-C$_5$H$_5$)$_2$Re(CH$_3$)(CH$_2$Si(CH$_3$)$_3$)]BF$_4$$ (8). A small glass vessel with an 8 mm Kontes valve was charged with ($\eta^5$-C$_5$H$_5$)$_2$Re(CH$_2$Si(CH$_3$)$_3$) (50 mg, 0.124 mmol) and [Me$_3$O]BF$_4$ (18 mg, 0.124 mmol). Acetonitrile (10 mL) was vacuum transferred to the flask and the solution was stirred for 1 hour at room temperature. The solvent was removed in vacuo to give an orange/brown solid. Methylene chloride (5 mL) was vacuum transferred to the flask followed by 5 mL of pentane and an orange precipitate formed. $^1$H NMR (CD$_2$Cl$_2$): 5.43 (s, 10 H, $\eta^5$-C$_5$H$_5$); 0.98 (s, 3 H, Re-CH$_3$); 0.31 (s, 2 H, Re-CH$_2$-); 0.06 (s, 9 H, -Si(CH$_3$)$_3$). $^{13}$C NMR (CD$_2$Cl$_2$): 91.5 (d of quart, $^1$J$_{CH}$ = 188 Hz, J$_{CH}$ = 6 Hz, $\eta^5$-C$_5$H$_5$); 2 (quart, -Si(CH$_3$)$_3$); -21.9 (quart, J$_{CH}$ = 136 Hz, Re-CH$_3$); -23.1 (t, J$_{CH}$ = 119 Hz, Re-CH$_2$-).

$$[(\eta^5$-C$_5$H$_5$)$_2$ReH$_2$]B(Ar')$_4$$ A small glass vessel with an 8 mm Kontes valve was charged with ($\eta^5$-C$_5$H$_5$)$_2$ReH (100 mg, 0.315 mmol) and [H(Et$_2$O)$_2$]B(Ar')$_4$ (319 mg, 0.315 mmol). Diethyl ether (10 mL) was vacuum transferred to the vessel and the colorless solution was stirred at room temperature for 30 minutes. The volume of solvent was reduced to 1 mL and pentane (4 mL) was vacuum transferred to the vessel to give a white precipitate. The solvent was removed by cannula and the solid was dried under
vacuum. The white solid was collected in 95% yield (352 mg). \(^1\)H NMR (CD\(_2\)Cl\(_2\)): 5.34 (s, 10 H, \(\eta^5\)-C\(_5\)H\(_5\)); -13.80 (s, 2 H, ReH\(_2\)).

\(\left[\left(\eta^5\text{-C}_5\text{H}_5\right)_2\text{ReH}_2\right]\text{OTf}\) A small glass vessel with an 8 mm Kontes valve was charged with \(\left(\eta^5\text{-C}_5\text{H}_5\right)_2\text{ReH}\) (50 mg, 0.157 mmol). Diethyl ether (5 mL) was vacuum transferred to the vessel and the solution was warmed to 0 °C. Under an argon flow, HOTf (14 \(\mu\)L, 0.157 mmol) was added via a gas tight syringe. A pale purple solid precipitated and the solvent was removed by cannula. The solid was rinsed with 3 x 5 mL portions of Et\(_2\)O and dried under vacuum. The solid was collected in 72% yield (53 mg). \(^1\)H NMR (CD\(_2\)Cl\(_2\)): 5.48 (s, 10 H, \(\eta^5\)-C\(_5\)H\(_5\)); -13.98 (s, 2 H, ReH\(_2\)).

\(\left[\left(\eta^5\text{-C}_5\text{H}_5\right)_2\text{Re(H)Cl}\right]\text{B(Ar)}^\prime\text{4}\) A small glass vessel with an 8 mm Kontes valve was charged with \(\left(\eta^5\text{-C}_5\text{H}_5\right)_2\text{ReCl}\) (17.4 mg, 0.049 mmol) and \([\text{H(Et}_2\text{O)}_2]\text{B(Ar)}^\prime\text{4}\) (50 mg, 0.049 mmol). Methylene chloride (10 mL) was vacuum transferred to the flask and the solution was stirred for 30 minutes. The solvent was removed in vacuo to give a 54 mg (91 %) of brown powder. \(^1\)H NMR (CD\(_2\)Cl\(_2\)): 5.85 (s, 10 H, \(\eta^5\)-C\(_5\)H\(_5\)); -11.84 (s, 1 H, Re-H).

\([\text{TI}]\text{B(Ar'}^\prime\text{4)}\) A small glass vessel with an 8 mm Kontes valve was charged with \([\text{H(Et}_2\text{O)}_2]\text{B(Ar'}^\prime\text{4)}\) (225mg, 0.222 mmol). Diethyl ether (5 mL) was vacuum transferred to the vessel and kept at -78 °C. A degassed solution of TlOEt (16 \(\mu\)L, 0.222 mmol) in 5 mL of diethyl ether was slowly cannula transferred to the \([\text{H(Et}_2\text{O)}_2]\text{B(Ar'}^\prime\text{4)}\) solution. The solution was stirred vigorously and slowly warmed to room temperature. The solvent volume was reduced to 3 mL and pentane (5 mL) was vacuum transferred to the flask to precipitate a white solid. The solvent was decanted away and the solid was rinsed with an additional 3 mL of pentane. The solid was dried under dynamic vacuum
for 2 hours. The white solid was collected in 89% yield (210 mg). $^1$H NMR (CD$_3$CN):

7.70 (br, B(Ar')$_4$).
Notes to Chapter 2.


(19) (TMS)$_2$NLi has been observed to deprotonate [Cp$_2$Re(CH$_3$)$_2$]PF$_6$.¹³


(30) The formation of [Cp2Re(NCCD3)]+ results from [Cp2Re(CH3)H]+ which was observed by low temperature 1H NMR experiments; Gould G. L.; unpublished observations.

(31) Gould G. L.; unpublished observations.


The electrochemistry of Cp₂ReCH₃ has been observed to undergo a reversible 1e⁻ oxidation in CH₃CN which presumably forms [Cp₂ReCH₃]⁺. Gould, G. L., Unpublished results.

(43) Connelly, N. G.; Geiger, W. E. Chem. Rev. 1996, 96, 877-910. Several preparations of Cp₂Fe⁺ are reported in the appendix of this paper.


(48) Reaction of Cp₂ReCH₂Ph with [Ph₃C]BF₄ appears to form PhCH₂CPh₃, with no evidence of the benzylidene complex. Gould, G. L., Unpublished observations.


(60)  See chapter 4 for synthesis and characterization.

CHAPTER 3

REACTIVITY OF A CATIONIC METHYLENE COMPLEX OF RHENOCENE

Introduction

Fischer and Maasbol first reported the direct synthesis of a stable carbene complex in 1964 by reaction of an alkyl lithium reagent with W(CO)₆ followed by protonation and addition of diazomethane to give (CO)₅W=CR(OMe).¹ "Fischer-type" carbene complexes are electrophilic and are typically stabilized by π donation from a heteroatom substituent. The neutral carbene ligand donates electron density to the metal center and backdonation from a filled metal π orbital to the carbene forms the double bond. Schrock isolated the first alkyldiene complex in 1975 by the addition of two equivalents of neopentyl lithium to Ta(neopentyl)₃Cl₂ to form (BU₄CH₂)₃Ta=CHBu and neopentane.² Unlike the Fischer carbenes, the alkyldiene ligands formally have a 2⁻ charge and are typically formed on high valent, early transition metals. Typically the Schrock alkyldienes contain only alkyl or H substituents and are nucleophilic.

Schrock alkyldienes and Fischer carbenes represent two extremes of carbene ligands while several other complexes do not strictly fall into these categories. The cationic charge of the unstable [Cp₂W(=CH₂)H]⁺ results in electrophilic reactivity such as formation of phosphine-ylide complexes.³ Fewer complexes have been reported to have amphiphilic reactivity. Roper and coworkers have reported that Ru(=CF₂)(PPh₃)(CO)₂ reacts with both MeNH₂ and HCl, although, reaction with the latter may occur at the metal center rather than the carbene carbon.⁴ Casey and coworkers have reported the reaction of CpRe(=CHR)(CO)₂ with HCl to form a alkyl chloride complex as well as deprotonation of the carbene with KOCHMe₂ to form a vinyl complex.⁵
The reactivity of carbene complexes with acids and bases is quite common, but few complexes are shown to have both electrophilic and nucleophilic character.

Despite the rapid development of carbene chemistry in the last 33 years,\textsuperscript{6-8} few examples have been completely characterized due to their reactivity. The methylene ligand, \( L_nM=\text{CH}_2 \), is the simplest type of carbene ligand and the study of methylene ligands still remains quite rare. The first methylene complex was synthesized by deprotonation of \([\text{Cp}_2\text{TaMe}_2]^+\) to give \( \text{Cp}_2\text{TaCH}_3(=\text{CH}_2) \).\textsuperscript{9} This reaction was reported by Schrock in 1975 and the number of isolable methylene complexes has grown slowly since this time. Several routes have been observed to produce methylene complexes. In addition to proton abstraction from a cationic methyl group, a common route is hydride abstraction from a methyl group using \([\text{Ph}_3\text{C}]^+\). Gladysz and coworkers have successfully abstracted an \( \alpha \)-hydride from \( \text{Cp}^*\text{Re(NO)(PPh}_3)(\text{CH}_3) \) using \([\text{Ph}_3\text{C}]^+\) to give a stable methylene complex which has been structurally characterized.\textsuperscript{10} Despite the usefulness of hydride abstraction by \([\text{Ph}_3\text{C}]^+\), several of the methylene complexes generated could only be characterized by spectroscopic methods or proposed as intermediates based on the appearance of bimolecular decomposition products such as \( L_nM(n^2-\text{C}_2\text{H}_4) \). A number of unstable iron methylene complexes of the type \([\text{CpFe}(=\text{CH}_2)L_2]^+\) (\( L = \text{PR}_3 \) or CO) have been reported by the addition of a Lewis acid to a \( \text{CpFe(CH}_2\text{OR})L_2 \) precursor.\textsuperscript{11} Recently a stable complex was isolated in this series, \([\text{Cp}^*\text{Fe(dppe)}(=\text{CH}_2)]\text{BF}_4 \); apparently the bulkier \( \text{Cp}^* \) ligand and the more basic ligand set increase the stability of this complex.\textsuperscript{12} Roper and coworkers have utilized diazomethane as a methylene transfer reagent to several coordinatively unsaturated Ru, Os and Ir complexes.\textsuperscript{13} Iridium methylene complexes are rare and have been only reported by the Bergman, Roper, and Fryzuk groups. Bergman has reported that the photolysis of \( \text{Cp}^*\text{Ir(PMe}_3)(2-\text{oxametallacyclobutane}) \)\textsuperscript{14} generates \( \text{Cp}^*\text{Ir(PMe}_3)(=\text{CH}_2) \) and eliminates acetone (eq 3.1).\textsuperscript{15} The methylene complex is unstable in solution but has been
characterized by $^1$H and $^{13}$C NMR spectroscopy and a number of isolable derivatives have been formed by reaction with acidic compounds.

\[
\text{Me}_3\text{P} \quad \xrightarrow{\text{hv}/-60 \, ^\circ\text{C}} \quad \text{Me}_3\text{P} \quad -\text{(CH}_3\text{)}\text{CO}
\]

Fryzuk has reported that photolysis of $[\text{N(SiMe}_2\text{CH}_2\text{PPPh}_3\text{)_2}](\text{CH}_3)(\text{CH}_2\text{CMe}_3)$ eliminates neopentane to form the stable, 16 electron $[\text{N(SiMe}_2\text{CH}_2\text{PPPh}_3\text{)_2}]\text{Ir(CH}_2\text{)}$ (eq 3.2).$^{16,17}$

Ylide complexes can be formed by the addition of PR$_3$, NR$_3$ or SR$_2$ compounds to electrophilic carbene complexes. Often the nucleophile can help stabilize carbene complexes which would otherwise be too reactive to isolate or characterize.$^{18}$ The ylide complexes are often observed to be in equilibrium with the free carbene complex. The extent of the equilibrium depends upon the metal complex as well as the nucleophile, therefore, more basic trialkyl phosphines are likely to form stronger ylide complexes than triphenylphosphine. This equilibrium can be useful in allowing an ylide complex to react as a free carbene. CpFeL$_2$(CH$_2$SMe)$_2$ has been shown to undergo cyclopropagation reactions by providing a masked form of the unstable CpFeL$_2$(=CH$_2$)$_2$ complex.$^{19}$ We
have found that [Cp₂Re=CH₂]B(Ar⁺)₄ (1) reacts with nucleophiles to provide ylide complexes.

Results and Discussion

Reaction of [Cp₂Re=CH₂]B(Ar⁺)₄ (1) with Nucleophiles. Addition of one equivalent of PPh₃ to a solution of 1 in methylene chloride results in an immediate color change from pink to pale orange. A crystalline solid is precipitated in 90% yield by addition of pentane. ¹H, ³¹P{aromatic ¹H}, and ¹³C NMR data are consistent with the formation of the expected phosphine–ylide complex, [Cp₂Re(CH₂PPh₃)]B(Ar⁺)₄ (9) (eq 3.3).

The ¹H and ¹³C NMR resonances of the methylene ligand have shifted considerably to higher field at 2.58 and −32.7 ppm respectively. The ¹H NMR spectrum of the methylene resonance appears as a doublet due to ³¹P coupling of 10.8 Hz. This is confirmed by the ³¹P NMR spectrum which has been decoupled in the aromatic proton region to give a triplet due to coupling of the two equivalent methylene protons. The methylene resonance in the ¹³C NMR spectrum appears as a doublet of triplets due to ³¹P and ¹H coupling (J_{CP} = 25.6 Hz, J_{CH} = 26.2 Hz).

Addition of three equivalents of pyridine (py) to 1 in CD₂Cl₂ resulted in the formation of a pyridine-ylide complex, [Cp₂Re(CH₂NC₅H₅)]B(Ar⁺)₄ (10) (eq 3.4).
The $^1$H NMR resonance of the methylene protons was shifted to 5.86 ppm and a singlet for the cyclopentadienyl protons was observed at 4.51 ppm. Attempts to isolate this complex as a solid were unsuccessful. When pentane was added to a methylene chloride solution of 5, a pale peach solid precipitated. The $^1$H NMR spectrum of the solid dissolved in CD$_2$Cl$_2$ gave broadened resonances for the cyclopentadienyl and the methylene protons which were intermediate between the resonances for 5 and [Cp$_2$Re=CH$_2$]$.^+$ (1). Addition of excess pyridine to the solution resulted in conversion back to the sharp $^1$H NMR resonances of 5 as noted above.

The weaker binding of pyridine is not surprising and the use of a more donating amine such as triethylamine might provide an isolable complex. Complex 1 shows no reaction in the presence of a large excess of dimethyl sulfide. In a similar system, Gladysz and coworkers have found that isolable ylide complexes can be generated by reactions of the unstable [CpRe=CH$_2$(NO)(PPh$_3$)]$^+$ with PPh$_3$, NC$_5$H$_5$ and SMe$_2$. The dimethylsulfide is labile in solution and is easily displaced by PPh$_3$ or NC$_5$H$_5$.

Addition of tBuNC to a CH$_2$Cl$_2$ solution of 1 gives a pale orange solution from which [Cp$_2$ReCH$_2$CNtBu]B(Ar')$_4$ (11) is isolated in 86% yield (eq 3.5).
The $^1$H NMR resonance of the methylene protons was observed at 1.64 ppm and the carbon resonance was observed as a triplet ($J_{CH} = 164$ Hz) at -31.8 ppm in the $^{13}$C NMR spectrum. An IR spectrum of 6 as a Nujol mull exhibited a strong band at 1780 cm$^{-1}$ which is consistent with a ketenimine structure with a CN double bond. The IR of free alkyl isonitriles exhibit bands of approximately 2150 cm$^{-1}$ for $\nu_{CN}$.$^{12}$ This band will shift to lower wavenumbers by 60-340 cm$^{-1}$ upon coordination to a transition metal complex as a terminal ligand. Similar to CO, isonitriles can also coordinate to two transition metal centers as bridging ligands which will result in $\nu_{CN}$ bands of 1870-1580 cm$^{-1}$. The IR band for complex 6 is consistent with the latter structure indicating a significant decrease in the CN bonding order.

Roper and coworkers have briefly reported the reactivity of CNptolyl and CO with Os=CH$_2$(PPh$_3$)$_2$(NO)(Cl) to give ketenimine and ketene structures respectively.$^{13}$ We find that complex 1 does not react with CO, CH$_3$CN, PhNCO, CO$_2$, or CS$_2$.

**Reaction of 1 with Halogens.** Based on our earlier observation of the trapping of "Cp$_2$Re+" by CH$_2$Cl$_2$ to form [Cp$_2$Re(CH$_2$Cl)$_2$Cl]$^+$ (5), we sought to confirm the identity of the product via another synthetic route. We have observed that [Cp$_2$Re=CH$_2$]B(Ar)$_4$ (1) reacts readily with Cl$_2$ in CH$_2$Cl$_2$ to form complex 5. The reaction is very clean although excess Cl$_2$ must be removed immediately as it will begin to react with B(Ar')$_4$ as indicated by $^1$H NMR spectroscopy. The reaction can also be
reversed by sonicating a CD₂Cl₂ solution of 5 for two hours in the presence of Mg to form [Cp₂Re=CH₂]⁺ (1). Complex 5 does not react under similar conditions with Hg. The bromine and iodine analogs, [Cp₂Re(CH₂X)X]B(Ar')₄ (12,Br; 13,I), have been formed upon addition of Br₂ or I₂ to CH₂Cl₂ solutions of 1 (eq 3.6).

\[
\begin{align*}
\text{Cp₂Re=CH₂} & \xrightarrow{\text{X₂}} \text{Cp₂Re-CH₂X} \\
\text{1} & \text{2} \\
\end{align*}
\]

\[X = \text{Cl (5), Br (12), I (13)}\]

Complexes 5, 12 and 13 have been isolated by recrystallization from CH₂Cl₂/pentane and completely characterized by ¹H and ¹³C NMR spectroscopy and elemental analysis. The ¹H and ¹³C NMR resonances of the methylene group are observed to shift to higher field as the halogens become less electronegative (Cl>Br>I).

\[\text{N-chlorosuccinimide (NCS) reacts slowly with complex 1 at 50 °C. A new complex is generated which exhibits a ¹H NMR spectrum which closely resembles the spectrum of [Cp₂Re(CH₂Cl)Cl]⁺ (5). NCS is known to be a good chlorine atom donor reagent and the product formed is consistent with [Cp₂Re(CH₂Cl)[NC(O)CH₂CH₂C(O)]⁺.}\]

\[
\begin{align*}
\text{Cp₂Re=CH₂} & \xrightarrow{\text{NCS}} \text{Cp₂ReCH₂Cl} \\
\text{1} & \text{3} \\
\end{align*}
\]

\[\text{NCS} \]

\[\text{3.7}\]
Bergman and Klein have reported that Cp*Ir(PMe3)(=CH2) reacts with several Lewis acids including succinimide which forms Cp*Ir(PMe3)[NC(O)CH2CH2C(O)](CH3).\textsuperscript{15} Complex 1 shows no reactivity with succinimide and decomposes to several products in the presence of N-bromosuccinimide and N-iodosuccinimide. Cp*Ir(PMe3)(=CH2) was also found to oxidatively add HCl and H2, neither of which reacted with [Cp2Re=CH2]\textsuperscript{+}.

Roper and coworkers have reported that Os(=CH2)(PPh3)\textsubscript{2}(NO)(Cl) reacts with chlorine to form a chloromethyl-chloride complex, Os(CH2Cl)(PPh3)\textsubscript{2}(NO)Cl\textsubscript{2}.\textsuperscript{13} This complex undergoes further rearrangement to an ylide complex, Os(CH2PPh3)(PPh3)(NO)Cl\textsubscript{3}. It is not uncommon for neutral halomethyl complexes to react with phosphines to form cationic ylide complexes, [L\textsubscript{m}MCH2PR\textsubscript{3}]Cl

The synthesis of chloromethyl-chloride complexes have been reported by several groups. Quite often these complexes are formed as a result of oxidative addition of CH2Cl\textsubscript{2} to a coordinatively unsaturated metal complex.\textsuperscript{23-27} These reactions often proceed by the thermal or photochemical reductive elimination of ligands in CH2Cl\textsubscript{2} or by the reaction of Pt\textsuperscript{0} square planar complexes with CH2Cl\textsubscript{2}. Hubbard and coworkers have reported the stepwise addition of diazomethane to Cp*Ru(NO)Cl\textsubscript{2} (eq 3.8).\textsuperscript{28}
The chloromethyl-chloride complex has been shown to form polymethylene upon thermolysis or photolysis, while the bis(chloromethyl) complex extrudes ethylene. In both cases the dichloride complex is formed. Thermolysis of complex 7 did not result in any conversion to the known \([\text{Cp}_2\text{ReCl}_2]^+\).

**Reaction of 1 with Pyridine N-oxide: Formation of an \(\eta^2-\)**

**Formaldehyde Complex.**

Roper and coworkers reported the first synthesis of a formaldehyde complex in 1979 by reaction of Os(CO)_2(PPh_3)_2 with an aqueous formaldehyde solution.\(^{30}\) The sidebound nature of the formaldehyde ligand was confirmed by the X-ray structure of Os(\(\eta^2-\text{H}_2\text{C}=\text{O})\)(CO)_2(PPh_3)_2. Several formaldehyde complexes have been synthesized by the reaction of formaldehyde or paraformaldehyde with unsaturated complexes or complexes with labile ligands.\(^{31}\) Gladysz and coworkers developed a new route by reaction of a nucleophilic oxygen atom donor with an electrophilic methylene complex.\(^{32}\)

All mononuclear formaldehyde complexes have been observed to be side-bound, unlike aldehyde and ketone complexes which can bind \(\eta^1\) or \(\eta^2\). Gladysz and Huang have reviewed the field of formaldehyde, aldehyde and ketone complexes from work in their lab and others.\(^{33}\)

\([\text{Cp}_2\text{Re}=\text{CH}_2]\text{B}(\text{Ar}^\prime)_4\) (1) reacts cleanly with pyridine N-oxide (pyO) to form \([\text{Cp}_2\text{Re}(\eta^2-\text{CH}_2\text{O})]\text{B}(\text{Ar}^\prime)_4\) (14) in CH_2Cl_2 (eq 3.9). Complex 14 was isolated as a pale orange solid in 93% yield by crystallization from CH_2Cl_2/pentane followed by filtration.
The $^1$H NMR spectrum shows a single Cp resonance at 5.49 ppm and a resonance at 3.69 ppm for the methylene protons. The highfield $^1$C NMR resonance of the formaldehyde ligand at 46.2 ppm is consistent with an $\eta^2$-CH$_2$O structure. The IR spectra of [Cp$_2$Re=CH$_2$]B(Ar')$_4$ and [Cp$_2$Re($\eta^2$-H$_2$C=O)]B(Ar')$_4$ were compared, but a band for vCO could not be located in the expected region between 1300-1000 cm$^{-1}$ which was obscured by bands from the anion. However, the lack of a CO stretch in the IR spectrum between 1400 and 1600 cm$^{-1}$ rules out an end-bound formaldehyde ligand. An intense band for vCO was observed in the IR spectrum for Cp$_2$V($\eta^2$-H$_2$C=O) at 1160 cm$^{-1}$ and for Cp$_2$Mo($\eta^2$-H$_2$C=O) at 1155 cm$^{-1}$.$^{31a-c}$

The reactivity of complex 1 with other oxygen atom donor reagents was not successful.$^{34}$ Complex 1 slowly decomposed in the presence of a large excess of dimethyl sulfoxide and complex 1 quickly decomposed upon addition of Me$_3$NO. The reaction of Cp$_2$ReOCH$_3$ with [Ph$_3$C]B(Ar')$_4$ led to decomposition, although a resonance in the $^1$H NMR spectrum identified Ph$_3$COCH$_3$ as a minor product.$^{32}$

The formaldehyde ligand can be displaced by reaction with solvent or nucleophiles. Heating a solution of 14 in CD$_3$CN at 55 °C for several days eventually led to the formation of [Cp$_2$ReNCCD$_3$]$^+$. Complex 14 reacts similarly with CD$_2$Cl$_2$ to form [Cp$_2$Re(CD$_2$Cl)$_2$Cl]$^+$ (5) after several days at 55 °C. A solution of 14 and PPh$_3$ in CD$_2$Cl$_2$ slowly forms [Cp$_2$RePPh$_3$]$^+$ after a week at room temperature. [Cp$_2$RePPh$_3$]$^+$ has been previously prepared by thermolysis of [Cp$_2$ReH$_2$]$^+$ with PPh$_3$ at 100 °C in
DMSO. This reactivity suggests that complex 14 may be useful in the synthesis of new complexes by displacement of the relatively weak formaldehyde ligand.

Pyridine N-oxide reacts slowly over several days with the phosphine ylide complex, [Cp₂ReCH₂PPh₃]⁺, to form 14. Consistent with the above observations of the displacement of the formaldehyde ligand, complex 14 reacts with the free PPh₃ in solution and [Cp₂RePPh₃]⁺ is the final product. Although pyridine and PPh₃ are present in solution in equal amounts, there is no evidence for the formation of [Cp₂Re(py)]⁺.³⁵ [Cp₂ReCH₂CN³Bu]⁺ does not react with pyO at room temperature in CD₂Cl₂ and heating to 55 °C leads to decomposition after several days.

Preliminary investigations suggest that the formaldehyde complex can be deprotonated. Complex 14 reacts with KOH, Proton-Sponge® (1,8-bis(dimethylamino)naphthalene) or LiNHP₃⁺ which all lead to the disappearance of the starting material. A new peak is observed in the ¹H NMR spectra at 4.5 ppm which is consistent with the formation of a neutral phenolene complex. A likely product would be the neutral formyl complex, Cp₂Re(HCO), but a downfield resonance for the -CHO group has not been located in the ¹H NMR spectra. Gladysz and coworkers have reported the synthesis of Cp-Re(NO)(PPh₃)(CHO) for which the ¹H NMR spectrum reveals a resonance for the formyl ligand at 16.5 ppm.²⁰ Compound 14 does not react with CS₂, H₂, or H₂O and heating in CD₂Cl₂ at 55 °C eventually leads to [Cp₂Re(CD₂Cl)Cl]⁺ (5) as the only product.

Reaction of 1 with Sulfur-Atom Donors: Formation of an η²-Thioformaldehyde Complex. The synthesis of a series of chalcogen η²-H₂C=E (E = S, Se, Te) complexes have been reported by several groups. Roper and coworkers have reported that Os(=CH₂)(PPh₃)₂(NO)(CI) reacts slowly with elemental S, Se, and Te to form chalciformaldehyde complexes.⁴ Werner and Paul have reported a similar series
by reaction of NaEH (E = S, Se, Te) with CpRh(PMe3)(CH2I)I. Reports from the groups of Gladysz and Grubbs have reported that thioformaldehyde complexes can be formed by the reaction of methylene complexes with several different sulfur donor reagents; cyclohexene sulfide, styrene sulfide, S=PPPh3, and S8. Complex 1 reacts with excess sulfur in CD2Cl2 for 3 hours at 50 °C and leads to the clean formation of a thioformaldehyde complex. [Cp2Re(η2-C2H2S)]B(Ar')4 (15) can be more conveniently formed by reaction of 1 with excess ethylene sulfide at room temperature (eq 3.10). A bright orange/yellow solid is isolated in 89% yield by crystallization from CH2Cl2/pentane followed by filtration.

\[
\begin{align*}
\text{Re} & \quad \text{C} \quad \text{H} \\
\text{Cyclohexadienyl} + \text{B(Ar')}_4^- & \quad \text{C}_2\text{H}_4\text{S} \\
\text{1} & \quad \text{C}_2\text{H}_4\text{S} \\
\text{Re} & \quad \text{C} \quad \text{H} \\
\text{15} & \quad \text{B(Ar')}_4^- \\
\end{align*}
\]

The 1H NMR spectrum shows a cyclopentadienyl resonance at 5.47 ppm and a methylene resonance for the thioformaldehyde ligand at 3.41 ppm. The 13C NMR spectrum reveals a cyclopentadienyl resonance at 88.2 ppm and a triplet at 13.7 ppm for CH2S with JCH = 168 Hz.

The phosphonium ylide complex, [Cp2ReCH2PPPh3]+ (9), reacts rapidly with excess ethylene sulfide to form complex 15 and S=PPPh3. Addition of S=PPPh3 to complex 1 produces a 50/50 mixture of [Cp2ReCH2PPPh3]+ (9) and [Cp2Re(η2-H2C=S)]+ (15). Complex 9 is likely formed by the rapid reaction of 1 with the free PPPh3 after transfer of the sulfur atom since there is no reaction of 15 with S=PPPh3 to form 9. Similar results have been observed by Gladysz and coworkers. Also
consistent with the observations of Gladysz and coworkers, the thioformaldehyde ligand is less labile than the formaldehyde ligand. Heating complex 15 in CD$_3$CN for 2 weeks at 50 °C shows no formation of [Cp$_2$Re(NCCD$_3$)]$.^+$ The thioformaldehyde ligand is not displaced by PPh$_3$, but reacts rapidly to form [Cp$_2$ReCH$_2$PPh$_3$]$^+$ and $S$=PPh$_3$.

**Reaction of 1 with (Trimethylsilyl)diazomethane: Formation of an Olefin Complex.** The use of diazoalkane reagents to transfer carbenes to transition metal complexes to form bridging or mononuclear carbene complexes has been often explored.$^{39}$ Gladysz and Wang have recently demonstrated the utility of diazoalkane reagents for generating alkene complexes from electrophilic carbene complexes.$^{40}$

Addition of N$_2$CHSiMe$_3$ (2M in hexanes) to a methylene chloride solution of complex 1 results in color change from pink to light tan and the solution is observed to rapidly evolve N$_2$. [Cp$_2$Re(CH$_2$=CHSiMe$_3$)]B(Ar')$_4$ (16) is isolated in 69% yield by crystallization from a concentrated CH$_2$Cl$_2$ solution layered with pentane.

\[
\text{Cp}_2\text{Re=CH} + \text{N}_2\text{CHSiMe}_3 \rightarrow \text{Cp}_2\text{Re}+\text{CHSiMe}_3
\]

The $^1$H NMR spectrum exhibits two cyclopentadienyl resonances at 5.13 and 5.10 ppm indicating hindered rotation of the olefin ligand. Three doublet of doublet resonances are observed for the olefinic protons and are assigned in the experimental section.

The reactivity of diazoalkane reagents with [Cp$_2$Re=CH$_2$]B(Ar')$_4$ (1) is a potentially useful method for generating substituted alkene complexes. Currently the only
methods for generating cationic olefin complexes of rhenocene are the reaction of 
Cp₂Re(CH₂CH=CH₂) with electrophiles and the isomerization of the cationic ethylidenic 
complex to [Cp₂Re(η²-C₂H₄)]⁺ (see Chapter 2). The isolation of [Cp₂Re(η²-C₂H₄)]⁺ 
was achieved in poor yield (41% before recrystallization)⁴¹ and the reaction of 1 with 
diazomethane may provide a more convenient route to this complex. The reactivity of the 
ethylene complex has not been investigated although it is a potentially useful starting 
material for several new complexes in rhenocene chemistry.

Conclusions

The number of stable transition metal methylene complexes which have been 
completely characterized are few. The successful synthesis and isolation of 
[Cp₂Re=CH₂]B(Ar')₄ (1), as described in Chapter 2, has led to a rare opportunity to 
study the reactivity of this complex with several small molecules. In contrast to the first 
methylene complex, Cp₂TaCH₃(=CH₂), reported by Schrock over 20 years ago, 
complex 1 has an electrophilic carbene ligand. This is demonstrated by reactivity of 1 
with nucleophiles such as PPh₃ and NC₅H₅ to form ylide complexes. The coordination 
of pyridine is quite weak and dimethyl sulfide does not form an ylide complex unlike 
several other electrophilic carbene complexes. Complex 1 has similar reactivity to a 
related methylene complex, [CpRe(NO)(PPh₃)(=CH₂)]⁺, which has been studied for 
many years by Gladysz and coworkers.¹⁰,²⁰,²¹,³²,³³,³³,₃₇,₄⁰ Complex 1 reacts with Cl₂, 
Br₂, I₂ by 1,2-addition across the Re-C double bond to form halomethyl halide 
complexes. Complex 1 has also been shown to react with oxygen, sulfur and carbene 
donor reagents to form η²-formaldehyde, η²-thioformaldehyde and η²-olefin complexes. 
The reactivity of [Cp₂Re=CH₂]B(Ar')₄ (1) with various reagents has led to the isolation
and characterization of many new complexes and will remain an important synthetic precursor for new classes of bis(cyclopentadienyl)rhenium complexes.

Experimental Section

**General Considerations.** General experimental techniques have been described in Chapter 1. The synthesis of \([\text{Cp}_2\text{Re} = \text{CH}_2]\text{B(Ar')}_4\) (1) is reported in Chapter 2. The \(^1\text{H}\) and \(^{13}\text{C}\) NMR resonances for \(\text{B(Ar')}_4\) are identical with those reported for complex \(1-\text{B(Ar')}_4\) in Chapter 2 and have been omitted from subsequent complexes. Pyridine \(N\)-oxide was sublimed and stored in an inert atmosphere. SPPh\(_3\) was prepared by reported procedure.\(^{42}\) All other reagents were purchased from Aldrich and used as received.

**Synthesis of Complexes.**

\([\eta^5\text{-C}_5\text{H}_5]\text{ReCH}_2\text{PPh}_3]\text{B(Ar')}_4\) (9). A small glass vessel with an 8 mm Kontes valve was charged with \([\text{Cp}_2\text{Re} = \text{CH}_2]\text{B(Ar')}_4\) (50 mg, 0.0419 mmol) and PPh\(_3\) (11 mg, 0.0419 mmol). Dichloromethane (15 mL) was vacuum transferred to the vessel and the solution was stirred for 10 minutes. The volume of solvent was reduced to 2 mL and 10 mL of pentane was vacuum transferred to the vessel to give a pale orange precipitate. The solvent was removed by cannula and the solid was dried under dynamic vacuum. The pale orange solid was collected in 90% yield (55 mg). \(^1\text{H}\) NMR (CD\(_2\)Cl\(_2\)): 7.4 to 7.9 (m, 15 H, PPh\(_3\)); 4.16 (s, 10 H, \(\eta^5\text{-C}_5\text{H}_5\)); 2.58 (d, 2 H, J\(_{PH} = 10.8\) Hz, Re-CH\(_2\)). \(^31\text{P}\{\text{aromatic} \, ^1\text{H}\}\) NMR (CD\(_2\)Cl\(_2\)): 32.6 (t, PPh\(_3\)). \(^{13}\text{C}\) NMR (CD\(_2\)Cl\(_2\)): 134.5 (s, \(\text{p-PPh}_3\)); 134.3 (d, J\(_{CP} = 8.9\) Hz, \(\text{o-PPh}_3\)); 129.9 (d, J\(_{CP} = 163\) Hz, \(\text{m-PPh}_3\)); 123.5 (d, J\(_{CP} = 81.3\) Hz, ipso PPh\(_3\)); 73.7 ( d of quint, J\(_{CH} = 182.2\) Hz, J\(_{CH} = 6.5\) Hz, \(\eta^5\)-
C₅H₅); -32.7 (d of t, J Cp = 25.6 Hz, J CH = 26.2 Hz, Re-CH₂). Anal. Calcd for C₆₁H₃₉BF₂₄PRe: C, 50.32; H, 2.70. Found: C, 49.48; H, 2.68.

\[ [(\eta^5-C₅H₅)_2ReCH₂CN'Bu]B(\text{Ar}^\prime)_4 \] (11). A small glass vessel with an 8 mm Kontes valve was charged with \[ [(\eta^5-C₅H₅)_2Re=CH₂]B(\text{Ar}^\prime)_4 \] (60 mg, 0.0503 mmol). Dichloromethane (15mL) was vacuum transferred to the vessel. Under an argon flow, CN'Bu (6 µL, 0.0503 mmol) was added via a gas tight syringe. The solution was stirred for 10 minutes and the volume of solvent was reduced to 2 mL. Pentane (10 mL) was vacuum transferred to the vessel to give a pale orange precipitate. The solvent was removed by cannula and the solid was dried under vacuum. The pale orange solid was collected in 86% yield (55 mg). ¹H NMR (CD₂Cl₂): 5.15 (s, 10 H, \(\eta^5\)-C₅H₅); 1.64 (s, 2 H, Re-CH₂); 1.26 (s, 9 H, CN'Bu). ¹³C NMR (CD₂Cl₂): 158.5 (s, CN'Bu); 84.0 (d of quint, J CH = 188 Hz, J CH = 6.4 Hz, \(\eta^5\)-C₅H₅); 28.8 (quart, J CH = 125.9 Hz, CN'Bu); -31.8 (t, J CH = 163.8, Re-CH₂). IR (cm⁻¹, Nujol, νCN): 1780. Anal. Calcd for C₄₈H₃₃BF₂₄NRe: C, 45.16; H, 2.60; N, 1.10. Found: C, 44.82; H, 2.55; N, 1.15.

Reaction of \[ [(\eta^5-C₅H₅)_2Re(=CH₂)]B(\text{Ar}^\prime)_4 \] with pyridine A sealable NMR tube was charged with \[ [(\eta^5-C₅H₅)_2Re(=CH₂)]B(\text{Ar}^\prime)_4 \] (5 mg, 0.004 mmol). Methylene chloride-\(d_2\) (0.5 mL) was vacuum transferred to the tube. Under an argon flow excess pyridine (1 µL, 0.013 mmol) was added via a gas tight syringe. The solution was degassed by three freeze-pump-thaw cycles and the tube was sealed. ¹H NMR (CD₂Cl₂): 8.6 and 7.2 (m, free and coordinated NC₅H₅); 5.86 (br, 2 H, Re-CH₂-); 4.51 (s, 10 H, \(\eta^5\)-C₅H₅).
[(η⁵-C₅H₅)₂Re(CH₂Cl)Cl]B(Ar')₄ (5). A scalable NMR tube was charged with [(η⁵-C₅H₅)₂Re(≡CH₂)]B(Ar')₄ (5 mg, 0.004 mmol). Methylene chloride-\(d_2\) (0.5 mL) was vacuum transferred to the tube. The solution was briefly purged with chlorine gas and the color changed from bright pink to yellow. The solution was subjected to three freeze-pump-thaw cycles and the tube was sealed. \(^1\)H NMR (CD₂Cl₂): 6.02 (s, 10H, η⁵-C₅H₅); 4.40 (s, Re-CH₂Cl). \(^13\)C NMR data and elemental analysis for this complex are reported in Chapter 2.

[(η⁵-C₅H₅)₂Re(CH₂Br)Br]B(Ar')₄ (12). A small glass vessel with an 8 mm Kontes valve was charged with [(η⁵-C₅H₅)₂Re=CH₂]B(Ar')₄ (60 mg, 0.0503 mmol). Dichloromethane (10 mL) was vacuum transferred to the vessel. The solution was titrated with a Br₂/CH₂Cl₂ solution until the pink color of the carbene complex was gone. The solution was stirred for ten minutes and the volatiles were removed in vacuo. The peach colored solid was recrystallized from CH₂Cl₂ and pentane and isolated in 81% yield (55 mg). \(^1\)H NMR (CD₂Cl₂): 6.06 (s, 10 H, η⁵-C₅H₅); 4.26 (s, 2 H, Re-CH₂Br). \(^13\)C NMR (CD₂Cl₂): 98.1 (d of quint, \(J_{CH} = 191.8\) Hz, \(J_{CH} = 6.1\) Hz, η⁵-C₅H₅); -5.58 (t, \(J_{CH} = 162.4\) Hz, Re-CH₂Br). Anal. Calcd for C₄₃H₂₄Br₂F₂₄Re: C, 38.16; H, 1.79. Found: C, 37.95; H, 1.80.

[(η⁵-C₅H₅)₂Re(CH₂I)I]B(Ar'')₄ (13). A small glass vessel with an 8 mm Kontes valve was charged with [(η⁵-C₅H₅)₂Re≡CH₂]B(Ar')₄ (60 mg, 0.0503 mmol). Dichloromethane (10 mL) was vacuum transferred to the vessel. Under an argon flow I₂ (17 mg, 0.067 mmol) was added to give a deep red solution. The volatiles were removed in vacuo and the solid was recrystallized from CH₂Cl₂ and pentane. The product was isolated as a light green solid in 86% yield (63 mg). \(^1\)H NMR (CD₂Cl₂): 6.06 (s, 10 H, η⁵-C₅H₅); 3.84 (s, 2 H, Re-CH₂I). \(^13\)C NMR (CD₂Cl₂): 96.18 (d of quint, \(J_{CH} = \)}
191.4 Hz, $J_{\text{CH}} = 6.2$ Hz, $\eta^5$-C$_5$H$_5$); -44.0 (t, $J_{\text{CH}} = 158.8$ Hz, Re-CH$_2$I). Anal. Calcd for C$_{43}$H$_{24}$BF$_{24}$I$_2$: C, 35.68; H, 1.67. Found: C, 35.57; H, 1.57.

**Reaction of $[(\eta^5$-C$_5$H$_5$)$_2$Re(=CH$_2$)]B(Ar')$_4$ with N-chlorosuccinimide.** A sealable NMR tube was charged with $[(\eta^5$-C$_5$H$_5$)$_2$Re(=CH$_2$)]B(Ar')$_4$ (7 mg, 0.006 mmol) and N-chlorosuccinimide (6 mg, 0.045 mmol). Methylene chloride-$d_2$ (0.5 mL) was vacuum transferred to the tube and sealed. The pink solution was heated at 50°C for 15 hours and the color became orange. $^1$H NMR (CD$_2$Cl$_2$): 6.25 (s, 10 H, $\eta^5$-C$_5$H$_5$); 4.68 (s, 2 H, Re-CH$_2$Cl); 2.8 (s, 4 H, Re-[NC(O)CH$_2$CH$_2$C(O)]).

$[(\eta^5$-C$_5$H$_5$)$_2$Re(H$_2$C=O)]B(Ar')$_4$ (14). A 20 mL round bottom flask was charged with $[(\eta^5$-C$_5$H$_5$)$_2$Re(=CH$_2$)]B(Ar')$_4$ (105 mg, 0.088 mmol), C$_5$H$_5$NO (8 mg, 0.088 mmol) and attached to a swivel frit apparatus. The swivel frit was attached to a vacuum line and 10 mL of CH$_2$Cl$_2$ was vacuum transferred at -78°C. The orange solution was warmed to room temperature and stirred for a few minutes. The solvent volume was reduced in vacuo to 2 mL. Pentane (10 mL) was vacuum transferred to the solution to give an orange precipitate. The solid was collected on the frit and washed with the filtrate four times. The pale orange solid was collected in 93% yield (99 mg). $^1$H NMR (CD$_2$Cl$_2$): 5.49 (s, 10 H, $\eta^5$-C$_5$H$_5$); 3.69 (s, 2 H, Re(H$_2$C=O)). $^{13}$C NMR (CD$_2$Cl$_2$): 88.4 (d of quint, $J_{\text{CH}} = 189$ Hz, J$_{\text{CH}} = 6.7$ Hz, $\eta^5$-C$_5$H$_5$); 46.2 (t, J$_{\text{CH}} = 178.7$ Hz, H$_2$CO). Anal. Calcd for C$_{43}$H$_{24}$BF$_{24}$ORe: C, 42.70; H, 2.00. Found: C, 42.57; H, 1.99.

**Reaction of $[(\eta^5$-C$_5$H$_5$)$_2$Re(H$_2$C=O)]B(Ar')$_4$ with PPh$_3$** A sealable NMR tube was charged with $[(\eta^5$-C$_5$H$_5$)$_2$Re(H$_2$C=O)]B(Ar')$_4$ (4 mg, 0.003 mmol) and
PPh₃ (1 mg, 0.004 mmol). Methylene chloride-₇₂ (0.5 mL) was vacuum transferred to the tube and sealed. After a week at room temperature the starting material had been completely consumed. ¹H NMR (CD₂Cl₂): 9.65 (s, free CH₂O), 7.7 to 7.3 (m, Re-PPh₃), 4.53 (d, J₉P = 3.83 Hz, η⁴-C₅H₅). ³¹P{¹H} NMR (CD₂Cl₂): 23.1 (s, Re-PPh₃).

**Reaction of [(η⁵-C₅H₅)₂Re(=CH₂)]B(Ar')₄ with S₈**  A sealable NMR tube was charged with [(η⁵-C₅H₅)₂Re(=CH₂)]B(Ar')₄ (5 mg, 0.004 mmol) and excess sulfur. Methylene chloride-₇₂ (0.5 mL) was vacuum transferred to the tube and sealed. An initial NMR spectrum showed no reaction. After heating at 50 °C for 3 hours the color had changed from pink to orange. ¹H NMR (CD₂Cl₂): 5.47 (s, 10 H, η⁵-C₅H₅); 3.41 (s, 2 H, Re(H₂C=S)).

[(η⁵-C₅H₅)₂Re(H₂C=S)]B(Ar')₄ (15). A 20 mL round bottom flask was charged with [(η⁵-C₅H₅)₂Re=CH₂]B(Ar')₄ (80 mg, 0.067 mmol) and attached to a swivel frit apparatus. The swivel frit was attached to a vacuum line and 5 mL of CH₂Cl₂ was vacuum transferred at -78°C. The pink solution was exposed to 120 Torr of ethylene sulfide and the color began turning orange. The solution was degassed by a freeze-pump-thaw cycle and exposed again to ethylene sulfide. Pentane (10 mL) was vacuum transferred to the solution to give a bright yellow/orange precipitate. The solid was collected by filtration and washed with the filtrate twice. The solid was collected in 89% yield (82 mg). ¹H NMR (CD₂Cl₂): 5.47 (s, 10 H, η⁵-C₅H₅); 3.41 (s, 2 H, Re(H₂C=S)). ¹³C NMR (CD₂Cl₂): 88.2 (d of quint, J₉CH = 189 Hz, J₇CH = 6.4 Hz, η⁵-C₅H₅); 13.7 (t, J₇CH = 168.4 Hz, H₂CS). Anal. Calcd for C₄₃H₄₂BF₂₄ReS: C, 42.14; H, 1.97. Found: C, 42.19; H, 1.97.
\([(\eta^5-C_5H_5)_2ReCH_2CH(SiMe_3)]B(Ar')_4\) (16). A small glass vessel with an 8 mm Kontes valve was charged with \([(\eta^5-C_5H_5)_2Re=CH_2]B(Ar')_4\) (100 mg, 0.0838 mmol). Dichloromethane (10 mL) was vacuum transferred to the vessel. Under an argon flow, \(N_2CHSiMe_3\) (45 µL, 2 M, 0.090 mmol) was added via a gas tight syringe. The solution was stirred for 10 minutes and the volume of solvent was reduced to 2 mL. Pentane (10 mL) was vacuum transferred to the vessel to give a pale tan precipitate. The solvent was removed by cannula and the solid was dried under vacuum. The solid was collected in 69% yield (74 mg). \(^1H\) NMR (CD_2Cl_2): 5.13 (s, \(\eta^5-C_5H_5\)); 5.10 (s, \(\eta^5-C_5H_5\)); 2.67 (d of d, \(J_{HH} = 12.1, 3.8\) Hz, \(CH_2HE\)); 2.24 (d of d, \(J_{HH} = 15.5, 4.0\) Hz, \(CH_2HE\)); 1.73 (d of d, \(J_{HH} = 15.1, 12.1\) Hz, \(CHSiMe_3\)); 0.18 (s, \(SiMe_3\)).
Notes to Chapter 3.

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(17) [N(SiMe2CH2PPh3)2]Ir(CH2) is more conveniently prepared by reaction of [N(SiMe2CH2PPh3)2]Ir(CH3)I with 2 equivalents of KOtBu (ref 15b).


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CHAPTER 4

SYNTHESIS, STRUCTURE AND REACTIVITY OF SUBSTITUTED DERIVATIVES OF RHENOCENE

Introduction

The number of metalloocene complexes in the organometallic literature is vast, although, there are an even larger number of structural variants which may be synthesized with substituted metalloocene complexes. These complexes can have different structures or reactivity with respect to the parent complexes, depending upon the identity of the substituent as well as the degree of substitution. The two most common methods to generate substituted metalloocene complexes involve the reaction of a substituted cyclopentadienide ligand with a metal halide to generate a metalloocene complex (eq 4.1) or the in situ substitution of a metalloocene complex (eq 4.2).

\[
\begin{align*}
2 \text{R-} & \quad \text{Li}^+ \\
\text{+ MX}_2 & \quad \rightarrow \\
\text{M} & \\
\end{align*}
\]

(4.1)

\[
\begin{align*}
\text{M} & \quad \text{+ 2 } \text{nBuLi} \\
\rightarrow & \quad \rightarrow \\
\text{+ 2 RX} & \\
\end{align*}
\]

(4.2)
Other synthetic methods are available and the synthesis and properties of substituted metalloocene complexes has recently been reviewed.\textsuperscript{1}

**Synthesis of Rhenocene Complexes from Substituted Cyclopentadienide.** The substitution chemistry of rhenocene complexes has been rather limited. Cloke and coworkers have reported the synthesis of bis($\eta$-pentamethyl cyclopentadienyl)rhenium hydride ($\text{Cp}_2^*\text{ReH}$) by the co-condensation of rhenium vapor and 1,2,3,4,5-pentamethylcyclopenta-1,3-diene ($\text{Cp}^*\text{H}$) at 77 K.\textsuperscript{2} Photolysis of $\text{Cp}_2^*\text{ReH}$ leads to decamethylrhenocene ($\text{Cp}_2^*\text{Re}$) which exists as a stable monomeric radical. This provides an interesting contrast in reactivity to the parent rhenocene complexes. When $\text{Cp}_2\text{ReH}$ is photolyzed in a low temperature matrix, $\text{Cp}_2\text{Re}$ is generated which is unstable at room temperature.\textsuperscript{3} Rhenocene dimer, [($\text{Cp}_2\text{Re}$)$_2$], has been generated by conventional methods\textsuperscript{4} and is presumably the fate of the unstable $\text{Cp}_2\text{Re}$ radical. This is consistent with the ability of $\text{Cp}^*$ to stabilize complexes which are coordinatively or electronically unsaturated.

Herrmann and coworkers have used conventional synthetic methods to generate the mixed-ring complexes, $\text{Cp}^*\text{CpReH}$ and ($\eta$\textsuperscript{5-}$\text{C}_5\text{Me}_4\text{Et}$)$\text{CpReH}$ (eq 4.3).\textsuperscript{5}

\[
\text{Cp}^*\text{ReCl}_4 + 4\ \text{NaBH}_4 + 2\ \text{NaCp} \rightarrow \text{Cp}^*\text{CpReH} \quad (4.3)
\]

Consistent with the increased basicity of the $\text{Cp}^*$ ligand, $\text{Cp}^*\text{CpReH}$ does not react with $^\text{b}\text{BuLi}$ or $^\text{t}\text{BuLi}$ to generate the [($\text{Cp}^*\text{CpRe}$)$^\text{−}$]. $\text{Cp}_2\text{ReH}$, however, reacts with $^\text{b}\text{BuLi}$+$\text{PMDT}$ to generate an isolable $\text{Cp}_2\text{ReLi}$+$\text{PMDT}$ complex\textsuperscript{6} and $\text{Cp}_2\text{ReLi}$ is often generated \textit{in situ} to synthesize a number of $\text{Cp}_2\text{ReR}$ derivatives.\textsuperscript{7} It was not reported whether $\text{Cp}_2^*\text{ReH}$ could be deprotonated by strong bases, but [($\text{Cp}_2^*\text{Re}$)$^\text{−}$] has been generated by the reaction of the 17 electron radical, $\text{Cp}_2^*\text{Re}$, with metallic potassium.\textsuperscript{2a}
Conventional methods to generate $\text{Cp}_2^*\text{WX}_2$ ($X = \text{H, Cl}$) complexes have been reported by Parkin and Bercaw. The reactivity of these complexes has been extensively explored. The Heinekey group has made several attempts to develop a synthetic method for the preparation of decamethylrhenocene complexes but none were found. Use of alkali metal Cp* reagents often results in over reduction of high valent metal halide complexes, therefore the use of lower valent starting materials and milder Cp* reagents such as $\text{Me}_3\text{SnCp}^*$ or $\text{TlCp}^*$ will be more likely to produce $\text{Cp}_2^*\text{ReH}$.

**Substitution of Cyclopentadienyl Complexes.** Green and coworkers have previously reported two examples of ring substitution by reaction of $\text{Cp}_2\text{ReH}$ with $\text{nBuLi}$. Addition of a large excess of $\text{nBuLi}$ (17 equiv.) to $\text{Cp}_2\text{ReH}$ followed by excess methyl iodide led to a product which was substituted at the metal center and a cyclopentadienyl ring (eq 4.4).

Addition of 2.5 equivalents of $\text{nBuLi}$ to $\text{Cp}_2\text{ReH}$ followed by HgCl$_2$ is reported to give a disubstituted rhenocene hydride, ($\eta^5$-$\text{C}_5\text{H}_4(\text{HgCl}))_2\text{ReH}$. This appears to contrast with the results of Ephritikhine, Stucky, and Heinekey which have all reported that $\text{Cp}_2\text{ReR}$ complexes are readily prepared by the deprotonation of $\text{Cp}_2\text{ReH}$ followed by the addition of alkyl halides. Gould has reported careful studies of the metallation of $\text{Cp}_2\text{ReH}$ which suggest that deprotonation of the metal center is kinetically preferred although ring substitution is an accessible pathway.
Gladysz and coworkers have reported that reaction of rhenium hydride complexes with strong bases can lead to reaction at the cyclopentadienyl ring. They have found that addition of $^n$BuLi to ($\eta^5$-C$_5$H$_5$)Re(NO)(PPh$_3$)$_2$H generates a ring lithiated complex at low temperature which then undergoes a proton transfer from the metal hydride complex to form a metal lithio complex. Both intermediates can be trapped by addition of Me$^+$ at the appropriate temperature. Chloride and alkyl complexes do not undergo similar migrations and the final product remains lithiated at the ring (Scheme 4.1).

![Chemical structures](image)

**Scheme 4.1**

**Alkane Elimination from Metallocene Complexes.** Previous work in the Heinekey group involved the investigation of alkane elimination from rhenocene alkyl
hydride cations, \([\text{Cp}_2\text{Re(R)H}]^+\). The elimination of methane from \([\text{Cp}_2\text{Re(CH}_3\text{)H}]^+\) with a variety of anions was observed in solution at low temperatures (1/2 ca. 2 hours at 0 °C). Similar reactivity has been reported for related metallocene complexes of group 6. Green and coworkers have reported that \(\text{Cp}_2\text{W(CH}_3\text{)H}\) eliminates methane at 40 °C and the intermediate "\(\text{Cp}_2\text{W}\)" complex can then react with various hydrocarbon complexes by oxidative addition of a CH bond. Parkin and Bercaw have also investigated methane elimination from \(\text{Cp}_2^*\text{W(CH}_3\text{)H}\). Each of these metallocene systems has provided important insights in the study of alkane activation.

The intermediacy of alkane molecule coordination to transition metal complexes has been proposed in systems which oxidatively add or reductively eliminate alkanes. Bergman and coworkers first provided evidence for intermediate alkane complexes for \(\text{Cp}^*\text{Ir(PMe}_3\text{)}(\text{C}_6\text{H}_{11}\text{)}\text{H}\) and \(\text{Cp}^*\text{Rh(PMe}_3\text{)}(\text{C}_2\text{H}_5\text{)}\text{H}\). Proof for the intermediacy of an alkane complex is based upon several criteria: 1) H/D exchange between the alkyl and hydride ligands without exchange with free alkane, 2) elimination of isotopically pure alkane (d⁰ and d⁵) from a mixture of pure isotopomers, showing no intermolecular isotope exchange, and 3) an inverse isotope effect \((k_1/k_D < 0)\) which indicates that alkane elimination does not proceed via a single concerted step, but likely involves a pre-equilibrium with an alkane complex. Each of the metallocene complexes mentioned above have been proposed to undergo methane elimination through an alkane complex based on these criteria. Until recently, \([\text{Cp}_2\text{Re(CH}_3\text{)H}]^+\) was the only cationic alkyl hydride system which had been reported to result in an intermediate alkane complex upon alkane elimination. This system is also important since H/D exchange and methane elimination occur at significantly different temperatures, -78 °C and 0 °C respectively, and the thermodynamic data for each process can be measured separately.
Green and coworkers have recently reported on the synthesis, structure and reactivity of \textit{ansa}-metallocene complexes of molybdenum and tungsten.\textsuperscript{24,25} The term \textit{ansa} has been popularized by Brütting to primarily define an inter-annular bridge between cyclopentadienyl rings in metallocene complexes.\textsuperscript{26} Green has found significant reactivity differences between the \textit{ansa} complexes and the well studied parent complexes (Scheme 4.2 and 4.3).

\begin{center}
\begin{tikzpicture}
\node at (0,0) [draw] {\includegraphics[width=0.3\textwidth]{ansa1.png}};
\node at (2,0) {$\Delta, \text{C}_6\text{H}_6$};
\node at (2,-0.5) {\small $- \text{CH}_4$};
\end{tikzpicture}
\end{center}

\begin{center}
\begin{tikzpicture}
\node at (0,0) [draw] {\includegraphics[width=0.3\textwidth]{ansa2.png}};
\node at (2,0) {$\Delta, \text{C}_6\text{H}_6$};
\node at (2,-0.5) {NR};
\end{tikzpicture}
\end{center}

\textbf{Scheme 4.2}

\begin{center}
\begin{tikzpicture}
\node at (0,0) [draw] {\includegraphics[width=0.3\textwidth]{ansa3.png}};
\node at (2,0) {$h\nu, \text{C}_6\text{H}_6$};
\node at (2,-0.5) {\small $- \text{H}_2$};
\end{tikzpicture}
\end{center}

\begin{center}
\begin{tikzpicture}
\node at (0,0) [draw] {\includegraphics[width=0.3\textwidth]{ansa4.png}};
\node at (2,0) {$h\nu, \text{C}_6\text{H}_6$};
\node at (2,-0.5) {NR};
\end{tikzpicture}
\end{center}

\textbf{Scheme 4.3}
The parent tungstenocene complexes eliminate methane upon heating the methyl hydride to 40 °C and dihydrogen is eliminated by photolysis of the dihydride. Conversely the ansa-bridged complexes show no reactivity under similar conditions; Me₂CCp₂W(CH₃)H has been heated to 150 °C with no observed methane elimination. Green has proposed that the ansa-bridged complexes are more stable to reductive elimination since they are restricted to a bent metallocene structure which will be a higher energy intermediate compared to the parent complex. We were intrigued by the dramatic results obtained from these studies and set out to synthesize and study the reactivity of ansa-bridged complexes of rhenocene.

Results and Discussion

Reactivity of Substituted Cyclopentadienide Salts with ReCl₄(THF)₂. Brintzinger has pioneered the use of ansa-bridged ligands for various metal complexes.²⁷ We first attempted the synthesis of ansa-bridged complexes of rhenium following the more conventional approach of synthesizing an appropriate chelating ligand followed by reactivity with a metal halide or amide complex. This approach is readily used for the synthesis of Group 4 ansa-metallocene complexes which are widely studied for their ability to catalyze stereospecific olefin polymerization.²⁸ The synthesis of a wide variety of ansa-bridged ligands has been published by several research groups.²⁹ We decided to synthesize a simple ligand containing a single silicon dimethyl linker between the rings (eq 4.5). This ligand was previously reported by Reddy and Petersen.³⁰
Addition of Li$_2$[Me$_2$SiCp$_2$] to a THF solution of ReCl$_4$(THF)$_2$ followed by LiBH$_4$ led to a black solution (eq 4.6). Attempts to sublime or extract a pure material from the mixture were unsuccessful.

\[
\text{Li}_2[\text{Me}_2\text{SiCp}_2] + \text{ReCl}_4(\text{THF})_2 + \text{LiBH}_4 \rightarrow \text{decomposition} \quad (4.6)
\]

One of the major drawbacks to this method is the use of a Re(IV) starting material when attempting to synthesize a Re(III) product. The preferred method is to use an appropriate metal halide or amide complex with the same oxidation state, to avoid the use of excess Cp$^-$ to reduce the metal center. Despite numerous attempts from this group to synthesize Cp$_2$ReH from various Re(III) halide complexes, the only successful methods to date are from either ReCl$_5$ or ReCl$_4$(THF)$_2$.\(^9\)

We have found that non-bridged, substituted cyclopentadienide can be successfully reacted with ReCl$_4$(THF)$_2$ to form a derivative of Cp$_2$ReH. The synthesis of K[MeCp] follows the standard thermolysis of methylcyclopentadiene dimer, to form the monomeric methyl substituted cyclopentadiene, followed by reduction with potassium metal. ReCl$_4$(THF)$_2$ reacts with three equivalents of K[MeCp] and LiBH$_4$ to form Cp'$_2$ReH (Cp' = MeC$_5$H$_4$) (eq 4.7). The product is isolated as a yellow solid in 33% yield by sublimation under dynamic vacuum.
Complex 17 has been characterized by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy and elemental analysis. The \(^1\text{H}\) NMR spectrum of \(\text{Cp}_2\text{ReH}\) reveals two pseudotriplets for the cyclopentadienyl protons which is consistent with the AA'BB' system. The resonances at \(\delta 4.21\) and \(4.09\) display a 2 Hz coupling. We have not assigned which resonance is for the protons in the 2,5 positions versus the protons which are in the 3,4 positions. A resonance at \(\delta 2.0\) integrates for the six protons of the two equivalent methyl groups. The hydride resonance comes at \(\delta -12.64\).

Although the attempt to react \(\text{ReCl}_4(\text{THF})_2\) with permethylated cyclopentadienide was unsuccessful,\(^9\) it appears that less substituted complexes can still be synthesized by this route in very good yield. As will be discussed later, this route may be particularly useful in the synthesis of \(\text{Cp}_2\text{Re}\) derivatives which are alkyl substituted or disubstituted on the cyclopentadienyl ring. Unfortunately the substituted rings may limit the usefulness of \(\text{Cp}'_2\text{ReH}\) toward further derivitization. The reaction of \((\eta^5-\text{C}_5\text{H}_4\text{Me})_2\text{ReH}\) with \(\text{nBuLi}\) followed by excess \(\text{CH}_3\text{Cl}\) led to the methyl complex which was contaminated with the hydride starting material.

**Synthesis and Characterization of \((\text{CH}_3)_2\text{Si(}\eta^5-\text{C}_5\text{H}_4)_2\text{ReCH}_3\) (18).**

Due to the lack of a suitable \(\text{Re(III)}\) starting material for reaction with \(\text{ansa}\)-bridged ligands we have explored the synthesis of \(\text{ansa}\)-metalocene complexes by derivitization of \(\text{Cp}_2\text{ReCH}_3\). The metalation of cyclopentadienyl complexes by \(\text{nBuLi}\) has been
reported by several groups. Consistent with our synthetic goals, there have been two reports of metalation of sandwich complexes followed by addition of dialkyldichlorosilane to generate ansa-bridged complexes.22,23

\[ \text{Fe} \quad \text{Li} \quad \text{Fe} \quad \text{TMEDA} + \text{SiPh}_2\text{Cl}_2 \rightarrow \text{Ph}_2\text{Si} \quad \text{Fe} \quad (4.8) \]

\[ \text{Ti} \quad \text{Li} \quad \text{Ti} \quad \text{TMEDA} + \text{SiMe}_2\text{Cl}_2 \rightarrow \text{Me}_2\text{Si} \quad \text{Ti} \quad (4.9) \]

We have observed that Cp₂ReCH₃ can be deprotonated twice by addition of 2 equivalents of nBuLi in THF at 0 °C. No change is observed to the bright orange solution and one equivalent of Me₂SiCl₂ is added to the solution and stirred for 15 minutes. Sublimation of the residue gave dark orange crystals of (CH₃)₂Si(η⁵-C₅H₅)₂ReCH₃ (18) in 84% yield (eq 4.10).

\[ \text{Re}--\text{CH}_3 \quad 2 \text{nBuLi} \rightarrow \text{Li} \quad \text{Re}--\text{CH}_3 \quad \text{Li} \]

\[ \text{Me}_2\text{SiCl}_2 \rightarrow \text{Me}_2\text{Si} \quad \text{Re}--\text{CH}_3 \quad (4.10) \]
Several $^1$H and $^{13}$C NMR experiments were conducted to conclusively identify the structure of 18. The $^1$H NMR spectrum of the cyclopentadienyl region reveals two doublet of doublet resonances ($\delta$ 4.82 and 4.21) which is consistent with the expected AA'BB' system ($J_{HH} = 1.6$ and 1.9 Hz). The $^{13}$C NMR spectrum of the cyclopentadienyl region contains two doublet of quartet resonances ($\delta$ 83.7 and 75.0) which exhibit a large one bond CH coupling ($^{1}J_{CH} = 180$ Hz) and an averaging of the two and three bond CH couplings ($J_{CH} = 7$ Hz) for the quartet.

![Scheme 4.4](image)

**Table 4.1.** $^1$H and $^{13}$C NMR Chemical Shifts (ppm) for Complex 18.

<table>
<thead>
<tr>
<th></th>
<th>$^1$H</th>
<th>$^{13}$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4.21</td>
<td>83.7</td>
</tr>
<tr>
<td>B</td>
<td>4.82</td>
<td>74.9</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>28.0</td>
</tr>
<tr>
<td>D</td>
<td>0.28</td>
<td>-34.0</td>
</tr>
<tr>
<td>E</td>
<td>0.18</td>
<td>-5.2</td>
</tr>
</tbody>
</table>
The $^1$H NMR chemical shifts for the 3,4 (A) and 2,5 (B) positions of the cyclopentadienyl rings were identified by NOE studies between the cyclopentadienyl protons and the methyl groups. The experiments determined that the resonance at $\delta$ 4.21 corresponds to protons at the 3,4 or A position which are nearer to the methyl group on the rhenium. Conversely the protons at the 2,5 or B position which are nearer to the methyl groups on the silicon bridge correspond to the resonance at $\delta$ 4.82. The $^{13}$C NMR chemical shifts of the cyclopentadienyl rings were correlated to the appropriate $^1$H NMR resonances by selective $^1$H decoupling of the $^{13}$C NMR spectrum. Therefore, by irradiating either the resonance at $\delta$ 4.21 or 4.82, the $^{13}$C NMR resonance of the corresponding carbon would collapse to a singlet, while the other resonance appeared as a doublet with decreased coupling.

**Structural Characterization of** $\{(\eta^5$-C$_5$H$_4$-Si(CH$_3$)$_2$-$\eta^5$-C$_5$H$_4$)ReCH$_3$\} (18). Crystals suitable for x-ray diffraction were obtained by slow sublimation under dynamic vacuum from the crude reaction material at 50 °C to a probe cooled with ice water. An ORTEP drawing is shown in Figure 4.1. The summary of crystallographic data is given in Table 4.2 and selected bond distances and angles are listed in Table 4.3. Appendix A contains tables of atomic coordinates, isotopic and anisotropic displacement coefficients.
Figure 4.1. ORTEP representation of \( ((\eta^5-C_5H_4-Si(Me_2)-\eta^5-C_5H_4)ReCH_3 \) (18). Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity.
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical Formula</strong></td>
<td>C\textsubscript{13}H\textsubscript{17}ReSi</td>
</tr>
<tr>
<td><strong>Color; Habit</strong></td>
<td>Orange Needle</td>
</tr>
<tr>
<td><strong>Crystal Size (mm)</strong></td>
<td>0.15 x 0.20 x 0.35</td>
</tr>
<tr>
<td><strong>Crystal System</strong></td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space Group</strong></td>
<td>C\textsubscript{2}/c</td>
</tr>
<tr>
<td><strong>Unit Cell Dimensions</strong></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>11.242 (2) Å</td>
</tr>
<tr>
<td>b</td>
<td>14.118 (3) Å</td>
</tr>
<tr>
<td>c</td>
<td>7.885 (2) Å</td>
</tr>
<tr>
<td>(\beta)</td>
<td>108.19 (3)°</td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td>1188.9 (4) Å(^3)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
</tr>
<tr>
<td><strong>Formula Weight</strong></td>
<td>387.6</td>
</tr>
<tr>
<td><strong>Density (calc.)</strong></td>
<td>2.165 Mg/m(^3)</td>
</tr>
<tr>
<td><strong>Absorption Coefficient</strong></td>
<td>10.285 mm(^{-1})</td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>736</td>
</tr>
<tr>
<td><strong>Radiation</strong></td>
<td>MoK(\alpha) ((\lambda = 0.71073 \text{ Å}))</td>
</tr>
<tr>
<td><strong>Temperature (K)</strong></td>
<td>183</td>
</tr>
<tr>
<td><strong>Monochromater</strong></td>
<td>Highly oriented graphite crystal</td>
</tr>
<tr>
<td><strong>2(\theta) Range</strong></td>
<td>2.0 to 50.0 °</td>
</tr>
<tr>
<td><strong>Scan Type</strong></td>
<td>2(\theta)</td>
</tr>
<tr>
<td><strong>Scan Speed</strong></td>
<td>Variable; 1.50 to 5.50°/min. in (\omega)</td>
</tr>
<tr>
<td><strong>Scan Range ((\omega))</strong></td>
<td>0.80 + 0.35((\tan \theta))°</td>
</tr>
<tr>
<td><strong>Reflections Collected</strong></td>
<td>1203</td>
</tr>
<tr>
<td><strong>Independent Reflections</strong></td>
<td>1054 ((R_{int} = 10.05%))</td>
</tr>
<tr>
<td><strong>Observed Reflections</strong></td>
<td>981 ((F &gt; 4.0\sigma(F)))</td>
</tr>
<tr>
<td><strong>Number of Parameters Refined</strong></td>
<td>71</td>
</tr>
<tr>
<td><strong>Final R Indices (obs. data)</strong></td>
<td>R = 6.57 %, wR = 8.18 %</td>
</tr>
<tr>
<td><strong>R Indices (all data)</strong></td>
<td>R = 6.57 %, wR = 8.40 %</td>
</tr>
<tr>
<td><strong>Goodness-of -Fit</strong></td>
<td>1.14</td>
</tr>
</tbody>
</table>
Table 4.3. Selected Bond Distances and Angles for 18.

<table>
<thead>
<tr>
<th>Distances, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re-C(1)</td>
</tr>
<tr>
<td>Re-C(4)</td>
</tr>
<tr>
<td>Re-C(6)</td>
</tr>
<tr>
<td>Si-C(3)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
</tr>
<tr>
<td>C(3)-C(7)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Angles, deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(3)-Si-C(3a)</td>
</tr>
<tr>
<td>C(3)-C(7)-C(6)</td>
</tr>
<tr>
<td>C(5)-C(6)-C(7)</td>
</tr>
<tr>
<td>C(4)-C(5)-C(6)</td>
</tr>
</tbody>
</table>

The variety of structural parameters which have been reported for metallocene complexes can be quite confusing. In order to derive meaningful comparisons between structures a consistent set of angles and distances must be defined. Fortunately, the recent review of substituted metallocene complexes by Hays and Hanusa has defined several relevant angles for describing the structures of these complexes as depicted in Figure 4.2.1
Figure 4.2. Pictorial representation of bending angles for metalloocene complexes. Adapted from reference 1.

The bending angle of the cyclopentadienyl rings is a crucial structural factor and can be defined in two ways. The $\alpha$ angle is between the vectors to ring centroids from the metal while the $\beta$ angle is between the vectors to the normal of the ring from the metal. These two angles are not necessarily coincidental, but will be close if there is little structural distortion of the metalloocene complex. This distortion will also be evident by the $M$-$C$ distances of the Cp ligand which will vary if the $\alpha$ and $\beta$ angles differ. The deviation from the centroid of the Cp ring and the normal to the ring can be also measured by $\delta$ which will be 90° if $\alpha$ and $\beta$ are equal. The angle between the cyclopentadienyl planes ($\gamma$) is supplementary to $\beta$. Table 4.4 lists several relevant angles and distances for complex 2. Although the structure of the parent complex, $\text{Cp}_2\text{ReCH}_3$, has not been crystallographically determined, we can observe that the ansa ligand of complex 18 has not severely distorted the structure. The 5° difference between the $\alpha$ and $\beta$ angles is quite modest. The distances between the rhenium and the carbons of the cyclopentadienyl ring
are quite similar and the δ angle is slightly less than 90° indicating that the metal to Cp centroid vector is nearly coincidental with the normal to the ring.

Table 4.4. Selected Structural Data for Complex 18.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp(cen)−M−Cp(cen) (α)</td>
<td>145.2°</td>
</tr>
<tr>
<td>Cp (normal)−M−Cp(normal) (β)</td>
<td>140.0°</td>
</tr>
<tr>
<td>angle between Cp planes (γ)</td>
<td>40.0°</td>
</tr>
<tr>
<td>angle between Cp plane and vector to centroid (δ)</td>
<td>87.4°</td>
</tr>
<tr>
<td>M−Cp(cen)</td>
<td>1.869 Å</td>
</tr>
<tr>
<td>M−C (Cp) (range)</td>
<td>2.262−2.193 Å</td>
</tr>
<tr>
<td>Δ M-C (Cp)</td>
<td>0.17 Å or 7.5%</td>
</tr>
</tbody>
</table>

Relevant angles and distances for several crystallographically characterized derivatives of rheneocene are listed in Table 4.5. The Cp−M−Cp bending angles usually fall between 140° and 150°. There appears to be no consistent protocol for reporting the bending angle as most references randomly report either α or β. For most of these compounds there is not expected to be a large difference between these angles. The average distance between rhenium and the carbon atoms of the ring as well as the rhenium to centroid distances are very consistent between the various structures as well as being similar to complex 18. The Re-C(sp³) distances for the Alcock and Caulton structures are quite similar at 2.24 and 2.27 Å respectively. This distance decreases by 0.10 Å for the Re-C(sp²) structures reported by Herberich. The Re−CH₃ bond length for complex 18 (2.12 Å) is short by comparison, but is not unusual for a Re-C(sp³) bond distance.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Cp-Re-Cp, deg</th>
<th>Re-Cp av., Å</th>
<th>Re-Cp(cen), Å</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_5H_5)(C_5H_5Me)Re(OMe)_2</td>
<td>145.7^a</td>
<td>2.18</td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>[CpReH_2]_2BF_4</td>
<td>139.5^a</td>
<td>2.01</td>
<td>1.88</td>
<td>35</td>
</tr>
<tr>
<td>[CpReBr_2]_2BF_4</td>
<td>147.6^b</td>
<td>2.26</td>
<td>2.22</td>
<td>36</td>
</tr>
<tr>
<td>Cp_2ReCl_2</td>
<td>147.5^a, 150.1^b</td>
<td>2.24</td>
<td>2.28</td>
<td>37</td>
</tr>
<tr>
<td>[CpReCuCl_2]_2</td>
<td>158.0^b</td>
<td>1.87</td>
<td>1.90</td>
<td>38</td>
</tr>
<tr>
<td>[CpReH(CMe)_2]_2</td>
<td>150.5^b</td>
<td>2.24</td>
<td>2.24</td>
<td>39</td>
</tr>
<tr>
<td>CpRe(alkeny)_2</td>
<td>146.2^a</td>
<td>2.25</td>
<td>1.90</td>
<td>40</td>
</tr>
<tr>
<td>CpRe(alkeny)_2</td>
<td>146.8^b</td>
<td>2.23</td>
<td>2.27</td>
<td>41</td>
</tr>
<tr>
<td>a Cp(normal)M-Cp(normal) (a)</td>
<td></td>
<td>2.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b Cp(cen)M-Cp(cen) (b)</td>
<td></td>
<td>2.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c Cp_2Re[1-(2-CO_2Me)=CH(CO_2Me)] (c)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Green and coworkers have compared the structures of *ansa*-bridged complexes of molybdenum with the parent complexes.\textsuperscript{23} They have observed that the *ansa*-bridged complexes exhibit a difference between the α and β angles of 10°. This indicates a greater distortion than that observed for complex 18. The β angle dramatically decreases by 15-26° from the parent metalloocene to the *ansa*-bridged complexes. The significant structural changes observed for the Green complexes is attributed to the use of carbon bridges; \(-\text{C(Me)}_2\) and \(-\text{C(CH}_2\text{)}_4\). The carbon bridge should affect a larger difference than a silicon bridge upon the metalloocene structure due to the expected shorter bond distances between carbon and the cyclopentadienyl rings. The Si-C(Cp) distance for complex 18 is 1.880Å while the C-C(Cp) distance for Me\textsubscript{2}C-(η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{4})\textsubscript{2}WH\textsubscript{2} is 1.529Å.\textsuperscript{24}

Corey and coworkers have recently reported a comparison of several metalloocene complexes with silicon and carbon bridges.\textsuperscript{42} They have synthesized and reported the crystal structures for Me\textsubscript{2}C(C\textsubscript{5}H\textsubscript{4})\textsubscript{2}MCl\textsubscript{2} (M = Ti, Zr, Hf) and compared them to the known parent structures as well as the analogous -SiMe\textsubscript{2} structures. They found the silicon bridge decreases the Cp-M-Cp bending angle by an average of 3-4° while the angle for the carbon bridge is 10-13° smaller than the parent compound. The single carbon bridges also force the metal center out from the cyclopentadienyl rings leaving it less protected. This may result in increased reactivity in some complexes. Most of the other angles and distances do not change dramatically.

**Synthesis and Characterization of** \(((\text{CH}_3)_2\text{Si})_2-\eta^5\text{-C}_5\text{H}_4)_2\text{ReCH}_3\) (19). The synthesis of an *ansa*-bridged complex with a two silicon bridge was accomplished by the same route as complex 18. One equivalent of (Me\textsubscript{2}Si)\textsubscript{2}Cl\textsubscript{2} was added to a THF solution of (η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{4}Li)\textsubscript{2}ReCH\textsubscript{3} at 0 °C and allowed to stir for 15 minutes. The solvent was removed from the bright orange solution *in vacuo* and compound 3 was sublimed from the residue at 50 °C under dynamic vacuum.
The $^1$H and $^{13}$C NMR spectra were similar to that observed for compound 18. Two pseudotriplet resonances ($\delta$ 4.42 and 4.37) were observed in the $^1$H NMR spectrum for the cyclopentadienyl protons. The methyl protons were observed at $\delta$ 0.36 (3 H) and $\delta$ 0.25 (12 H) in the $^1$H NMR spectrum indicating the methyl groups of the ansa-bridge are equivalent.

**Synthesis and Characterization of** $((\text{CH}_3)_3\text{Si-}\eta^5\text{-C}_5\text{H}_4)_2\text{ReCH}_3$ (20).

A substituted analog can also be synthesized which does not contain an ansa-bridge. The addition of two trimethylsilyl ligands to the cyclopentadienyl rings would presumably provide a similar electronic environment compared to compounds 18 and 19 without restricting the metallocene to a bent geometry. Excess Me$_3$SiCl is vacuum transferred to a THF solution of ($\eta^5\text{-C}_5\text{H}_4\text{Li}$)$_2\text{ReCH}_3$ at 0 °C. The solvent was removed in vacuo and compound 20 was isolated in 87% yield as an orange solid by vacuum sublimation.
Compound 20 was characterized by $^1$H and $^{13}$C NMR spectroscopy and was found to be similar to complexes 18 and 19. Two pseudotriplet resonances ($\delta$ 4.52 and 3.52) were observed in the $^1$H NMR spectrum for the cyclopentadienyl protons. The methyl protons were observed at $\delta$ 0.19 (18 H) and $\delta$ 0.18 (3 H) in the $^1$H NMR spectrum for the SiMe$_3$ and Re-Me groups respectively.

**Protonation of Substituted Rhenocene Complexes 18-20.** Addition of one equivalent of [H(Et$_2$O)$_2$]B(Ar$^+$)$_4$ to complexes 18-20 led to clean formation of cationic methyl hydride complexes, 22-24 (Scheme 4.5). The methyl hydride complexes have been characterized by $^1$H NMR spectroscopy at 250 K in both CD$_2$Cl$_2$ and CD$_3$CN. The $^1$H and $^{13}$C NMR spectra of the two ansa-bridged complexes, 22 and 23, are observed to have decreased symmetry compared to the neutral methyl complexes. The $^1$H NMR spectra of the cyclopentadienyl rings now exhibit 4 broad resonances due to the chemically inequivalent protons. Two resonances are observed for the methyl groups of the silicon bridge which become inequivalent with one group cisoid to the rhenium methyl
group and the other cisoid to the hydride. This asymmetry for the SiMe₃ protons is not observed for complex 24 since the cyclopentadienyl ligands are able to freely rotate.

![Chemical structures](image)

**Scheme 4.5**

The solutions of complexes 22-24 are colorless while the neutral methyl complexes are bright orange. As the solutions are warmed to room temperature they become dark orange and decomposition is evident in the $^1$H NMR spectra. The products of methane elimination often gave complicated $^1$H NMR spectra. The decomposition of complex 23 in CD$_3$CN gave a simple $^1$H NMR spectrum consistent with a single product, $[((\text{CH}_3)_2\text{Si})_2(\eta^5\text{-C}_5\text{H}_4)_2\text{Re(NCCD}_3)]\text{B(Ar')}_4$ (25).

**Methane Elimination from Complexes 21-24.** The methane elimination from complexes 22-24 and [Cp₂Re(CH₃)H]B(Ar')₄ (21) was monitored between 250 K and 298 K. At 250 K the complexes appeared to be stable and $^{13}$C NMR spectra of complexes 21 and 22 were obtained at this temperature without noticeable decomposition. As solutions of 21-24 were warmed to 0 °C, noticeable decomposition was occurring for complexes 21, 23 and 24. Complex 22 was stable at this temperature and decomposition was only evident when the sample was warmed to room temperature, $t_{1/2} = 1$-2 hours. Complexes 21, 23 and 24 decompose rapidly at room temperature and cannot be observed.
The reactivity differences between complexes 21-24 are subtle, but it appears that the single Si ansa bridge does increase the thermal stability of the methyl hydride complexes toward methane elimination. Green and coworkers have observed a more drastic reactivity difference between Cp₂W(CH₃)H and ansa-Çp₂W(CH₃)H. The parent compounds have been shown to reductively eliminate methane at 40 °C while the ansa complexes show no reactivity up to 150 °C.²⁴ Green et al. have proposed that this reactivity difference is the result between the ability of the "Çp₂W" intermediate to attain a parallel structure following reductive elimination of methane and the inability of "ansaÇp₂W" to attain a parallel structure.

Perutz and coworkers have obtained evidence that complexes such as Cp₂W and Cp₂Mo have parallel structures rather than bent structures. The 16 electron metallocenes are exceedingly reactive and can only be generated and studied under special conditions. The photolysis of Cp₂WH₂ and Cp₂MoH₂ led to the reductive elimination of H₂ and formation of Cp₂W and Cp₂Mo which can be studied in a low temperature matrix of argon.⁴³ A wide variety of spectroscopic methods can be used to characterize these unstable species and the results indicate that the metallocene complexes obtain a parallel ring structure similar to Cp₂Fe. Similar results have been observed for the photolysis of Cp₂ReH which emits a hydrogen atom to form the neutral radical, Cp₂Re.⁴⁴ The decamethyl analog, Cp₂*Re, is also formed by photolysis of Cp*₂ReH, but is stable at ambient temperature and the crystal structure has been shown to have parallel rings in an eclipsed conformation.²⁶

The products of methane elimination from the ansa-bridged metallocenes, ansa-Cp₂M (M = Mo, W, Re⁺), are confined to a bent geometry and the structure will depend upon the identity of the interannular bridge. Lauher and Hoffman have investigated the effect of bending a metallocene complex with a parallel ring structure, Cp₂Ti.⁴⁵ The energy of the frontier orbitals, calculated using extended Hückel theory, are observed to
increase as the bending angle is decreased. This would indicate that the bent geometry of the *ansa*-bridged complexes will have a higher barrier to reductive elimination due to the higher energy intermediate at the transition state. The proposed reaction coordinate for methane elimination from \([\text{Cp}_2\text{Re}(\text{CH}_3)\text{H}]^+\) (21) and \([\text{Me}_2\text{SiCp}_2\text{Re}(\text{CH}_3)\text{H}]^+\) (22) is depicted in Figure 4.3.

**Figure 4.3.** Proposed reaction coordinate depicting methane elimination from non-*ansa* and *ansa*-bridged rhenocene methyl hydride complexes (21 and 22). Adapted from references 9 and 24b.
As discussed previously, a single carbon bridge has been observed to have a greater effect upon the bending angle as compared to a single silicon bridge for several coordinatively saturated Cp₂MLₙ (n = 1 or 2) type complexes. Unfortunately, a direct comparison of the silicon versus carbon bridged complexes has yet to be made for metallocene complexes without ancillary ligands, Cp₂MLₙ (n = 0). The transition state of the bent ansaCp₂Re⁺ as depicted in Figure 4.3 may be higher in energy for a single carbon bridge compared to the single silicon bridge. A number of Group 8 metallocene complexes with various interannular bridges have been synthesized and structurally characterized. These complexes may provide some insight on the affect of the ansa-bridge upon the 16 electron transition state intermediates, ansa-Cp₂W and [ansa-Cp₂Re]⁺. The bending angles of Cp₂M (M = Fe, Ru) with various silicon and carbon bridges are shown in Scheme 4.5.46-51

\[
\begin{align*}
\text{Fe} & \quad \gamma = 0^\circ \\
\text{R}_2\text{Si} & \quad \text{Fe} \\
\text{Me}_2\text{Si} & \quad \text{Fe} \\
\end{align*}
\]

\[
\begin{align*}
\text{R} = \text{Me}; \gamma = 20.8^\circ \\
\text{R} = \text{Ph}; \gamma = 19.2^\circ \\
\gamma = 4.19^\circ \\
\end{align*}
\]

\[
\begin{align*}
\text{R}_2\text{C} & \quad \text{Fe} \\
\text{R}_2\text{C} & \quad \text{Fe} \\
\text{H}_2\text{C} & \quad \text{Ru} \\
\end{align*}
\]

\[
\begin{align*}
\text{R} = \text{H}; \gamma = 21.6^\circ \\
\text{R} = \text{Me}; \gamma = 23^\circ \\
\gamma = 29.6^\circ \\
\end{align*}
\]

Scheme 4.6
The bending angles (γ) for the complexes in Scheme 4.6 indicates the angle between the planes of the cyclopentadienyl rings. A single silicon bridge creates a bending angle of approximately 20° while a two silicon bridge bends the rings only very slightly. This contrasts with the two carbon bridge which has a much greater effect and is similar to the single silicon bridge. This is consistent with the fact that the two carbon bridge will have a shorter C-C bond length as well as shorter C-C(Cp) bonds to the ring. This makes it significantly more contracted than the two silicon bridge. Unfortunately, an example with a single carbon bridge has yet to be characterized but will probably enforce a greater bending angle upon the rings. The angles in Scheme 4.6 cannot be directly related to those for the ansa-Cp₂Re⁺ or ansa-Cp₂W complexes since the ligand will undergo greater stress encapsulating a metal atom with a larger radius. This is observed for the Ru complex which shows that the two carbon bridge has a larger bending angle compared to the iron analog.

The results of Scheme 4.6 suggest that complex 23 with the two silicon bridge may not have a large bending angle between the rings during the transition state. This would be consistent with the observation that methane elimination from 23 seems to occur at the same rate as for the complexes which do not contain an ansa-bridge, 21 and 24. Scheme 4.6 also suggest a single carbon bridge will have a greater impact upon the bending angle compared to a silicon bridge. It is unclear how much flexibility the bridges will have during the transition state. Recent ab initio calculations have observed that a -SiMe₂ bridge does have a certain degree of flexibility and can allow the Cp rings to move. Presumably a single carbon bridge would provide a more rigid ansa ligand and increase the barrier to methane elimination.

Since methane elimination was never observed for the W and Mo complexes studied by Green and coworkers, the rhenium system provides a potentially more
important probe of the affects that the *ansa* bridge might create. Unfortunately preliminary attempts to synthesize carbon *ansa*-bridged complexes of rhenocene have failed. Presumably the further study of alternate routes toward synthesizing complexes of rhenocene with C, B, S or Sn bridges would provide a very interesting system to study.

**Conclusions**

A high yield synthesis for the first *ansa*-bridged complexes of rhenocene has been developed. The addition of Me$_2$SiCl$_2$ or (Me$_2$Si)$_2$Cl$_2$ to a THF solution of (η$^5$-C$_5$H$_4$Li)$_2$ReCH$_3$ gives *ansa*-bridged complexes with a single or double silicon linker. A X-ray diffraction study was undertaken to confirm the structure of (η$^5$-C$_5$H$_4$-SiMe$_2$-η$^5$-C$_5$H$_4$)ReCH$_3$. Substituted derivatives of Cp$_2$ReX (X = H, CH$_3$) have also been synthesized with Me or SiMe$_3$ groups on each cyclopentadienyl ring. Several methyl hydride rhenocene complexes have been generated by protonation and characterized at low temperature by NMR spectroscopy. Methane elimination from these complexes occurs at ambient temperature, although [(η$^5$-C$_5$H$_4$-SiMe$_2$-η$^5$-C$_5$H$_4$)Re(CH$_3$)H]B(Ar')$_4$ has been observed to be more stable at room temperature then analogous complexes. This increased stability is attributed to a higher energy intermediate upon methane elimination due to restricting the structure as a bent metallocene.

**Experimental Section**

**General Considerations.** General experimental techniques have been described in Chapter 1. ReCl$_4$(THF)$_2$$^{53}$ Cp$_2$ReCH$_3$$^{74}$ and [H(Et$_2$O)$_2$]B(Ar')$_4$$^{54}$ were prepared by reported procedures. (Me$_2$Si)$_2$Cl$_2$ was purchased from Gelest and all other reagents were purchased from Aldrich. The $^1$H and $^{13}$C NMR resonances for B(Ar')$_4$
are identical with those reported from complex 1-B(Ar')₄ (chapter 2) and have been omitted from subsequent complexes.

**Synthesis of Complexes.**

(CH₃-η⁵-C₅H₄)₂ReH (17). A 250 mL round bottom flask was charged with KCp' (1.9 g, 0.016 mol) and 100 mL of dry DME was vacuum transferred to the flask. The solution was warmed to 0°C and ReCl₄(THF)₂ (2.5 g, 0.0053 mol) is added under an argon flow. The solution immediately becomes purple-brown and is stirred at 0°C for 2 hours. Under an argon flow LiBH₄ (0.115 g, 0.0053 mmol) is added and the solution is stirred at room temperature for 3 hours. The solvent was removed in vacuo and a yellow solid (640 mg) is sublimed at 80°C under dynamic vacuum. Resublimation gives pure Cp₂ReH is 33% yield (606 mg). ¹H NMR (CD₇D₈): 4.21 ("t", 4 H, J_HH = 1.7 Hz, η⁵-C₅H₄); 4.09 ("t", 4 H, J_HH = 2.4 Hz, η⁵-C₅H₄); 2.05 (s, 6 H, CH₃-η⁵-C₅H₄); -12.64 (s, 1 H, Re-H). ¹³C NMR (CD₇D₈): 84.0 (s, CH₃-η⁵-C₅H₄ ipso); 67.1 (d of m, J_CH = 180 Hz, η⁵-C₅H₄); 64.9 (d of quart, J_CH = 179 Hz, J_CH = 6.5 Hz, η⁵-C₅H₄); 16.0 (q, J_CH = 127 Hz, CH₃-η⁵-C₅H₄). Anal. Calcd for C₁₂H₁₅Re: C, 41.72; H, 4.38. Found: C, 41.29; H, 4.34.

(η⁵-C₅H₄-Si(CH₃)₂-η⁵-C₅H₄)ReCH₃ (18). A small glass vessel with an 8 mm Kontes valve was charged with Cp₂ReCH₃ (274 mg, 0.83 mmol). THF (20 mL) was vacuum transferred to the vessel and warmed to 0°C. Under an argon flow, 2 equivalents of nBuLi (1.03 mL, 1.6 M, 1.65 mmol) was added via a gas tight syringe. The solution was stirred at 0°C for 45 minutes. Under an argon flow, (CH₃)₂SiCl₂ (101 µL, 0.83 mmol) was added via a gas tight syringe and stirred at 0°C for 15 minutes. The solvent was removed in vacuo. The solid was sublimed to give 320 mg of dark orange crystals (84%). ¹H NMR (CD₂Cl₂): 4.82 (d of d, 4H, J_HH = 1.59 Hz, J_HH = 1.96 Hz,
\( \eta^5\text{-C}_5\text{H}_4 \), 4.21 (d of d, 4H, J_{HH} = 1.62 Hz, J_{HH} = 1.94 Hz, \( \eta^5\text{-C}_5\text{H}_4 \)), 0.28 (s, 3H, ReCH\(_3\)), 0.18 (s, 6H, Si(CH\(_3\))\(_2\))

\( ^1\text{H} \text{NMR (CD}_3\text{CN):} \, 4.86 \) ("t", 4H, J_{HH} = 1.8 Hz, \( \eta^5\text{-C}_5\text{H}_4 \)), 4.12 ("t", 4H, J_{HH} = 1.4 Hz, \( \eta^5\text{-C}_5\text{H}_4 \)), 0.22 (s, 3H, ReCH\(_3\)), 0.15 (s, 6H, Si(CH\(_3\))\(_2\))

\( ^13\text{C} \text{NMR (CD}_2\text{Cl}_2): \, 83.7 \) (d of quart, J\(_{CH} = 180\) Hz, J\(_{CH} = 6.6\) Hz, \( \eta^5\text{-C}_5\text{H}_4 \)), 75.0 (d of quart, J\(_{CH} = 183\) Hz, J\(_{CH} = 7.3\) Hz, \( \eta^5\text{-C}_5\text{H}_4 \)), 28 (s, \( \eta^5\text{-C}_5\text{H}_4 \)), -5.2 (quart, J\(_{CH} = 121\) Hz, Si(CH\(_3\))\(_2\)), -34.0 (quart, J\(_{CH} = 127\) Hz, ReCH\(_3\)).

Anal. Calcd for C\(_{13}\)H\(_{17}\)ReSi: C, 40.29; H, 4.42. Found: C, 40.31; H, 4.61.

\( (\eta^5\text{-C}_5\text{H}_4\text{-}(\text{Si(CH}_3)_2\text{)2-} \eta^5\text{-C}_5\text{H}_4)\text{ReCH}_3 \) (19). A small glass vessel with an 8 mm Kontes valve was charged with Cp\(_2\)ReCH\(_3\) (50 mg, 0.15 mmol). THF (15 mL) was vacuum transferred to the vessel and warmed to 0°C. Under an argon flow, 2 equivalents of nBuLi (0.19 mL, 1.6 M, 0.30 mmol) was added via a gas tight syringe. The solution was stirred at 0°C for 45 minutes. Under an argon flow, \( ((\text{CH}_3)_2\text{Si})_2\text{Cl}_2 \) (27 \( \mu\)L, 0.15 mmol) was added via a gas tight syringe and stirred at 0°C for 15 minutes. The solvent was removed in vacuo. The solid was sublimed to give 38 mg of orange solid (56%). \( ^1\text{H} \text{NMR (CD}_2\text{Cl}_2): \, 4.42 \) ("t", 4H, J_{HH} = 1.7 Hz, \( \eta^5\text{-C}_5\text{H}_4 \)), 4.37 ("t", 4H, J_{HH} = 1.7 Hz, \( \eta^5\text{-C}_5\text{H}_4 \)), 0.36 (s, 3H, ReCH\(_3\)), 0.25 (s, 12H, Si(CH\(_3\))\(_2\))

\( ^13\text{C} \text{NMR (CD}_2\text{Cl}_2): \, 83.91 \) (d of quart, J\(_{CH} = 181\) Hz, J\(_{CH} = 6.5\) Hz, \( \eta^5\text{-C}_5\text{H}_4 \)), 71.24 (d of quart, J\(_{CH} = 180\) Hz, J\(_{CH} = 7.3\) Hz, \( \eta^5\text{-C}_5\text{H}_4 \)), 75.01 (s, \( \eta^5\text{-C}_5\text{H}_4 \)), -1.4 (quart, J\(_{CH} = 121\) Hz, Si(CH\(_3\))\(_2\)), -36.77 (quart, J\(_{CH} = 129\) Hz, ReCH\(_3\)).


\( ((\text{CH}_3)_3\text{Si-} \eta^5\text{-C}_5\text{H}_4)_2\text{ReCH}_3 \) (20). A small glass vessel with an 8 mm Kontes valve was charged with Cp\(_2\)ReCH\(_3\) (120 mg, 0.362 mmol). THF (20 mL) was vacuum transferred to the vessel and warmed to 0°C. Under an argon flow, 2 equivalents of nBuLi (0.45 mL, 1.6 M, 0.724 mmol) was added via a gas tight syringe.
The solution was stirred at 0°C for 30 minutes and then degassed by three freeze-pump-thaw cycles. Trimethylsilylchloride (ca. 1 mL) was vacuum transferred to the solution at -78°C. The solution was slowly warmed to room temperature and the volatiles were removed in vacuo. The solid was sublimed at 60°C under dynamic vacuum to give 150 mg of orange solid (87%). ^1H NMR (CD2Cl2): 4.52 ('t', 4H, JHH = 1.91 Hz, η5-C5H4), 3.52 ('t', 4H, JHH = 1.93 Hz, η5-C5H4), 0.19 (s, 18H, Si(CH3)3), 0.18 (s, 3H, ReCH3);^13C NMR (CD2Cl2): 83.9 (d of quart, JCH = 175.9 Hz, JCH = 7.7 Hz, η5-C5H4), 68.7 (d of quart, JCH = 180.3 Hz, JCH = 6.5 Hz, η5-C5H4), 0.58 (quart, JCH = 118.9 Hz, Si(CH3)3). -36.3 (quart, JCH = 128.2 Hz, ReCH3). Anal. Calcd for C17H29ReSi2: C, 42.92; H, 6.14. Found: C, 42.04; H, 6.05.

[(η5-C5H5)2Re(CH3)H]B(Ar')4 (21). A sealable NMR tube was charged with (η5-C5H5)2ReCH3 (6 mg, 0.018 mmol) and [H(Et2O)2]B(Ar')4 (18.3 mg, 0.018 mmol). Methylene chloride-d2 (0.5 mL) was vacuum transferred to the tube and sealed. The tube was kept at -78°C until it was placed in the NMR probe. ^1H NMR (CD2Cl2, 250 K): 5.30 (s, 10 H, η5-C5H5); 0.53 (s, 3 H, Re-CH3); -11.88 (s, 1 H, Re-H).

^13C{^1H} (CD2Cl2): 84.0 (η5-C5H5); -40.1 (Re-CH3).

[(η5-C5H4-Si(CH3)2-η5-C5H4)Re(CH3)H]B(Ar')4 (22). A sealable NMR tube was charged with ((CH3)2SiCp2ReCH3 (2) (8 mg, 0.021 mmol) and [H(Et2O)2]B(Ar')4 (21 mg, 0.021 mmol). CD2Cl2 was vacuum transferred to the tube and sealed. The tube was kept at -78°C until it was placed in the NMR probe. ^1H NMR (CD2Cl2, 250 K): 5.81 (s, 2 H, η5-C5H4); 5.72 (s, 2 H, η5-C5H4); 5.32 (s, 2 H, η5-C5H4); 4.92 (s, 2 H, η5-C5H4); 0.53 (s, 3 H, Re-CH3); 0.35 (s, 3 H, Si-CH3); 0.30 (s, 3 H, Si-CH3); -10.47 (s, 1 H, Re-H); ^1H NMR (CD3CN): 7.68 (br, B(Ar')4); 5.99 (s, 2 H, η5-C5H4); 5.89 (s, 2 H, η5-C5H4); 5.48 (s, 2 H, η5-C5H4); 5.13 (s, 2 H, η5-
C₅H₄): 0.53 (s, 3 H, Re-CH₃); 0.33 (s, 3 H, Si-CH₃); 0.30 (s, 3 H, Si-CH₃); -10.96 (s, 1 H, Re-H); ¹³C (¹H) NMR (CD₂Cl₂, 250 K): 114.7 (η⁵-C₅H₄); 89.5 (η⁵-C₅H₄); 84.4 (η⁵-C₅H₄); 73.5 (η⁵-C₅H₄); 49.5 (ipso η⁵-C₅H₅); -6.3 (Si-CH₃); -6.4 (Si-CH₃); -41.0 (Re-CH₃).

\[ \left( \eta^5-C_5H_4-(Si(CH_3)_2)_2-\eta^5-C_5H_4 \right) \text{Re}(CH_3)BH(Ar')_4 \] (23). A seableable NMR tube was charged with \((CH_3)_2Si)_2Cp_2ReCH_3 \) (3) (3 mg, 6.7 x 10⁻⁳ mmol) and \([H(Et_2O)_2]B(Ar')_4 \) (6.8 mg, 6.7 x 10⁻³ mmol). CD₂Cl₂ was vacuum transferred to the tube and sealed. The tube was kept at -78 °C until it was placed in the NMR probe. \(^1H \text{NMR (CD}_2\text{Cl}_2, 250 K): \) 5.44 (s, 2H, η⁵-C₅H₄); 5.38 (s, 2H, η⁵-C₅H₄); 5.32 (s, 2H, η⁵-C₅H₄); 4.31 (s, 2H, η⁵-C₅H₄); 0.63 (s, 3H, Re-CH₃); 0.42 (s, 6H, Si-CH₃); 0.40 (s, 6H, Si-CH₃); -12.00 (s, 1 H, Re-H); \(^1H \text{NMR (CD}_3\text{CN, 250 K): \) 7.68 (br, B(Ar')₄); 5.66 (s, 2H, η⁵-C₅H₄); 5.54 (s, 2H, η⁵-C₅H₄); 5.44 (s, 2H, η⁵-C₅H₄); 5.38 (s, 2H, η⁵-C₅H₄); 0.57 (s, 3H, Re-CH₃); 0.39 (s, 6H, Si-CH₃); 0.34 (s, 6H, Si-CH₃); -12.24 (s, 1H, Re-H).

\[ \left( ((CH_3)_3Si-\eta^5-C_5H_4)_2Re(CH_3)BH(Ar')_4 \] (24). A seableable NMR tube was charged with \((CH_3)_3Si)_2Cp_2ReCH_3 \) (4) (12 mg, 0.025 mmol) and \([H(Et_2O)_2]B(Ar')_4 \) (26 mg, 0.025 mmol). CD₂Cl₂ was vacuum transferred to the tube and sealed. The tube was kept at -78 °C until it was placed in the NMR probe. \(^1H \text{NMR (CD}_2\text{Cl}_2, 250 K): \) 5.58 (br, 2 H, η⁵-C₅H₄); 5.41 (br, 2 H, η⁵-C₅H₄); 4.79 (m, 4 H, η⁵-C₅H₄); 0.40 (s, 3 H, ReCH₃); 0.25 (s, 18 H, Si(CH₃)_3), -12.10 (s, 1 H, Re-H); \(^1H \text{NMR (CD}_3\text{CN, 250 K): \) 7.68 (br, B(Ar')₄); 5.78 ("quart", 2H, η⁵-C₅H₄); 5.48 ("quart", 2H, η⁵-C₅H₄); 4.98 (m, 4H, η⁵-C₅H₄); 0.36 (s, 3H, Re-CH₃); 0.24 (s, 18H, Si-CH₃); -12.35 (s, 1H, Re-H).
[(η⁵-C₅H₄-(Si(CH₃)₂)-η⁵-C₅H₄)Re(CD₃CN)]B(Ar')₄ (25). Upon methane elimination from complex 7 at room temperature in CD₃CN a new complex was formed which is assigned as the acetonitrile adduct. ¹H NMR (CD₃CN, 298 K): 7.68 (br, B(Ar')₄); 5.12 ("t", 4H, η⁵-C₅H₅); 4.57 ("t", 4H, η⁵-C₅H₅); 0.32 (s, 12H, Si-CH₃).

X-ray Structure Determination of (η⁵-C₅H₄-Si(CH₃)₂)-η⁵-C₅H₄)ReCH₃ (18). Crystals were generated upon sublimation of the crude reaction material at 50 °C to a probe cooled with ice water under dynamic vacuum. Several dark orange crystal grew which appeared to be of appropriate size for X-ray structure analysis and were scraped from the sublimation probe. Several large crystals were placed in a petri dish containing Paratone oil. An orange needle of dimensions 0.15 x 0.20 x 0.35 mm was placed in a nitrogen stream at 183 K on an Enraf-Nonius CAD4 diffractometer using MoKα radiation with a graphite monochromator (λ = 0.71073 Å). Examination of the peaks by scanning indicated that there was a large mosaic spread in the crystal. Two Θeta-Omega scans gave good peak shape while Omega scans gave largely skewed peak shapes, indicative of mosaic spread. 20 reflections in the range 24 to 32 in 2θ were used and orientation matrix was determined providing for a well oriented cell with a volume of 1189. The data were collected for a monoclinic cell. A high-chi reflection was scanned to provide for an absorption correction, reducing the equivalency disagreement from 9% to 3%. The decay was negligible. Reduction of the data was carried out using XCAD4 and all further work was carried out using the Siemens version of SHELX. The structure was solved primarily from the Patterson map as refinement on the Re was obtained. The weighting scheme required a correction of 0.005. Hydrogens were introduced by calculation. The methyl carbon attached to the Re atom showed a large ellipsoid and by modeling disorder of the hydrogens bonded to the carbon it was considerably reduced.
The accuracy of the results are generally not affected by mosaictiy but the statistics lead to rather larger than normal errors. A final R of 6.3% with a GOF of 1.14 was obtained.
Notes to Chapter 4.


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Appendix A

Supplementary X-ray Data for

\[ \left( \eta^5\text{-C}_5\text{H}_4\text{-Si(CH}_3)_2\text{-}\eta^5\text{-C}_5\text{H}_4 \right)\text{ReCH}_3 \]
Table 1. Atomic coordinates ($\times 10^5$) and equivalent isotropic displacement coefficients ($\AA^2 \times 10^4$)

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* Equivalent isotropic U defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.
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### Table 4. Anisotropic displacement coefficients (Å² x 10^4)

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The anisotropic displacement exponent takes the form:

\[-2x^2(h^2a^2U_{11} + \ldots + 2hka*b^2U_{12})\]
Table 5. H-Atom coordinates ($x10^4$) and isotropic displacement coefficients ($A^2x10^3$)

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Catherine E. Radzewich was born July 18, 1970 in Long Beach, California. She attended Western Washington University in Bellingham, Washington from which she earned a Bachelor of Science in Chemistry in June 1992. In the fall of 1992, she began graduate work in chemistry at the University of Washington. Under the guidance of Professor D. M. Heinekey, she earned a Doctor of Philosophy in Inorganic Chemistry in February of 1997.