Activation of Small Molecules by Cationic Rhenium Complexes

by

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Abstract

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Thermolysis of $ReX(CO)_5$ (X = CH_3 or H) with PPh_3 and P^iPrPh_2 in toluene generates *trans-mer*-$Re(X)(PR_3)_2(CO)_3$ complexes. Protonation of *trans-mer*-$Re(X)(PR_3)_2(CO)_3$ with $[H(Et_2O)_2]B(Ar')_4$ (Ar' = $3,5(CF_3)_2C_6H_3$) under an H_2 atmosphere generates stable dihydrogen complexes, $[Re(H_2)(PR_3)_2(CO)_3]B(Ar')_4$ (PR_3 = PPh_3 (**4a**), P^iPrPh_2 (**4b**)). The large J_{HD} values (**4a** = 32 Hz, **4b** = 30 Hz) and short 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, $[Re(PR_3)_2(CO)_3]B(Ar')_4$ (**5**). Complexes **4** and **5** react with a variety of small molecules to form $[ReL(PR_3)_2(CO)_3]B(Ar')_4$ (L = H_2O, NH_3, C_2H_4, N_2, CO, Cl^-, PPh_3, THF).

$[Ph_3C]B(Ar')_4$ reacts with Cp_2ReCH_3 and $Cp_2ReCH_2CH_3$ to abstract an α-hydride from the alkyl ligand to generate carbene complexes, $[Cp_2Re{=}CH_2]B(Ar')_4$ (**1**) and $[Cp_2Re{=}CH(CH_3)]B(Ar')_4$ (**3**). Both complexes **1** and **3** decompose to $[Cp_2Re(C_2H_4)]^+$ and $[Cp_2Re(NCCD_3)]^+$ in acetonitrile upon addition of BF_4^- salts or thermolysis of the solutions at 50 °C for two weeks. $[Cp_2Re(CH_3)H]B(Ar')_4$ eliminates methane at 0 °C in CH_2Cl_2 to generate $[Cp_2Re(CH_2Cl)Cl]B(Ar')_4$. Addition of $[Me_3O]BF_4$ to Cp_2ReR (R = CH_3, CH_2CH_3, CH_2SiMe_3) in acetonitrile forms stable bis-alkyl complexes, $[Cp_2Re(CH_3)R]BF_4$.

$[Cp_2Re{=}CH_2]B(Ar')_4$ (1) reacts with triphenylphosphine and pyridine to generate ylide complexes. Complex 1 reacts with Cl_2, Br_2, I_2 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 η^2-formaldehyde, η^2-thioformaldehyde and η^2-olefin complexes.

The addition of Me_2SiCl_2 or $(Me_2Si)_2Cl_2$ to a THF solution of $(\eta^5\text{-}C_5H_4Li)_2ReCH_3$ gives *ansa*-bridged complexes with a single or double silicon linker. A X-ray diffraction study was undertaken to confirm the structure of $(\eta^5\text{-}C_5H_4\text{-}SiMe_2\text{-}\eta^5\text{-}C_5H_4)ReCH_3$. Substituted derivatives of Cp_2ReX (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 $[(\eta^5\text{-}C_5H_4\text{-}SiMe_2\text{-}\eta^5\text{-}C_5H_4)Re(CH_3)H]B(Ar')_4$ has been observed to be more stable at room temperature then analogous complexes.

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ABBREVIATIONS AND SYMBOLS

Å	angstrom
atm	atmosphere
$B(Ar')_4^-$	$B(3,5\text{-}(CF_3)_2C_6H_3)_4^-$
br	broad
Cp	cyclopentadienyl, $(\eta^5\text{-}C_5H_5)$-
Cp^*	pentamethylcyclopentadienyl, $(\eta^5\text{-}C_5(CH_3)_5)$-
Cp'	methylcyclopentadienyl, $(\eta^5\text{-}C_5H_4(CH_3))$-
Cy	cyclohexyl
Cyp	cyclopentyl
d	doublet
δ	chemical shift in ppm (NMR) or bending frequency (IR)
$\Delta G^{\ddagger}_{rot}$	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
ν	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", 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
τ	lifetime
^{t}Bu	*tert*-butyl
THF	tetrahydrofuran
TMEDA	tetramethylethylenediamine
TMS	tetramethylsilane
triphos	1,1,1-tris(diphenylphosphino)ethane

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

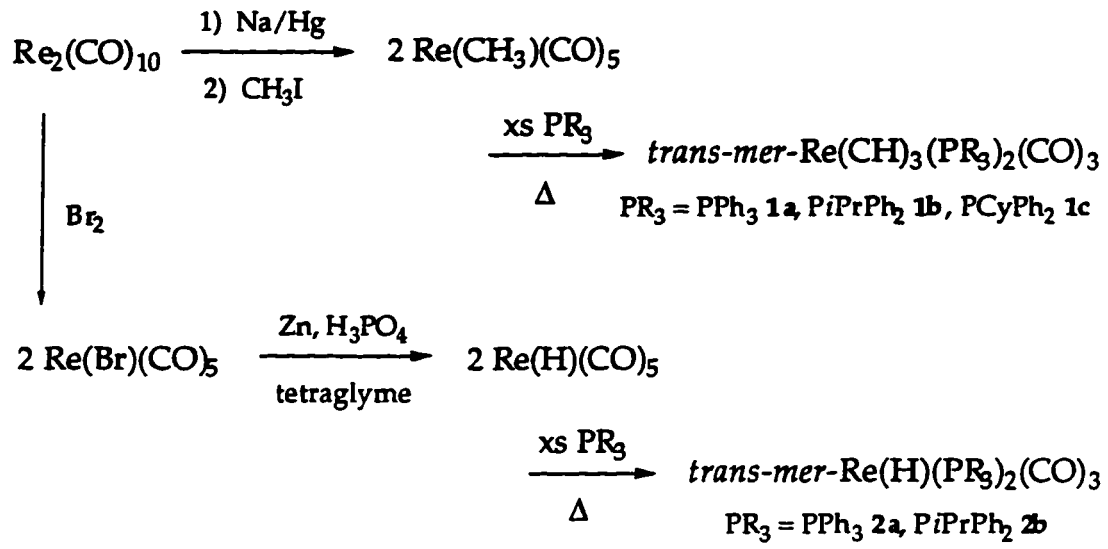
Since their initial discovery by Kubas,[1] H_2 complexes of transition metals have been the subject of intensive study by several research groups.[2] Cationic dihydrogen complexes, conveniently formed by protonation of neutral hydrides or by other routes, are now numerous. Recently, there have been several 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,[4,5] 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 $M(H_2)(PR_3)_2(CO)_3$ (M = W, Mo, Cr; PR_3 = PCy_3, P^iPr_3, $PCyp_3$),[1,10] the Heinekey group has embarked on a study of related Group 7 cationic analogs. A previous report of $[Re(H_2)(PMe_3)_2(CO)_3]BF_4$[11] 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 $[Re(H_2)(PCy_3)_2(CO)_3]BF_4$[12] also decomposes at low temperatures. We now report that the use of more weakly coordinating anions[13,14] 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*-$Re(H_2)(PR_3)_2(CO)_3$]$B(Ar')_4$ (PR_3 = PCy_3, P^iPr_3).[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 PCy_3 and P^iPr_3 analogs will also be presented. The Heinekey group has recently reported on a closely related series of dihydrogen complexes of the form, $[Re(H_2)(PR_3)_2(CNtBu)_3]^+$ (PR_3 = PCy_3, PPh_3), 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 $Re(X)(PR_3)_2(CO)_3$ (X = CH_3 (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 $Re(CH_3)(CO)_5$ or $Re(H)(CO)_5$ with excess phosphine in a thick walled glass vessel.



Scheme 1.1

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.[17] 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.[18,19]

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 stereochemical configurations depending upon conditions, phosphine, and X

group. Previous experiments from this group involved the thermolysis of $ReCH_3(CO)_5$ with PCy_3 and P^iPr_3 ligands. The reaction conditions required a higher temperature (130 °C) and longer reaction times (up to 140 hours). The isolated yield of $Re(CH_3)(PCy_3)_2(CO)_3$ was only 50% and can include up to 50% contamination by $ReH(PCy_3)_2(CO)_3$, 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, PPh_3 (145°) to PCy_3 (170°), produced complexes with trans phosphine 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 $^{31}P\{^1H\}$ NMR spectra show a single phosphorus signal for each complex. A typical $^{13}C\{^1H\}$ 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 phosphine ligands. The stereochemistry of the product was confirmed in one case by a crystal structure of $Re(CH_3)(PPh_3)_2(CO)_3$ (**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 $Re(Cl)(PR_3)_2(CO)_3$ in $CHCl_3$ or CH_2Cl_2 over a period of days (PR_3 = $PiPrPh_2$, PPh_3). The deuteride, $Re(D)(PiPrPh_2)_2(CO)_3$, can be formed by heating the hydride at 130 °C with several equivalents of D_2O in toluene.

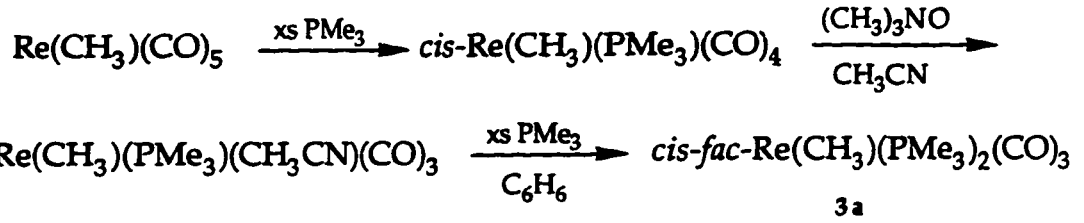
Table 1.1. Selected ^{1}H, $^{31}P\{^{1}H\}$ NMR and IR Data for Compounds **1** and **2**.

Compound	**1a**	**1b**	**2a**	**2b**
δ(M-CH_3)[a]	-1.06	-1.12		
δ(M-H)[a]			-5.20	-5.94
J_{PH}[b]	6.7	6.6	17.8	18.8
$\delta\,^{31}P$[a]	16.8	19.7	22.8	29.6
νCO(cm^{-1})[c]	2018(w),1915(s) 1878(m)	2018(w),1920(s) 1871(m)	2020(w),1925(s)	2020(w),1919(s)

[a] ^{1}H and $^{31}P\{^{1}H\}$ NMR chemical shifts in ppm, recorded at 298 K in $CDCl_3$ (**1a-b**) and C_6D_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° - PCy_3 170°). 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 °C over several days shows little further reaction. When heating was continued at 100 °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.

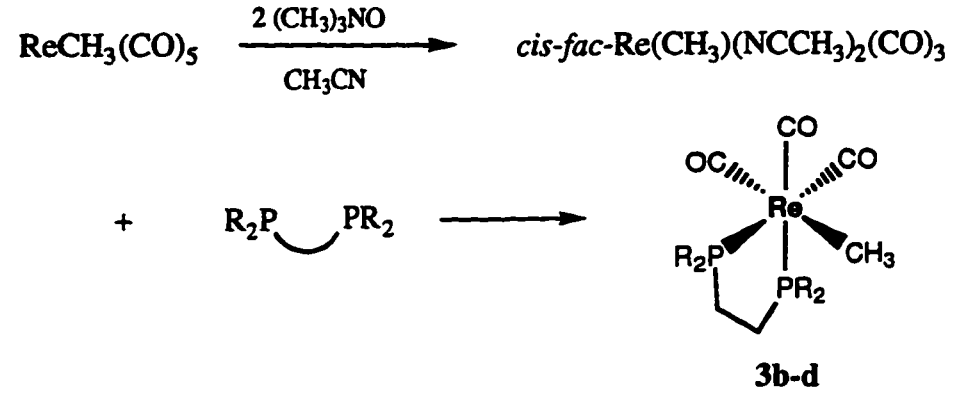
Recently, *cis-fac*-$Re(CH_3)(PPh_3)_2(CO)_3$ has been prepared by Bergman and Simpson by another synthetic method.[20] This method allows the addition of a second phosphine at low temperature by replacing a weakly bound CH_3CN instead of a more strongly coordinated CO. The synthesis of *cis-fac*-$Re(CH_3)(PMe_3)_2(CO)_3$ (**3a**) has been achieved in a similar method as outlined in Scheme 1.2.



Scheme 1.2

Addition of the first PMe_3 to $Re(CH_3)(CO)_5$ 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 CO_2 by nucleophilic attack at a carbonyl ligand. When this reaction is run in CH_3CN, the solvent will bind in place of the displaced CO ligand. The acetonitrile ligand is easily displaced upon addition of excess PMe_3 in benzene. The *cis-fac* configuration of the bisphosphine-substituted complex is confirmed by IR ν_{CO} 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 $ReCH_3(CO)_5$ in CH_3CN produces a new compound after stirring for 24 hours. The IR spectrum of the compound in CH_3CN 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 CH_3CN 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 ($Ph_2PCH_2CH_2PPh_2$), dcpe ($Cy_2PCH_2CH_2PCy_2$), and dnpe (($^tBuCH_2)_2PCH_2CH_2P(CH_2{}^tBu)_2$) 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.



Scheme 1.3

Table 1.2. IR Bond Stretching Frequencies of Related Neutral Carbonyl Complexes.

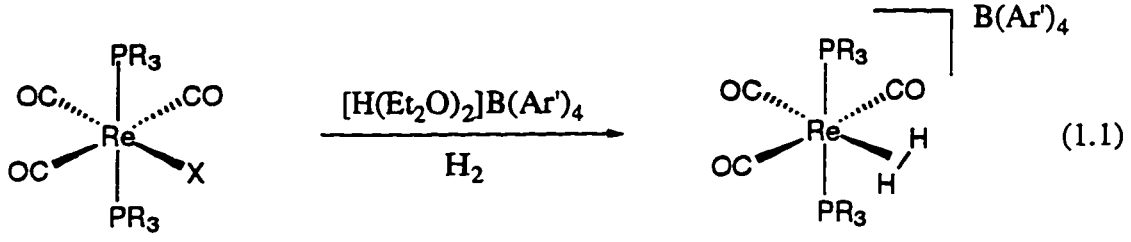
Compound	ν_{CO} (cm^{-1})[a]
cis-$ReCH_3(PMe_3)(CO)_4$	2073(w), 1983(s), 1967(vs), 1932(s)
cis-mer-$ReCH_3(CH_3CN)_2(CO)_3$	2006(s), 1925(s), 1892(s)
cis-mer-$ReCH_3(PMe_3)(CH_3CN)(CO)_3$	1999(s), 1902(s), 1874(s)
cis-mer-$Re(CH_3)(PMe_3)_2(CO)_3$ (**3a**)	2007(s), 1923(s), 1885(s)
cis-mer-$Re(CH_3)(PPh_3)_2(CO)_3$ (THF)	2005(s), 1922(s), 1885(s)[b]
cis-mer-$Re(CH_3)$(dppe)$(CO)_3$ (C_7H_8) (**3b**)	2006(s), 1925(s), 1892(s)
cis-mer-$Re(CH_3)$(dnpe)$(CO)_3$ (C_7H_8) (**3c**)	2000(s), 1915(s), 1876(s)
cis-mer-$Re(CH_3)$(dcpe)$(CO)_3$ (**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 *cis-mer-* $ReBr(PMe_3)_2(CO)_3$ at 150 °C for 10 hours affords *trans-mer-* $ReBr(PMe_3)_2(CO)_3$.[21] We have observed that heating *cis-mer*-$Re(CH_3)(PMe_3)_2(CO)_3$

does not show any reaction after several days at 50 °C and further heating to 100 °C leads to decomposition. However, *cis-mer*-$Re(CH_3)(PPh_3)_2(CO)_3$ can be cleanly converted to *trans-mer*-$Re(CH_3)(PPh_3)_2(CO)_3$ after several days at 50 °C. The lower barrier to isomerization for the PPh_3 complexes is consistent with a dissociative process which is preferred for the bulkier phosphine. Bergman and Simpson have shown that *cis-mer*-$Re(CH_3)(PPh_3)_2(CO)_3$ reacts with phenol and other alcohols by dissociation of a phosphine prior to coordination of the phenol.[20] The cis phosphines are quite labile due to the steric congestion in *cis-mer*-$Re(CH_3)(PPh_3)_2(CO)_3$ and consequently we found that the trans isomer shows no reaction with phenol under similar conditions.

Synthesis and Characterization of $[Re(H_2)(PR_3)_2(CO)_3]B(Ar')_4$ (PR_3 = PPh_3, 4a; $PiPrPh_2$, 4b). Protonation of complexes **1a,b** or **2a,b** with $[H(Et_2O)_2]B(Ar')_4$ under a hydrogen atmosphere in CH_2Cl_2 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 CD_2Cl_2.



(1.1)

X = CH_3 **1a,b**;
H **2a,b**

4a,b

Table 1.3 lists selected ^1H NMR data for the hydride region as well as data previously collected for the related PCy_3 (**4c**) and P^iPr_3 (**4d**) analogs.[22] All of the dihydrogen complexes are thermally robust and are stable indefinitely in halogenated solvents (CD_2Cl_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 ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. No change is observed for complexes **4a** and **4b** in the ^1H or $^{31}P\{^1H\}$ 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 1.3. ^1H NMR Data of the Hydride Region for Compounds **4a–4d**.[a]

Compound	δ(HH)[b]	δ(HD)[b]	J_{HD}[c]	Δδ[d,e]	T_{1min}[e,f]	$\Delta\nu_{1/2}$[e,j]
$[Re(H_2)(PPh_3)_2(CO)_3]^+$ **(4a)**	–3.86	–3.89	32	30	10.3[i]	54
$[Re(H_2)(PiPrPh_2)_2(CO)_3]^+$ **(4b)**	–4.26	–4.29	30	30	10.5[i]	52
$[Re(H_2)(PCy_3)_2(CO)_3]^+$ **(4c)**	–4.78	–4.81	32	34	9.3[g]	49
$[Re(H_2)(PiPr_3)_2(CO)_3]^+$ **(4d)**	–4.97	–5.01	33	37	9.6[h]	23

[a] All measurements recorded at 298 K in CD_2Cl_2 except where noted. [b] Chemical shift in ppm. [c] Coupling constant in Hz. [d] Isotope shift (Δδ = δ(HH) – δ(HD)) in ppb. [e] Recorded in a 500 MHz field. [f] T_{1min} 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_{HD} coupling due to the HD ligand. The observed ^1H 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 P^iPr_3 (**4d**) analogs were collected at 500 MHz in CD_2Cl_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_{1min} values for the neutral hydrides, **2a** and **2b**. Luo and coworkers have previously reported the variable temperature ^1H NMR T_1 data for $ReH(PPh_3)_2(CO)_3$ (**2a**).[18] They have observed the T_{1min} of 177 ms at 203 K in CD_2Cl_2 (250 MHz). The T_{1min} is proportional to the field of the magnet and the value becomes 354 ms at 500 MHz. We have determined the T_{1min} of $ReH(PiPrPh_2)_2(CO)_3$ (**2b**) to be 325 ms at 217 K in CD_2Cl_2 (500 MHz). The long T_{1min} 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_{1min} 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_{1min} 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_{HD} values greater than 25 Hz as well as reported T_{1min} 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 1.4 H-H Bond Lengths from T_{1min} Data in the Limit of Slow and Fast Rotation.

Compound	H–H (Å) slow rotation	H–H (Å) fast rotation
$[Re(H_2)(PPh_3)_2(CO)_3]^+$ (**4a**)[a,b]	0.95	0.75
$[Re(H_2)(P^iPrPh_2)_2(CO)_3]^+$ (**4b**)[a,c]	0.95	0.76
$[Re(H_2)(PCy_3)_2(CO)_3]^+$ (**4c**)	0.97	0.77
$[Re(H_2)(P^iPr_3)_2(CO)_3]^+$ (**4d**)	0.97	0.77

[a] Corrected for neutral hydride relaxation. [c] Measurement of the T_{1min} 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_{1min} of $Re(H)(PiPrPh_2)_2(CO)_3$ was 325 ms at 217 K in a 500 MHz field (CD_2Cl_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_{HD} values. Theoretical calculations by Hush and coworkers have also revealed a linear relationship between J_{HD} values and H–H distances.[28]

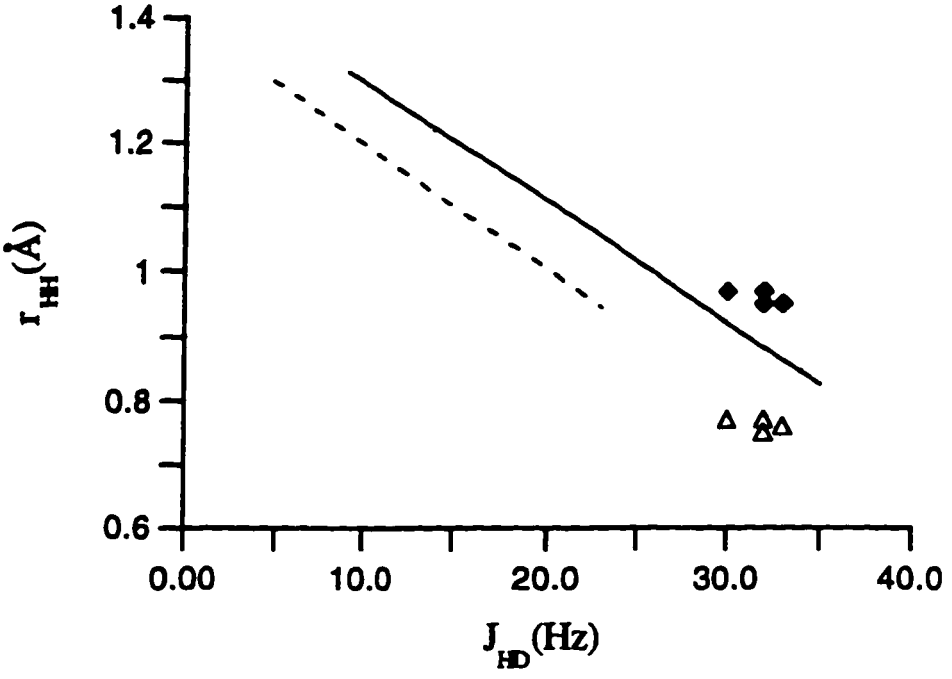


Figure 1.1. Plot of H–H bond distance (Å) versus J_{HD} (Hz). The solid line results from experimental data tabulated by Heinekey[2a] and Morris[27] for compounds with known H–H bond distances as determined by solid state NMR or neutron diffraction methods. The dashed line results from calculated bond 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_{1min} data for complexes **4a-d** (◆ = slow rotation) (Δ = 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_{1min} data. Surprisingly, 0.89Å 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

$[Mn(H_2)(CO)(dppe)_2]B(Ar')_4$[6] and 0.88 Å for the analogous neutral complex $Mo(H_2)(CO)(dppe)_2$ (dppe = $Ph_2PC_2H_4PPh_2$).[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 dicationic Os complexes, $[Os(NH_3)_4L(\eta^2\text{-}H_2)]^{n+}$, 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*-$Re(CH_3)P_2(CO)_3$ (P_2 = $(PMe_3)_2$ (3a), dppe (3b), dcpe (3c), dnpe (3d)). Addition of $[H(Et_2O)_2]B(Ar')_4$ to complexes **3a-d** under an H_2 atmosphere did not lead to new dihydrogen complexes. The ^1H NMR spectra did not reveal signals for coordinated hydrogen and the $^{31}P\{^1H\}$ 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 $M(CO)_5(H_2)$ (M = W, Mo, Cr)

complexes by matrix isolation methods.[31] Previous attempts have been made in the Heinekey group to synthesize $[Re(H_2)(CO)_5]^+$ by low temperature protonation of $ReH(CO)_5$.[32] A dihydrogen complex was never observed by ^1H NMR spectroscopy. Apparently these dihydrogen complexes are unstable due to the lack of sufficient backbonding from the electron poor metal center to the σ^* orbital of the dihydrogen ligand. In a similar system in which the carbonyl ligands are replaced by more basic isonitrile ligands, $[Re(H_2)(CN^tBu_3)_5]^+$ was observed at low temperature but was too unstable to isolate.[16] The greater stability of the $[Re(H_2)(CN^tBu_3)_5]^+$ complex is consistent with greater backbonding to the σ^* orbital of the dihydrogen ligand compared to the carbonyl complexes, but decomposition likely results by the inability of the CN^tBu ligands to provide an agostic interaction upon H_2 liberation.

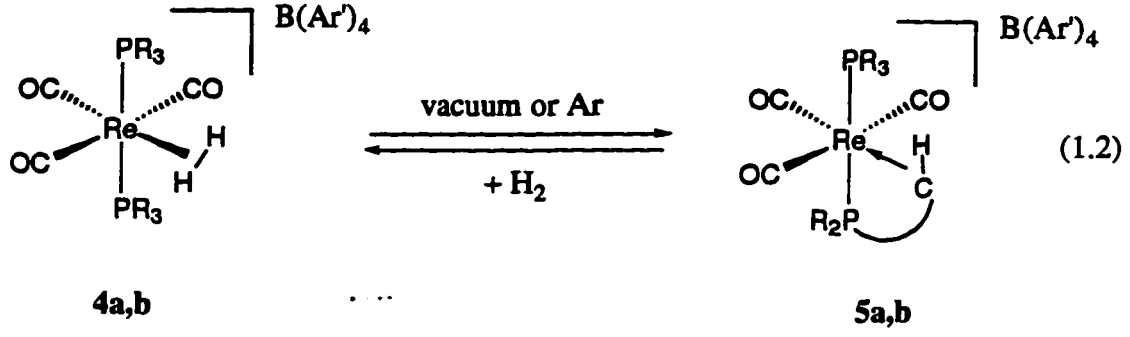
Kubas and coworkers have reported several studies upon the rotational barrier of the dihydrogen ligand when coordinated to various Group 6 complexes. The barrier is directly affected by the amount of π donation to the H_2 ligand rather than the σ bond which is considered more significant in the strength of the M-H_2 bond. In the most stable configuration for $W(P^iPr_3)_2(CO)_3(H_2)$, as evidenced by neutron diffraction, the H_2 molecule lies along the P-M-P axis. Rotation of the H_2 ligand by 90° would line the σ^* orbital along the same filled metal d orbital that is backbonding to the CO ligands. The orientation of the 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 π-back-bonding.

Another factor which may lead to unstable H_2 complexes is the instability of the complexes upon H_2 liberation. Complexes **4a-d** have been observed to have very labile H_2 ligands and a stable agostic complex is generated (*vide infra*) upon H_2 loss. Although complexes of the type *cis-mer*-$MP_2(CO)_3^{n+}$ (n = 0 (Cr, Mo, W); +1 (Mn, Re)) have not been investigated, $[Mn(dppe)_2(CO)]B(Ar')_4$ and $Mo(dppe)_2(CO)$ have been characterized

by X-ray crystallography and contain agostic interactions with an *ortho* -hydrogen of the phosphine ligand.[6,33] 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_2Cl_2 solution of the dihydrogen complex leads to immediate formation of the neutral hydride, $ReH(PCy_3)_2(CO)_3$.[34] The strong base KO*t*Bu will also deprotonate the dihydrogen complex, but only over the course of several days due to its low solubility in CD_2Cl_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 pentafluropyridine 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 $[H(Et_2O)_2]B(Ar')_4$ 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).



4a,b **5a,b** (1.2)

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}H and $^{31}P\{^{1}H\}$ 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_2O 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 (*vide infra*). These reactions are conveniently monitored by $^{31}P\{^{1}H\}$ 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 $[Re(PR_3)_2(CNtBu)_3]^+$ and $W(PR_3)_2(CO)_3$, 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 $ReCH_3(PR_3)_2(CO)_3$ with $[H(Et_2O)_2]B(Ar')_4$ in CD_2Cl_2. We have observed that the agostic complexes will undergo moderate to strong bonding of H_2O and THF and considered that the excess Et_2O in solution could behave as a potential ligand. The Et_2O can be removed from solutions of **5a** and **5b** by addition of CH_2Cl_2 followed by removal of the volatiles *in vacuo*. This process is repeated several times and the resulting ^1H NMR spectra indicate the absence of Et_2O in solution. The $^{31}P\{^1H\}$ NMR of the agostic complexes is invariant in the presence or absence of Et_2O.

Complexes **5a** and **5b** are soluble and stable in halogenated solvents. The $^{31}P\{^1H\}$ NMR chemical shifts for these complexes do not show a significant shift upon changing solvent (CD_2Cl_2, $CDCl_3$ or 1,2-$C_6F_2H_4$). There have been several recent reports on coordination of methylene chloride as well as complexes which oxidatively add CH_2Cl_2 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 $^{13}C\{^1H\}$ NMR spectrum of $[Cp^*Re(NO)(PPh_3)(ClCH_2Cl)]BF_4$ is associated with a bound CH_2Cl_2 and can be distinguished from the resonance for free CH_2Cl_2.[36a] We investigated the low temperature $^{13}C\{^1H\}$ NMR spectra of $[Re(PR_3)_2(CO)_3]B(Ar')_4$ in CH_2Cl_2 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^iPrPh_2) with $[Ph_3C]B(Ar')_4$. 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_2O_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 $[H(Et_2O)_2]B(Ar')_4$ 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 $^{31}P\{^1H\}$ NMR spectra. Recent reports from the Brookhart and Schrock groups have also observed difficulties in the attempted synthesis of cationic Et_2O complexes by protonation with $[H(Et_2O)_2]B(Ar')_4$.[37,38] These complexes are also very sensitive to the presence of water and it appears that $[H(Et_2O)_2]B(Ar')_4$ 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 $[Ph_3C]B(Ar')_4$ toward rhenium methyl and hydride complexes. Preliminary results indicate that $[Ph_3C]^+$ 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 $^{31}P\{^1H\}$ 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 ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. This seems to indicate that there is a possible interaction between the Ph_3CH or Ph_3CCH_3 that is formed and the five-coordinate cations. Attempts were made to isolate $[Re(P^iPrPh_2)_2(CO)_3]^+$ in a scaled up synthesis by recrystallization from CH_2Cl_2/pentane. After rinsing the product several times with pentane, the solid did become slightly orange and a ^1H NMR spectra of the filtrate indicated the formation of Ph_3CH. There is some precedence for coordination of Ph_3CH in an η^2-arene fashion by cationic rhenium complexes.[39,40] These complexes have been observed to have distinct ^1H NMR resonances for the hydrogens of the coordinated phenyl group. Contrary to this we have not observed any unusual resonances in the ^1H NMR spectra to indicate this type of coordination. Perhaps further investigation with a bulkier trityl reagent[41] with a ^{t}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; PCy_3, 6c). An $HCl{\cdot}Et_2O$ solution was added to $Re(CH_3)(PR_3)_2(CO)_3$ (PR_3 = PPh_3, PCy_3) in toluene or CH_2Cl_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 $^{31}P\{^1H\}$ 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 $ReCl(PCy_3)_2(CN^tBu)_3$ by H_2. We have conducted preliminary reactivity studies of the corresponding chloride

complexes in the carbonyl system. $ReCl(PCy_3)_2(CO)_3$ does not react in CD_2Cl_2 with ligands such as H_2 (3 atm) or CO (0.8 atm) and appears to be indefinitely stable in CD_2Cl_2. $ReCl(PCy_3)_2(CO)_3$ does react with $NaB(Ar')_4$ and gives quantitative formation of $[Re(PCy_3)_2(CO)_3]B(Ar')_4$ (**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 H_2 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 = $Ph_2PCH_2CH_2PPh_2$) reacts with $NaB(Ar')_4$ in CH_2Cl_2 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. $ReCl(PPh_3)_2(CO)_3$ (**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 $[Re(PPh_3)_2(CO)_3]B(Ar')_4$ (**5a**) was observed after 48 hours at room temperature. Heating this reaction caused extensive decomposition. $ReCl(P^iPrPh_2)_2(CO)_3$ (**6b**) has been observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy by reaction of HCl(g) with a CD_2Cl_2 solution of $Re(CH_3)(P^iPrPh_2)_2(CO)_3$ (**1b**).

Stability of Dihydrogen Complexes: H_2 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 $[Re(H_2)(PR_3)_2(CO)_3]^+$ system, that the choice of acid to form the dihydrogen complexes is crucial to their stability. The labile dihydrogen ligands in $[Re(H_2)(PR_3)_2(CO)_3]^+$ (**2**) can be easily displaced by anionic ligands such as chloride and triflate.[22] Even BF_4^-, which is often considered an unreactive anion, led to the

decomposition of **4c** at low temperature.[12] The use of the less reactive anion, $B(Ar')_4^-$, has allowed the formation of a stable series of dihydrogen complexes, $[Re(H_2)(PR_3)_2(CO)_3]B(Ar')_4$.

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 1.5 IR Bond Stretching Frequencies of Related Cationic Carbonyl Complexes.

Compound	ν_{CO} (cm^{-1}, Nujol)
$[Re(CO)_4(PPh_3)_2]^+$ (**7a**)	2002
$[Re(CO)_4(PCy_3)_2]^+$ (**7c**)	1983
$[Re(CO)(PCy_3)_2(CNtBu)_3]^+$ [43]	1900
$W(CO)_4(PiPr_3)_2$ [10c]	1870

There is now a large series of closely related cationic rhenium dihydrogen complexes which have been studied by several different research groups.[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 π acidic isonitrile ligands the reactivity is dramatically different. Not only is $[Re(H_2)(PCy_3)_2(CNtBu)_3]^+$ stable with a wider variety of anions, but the cationic dihydrogen complex can also be formed by chloride displacement from $ReCl(PCy_3)_2(CNtBu)_3$ by H_2.[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 nucleophillic anions such as BF_4^- and CF_3COO^-. Three of the complexes listed in Table 1.6 are reported to be thermally unstable and have only been investigated by low temperature ^1H 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 $W(H_2)(P^iPr_3)_2(CO)_3$ can briefly withstand dissolution in CD_2Cl_2 at low temperature (< –20 °C).[25] Even the rhenium isonitrile complexes, $[Re(H_2)(PCy_3)_2(CNtBu)_3]^+$, 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, $[ReCl(PCy_3)_2(CNtBu)_3]^+$, which forms by decomposition of $[Re(PCy_3)_2(CNtBu)_3]^+$ in chlorinated solvents (CD_2Cl_2, $CDCl_3$, $CDFCl_2$).[16] Similarly, $W(PCy_3)_2(CO)_3$ can also be oxidized by one electron to form a neutral 17 electron halide complex, $WI(PCy_3)_2(CO)_3$.[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 1.6. Reactivity of Related Dihydrogen Complexes.

Compounds	H_2 Lability	Halogentated Solvent	Dihydride Formation	Anions	Base
$W(H_2)(PCy_3)_2(CO)_3$[a]	labile	stable < –20 °C	equilibrium	—	Cu alkoxide
$[Re(H_2)(PCy_3)_2(CO)_3]^+$ (4c)	labile	stable	none	$B(Ar')_4^-$	(see text)
$[Re(H_2)(PCy_3)_2(CNtBu)_3]^+$[e]	slowly labile	stable for a few days	none	Cl^-, OTf^-, BF_4^-	KO*t*Bu
$[triphosRe(H_2)(CO)_2]^+$[b]	med. labile	stable	none	BF_4^-	NEt_3
$[Re(H_2)(PMe_3)_2(CO)_3]^+$[c]	thermally unstable	—	none	CF_3COO^-	—
$[Re(H_2)(PMe_3)_3(CO)_2]^+$[c]	thermally unstable	—	none	CF_3COO^-	—
$[Re(H_2)(PMePh_2)_3(CO)_2]^+$[d]	thermally unstable	—	equil/dihydride at higher T	BF_4^-	NEt_3
$[ReH_2(PMePh_2)_4(CO)]^+$[d]	no H_2 loss	stable	dihydride	BF_4^-	KOH
$[ReH_2(PMe_3)_4(CO)]^+$[c]	no H_2 loss	stable	equil/dihydride at RT	CF_3COO^-	—

[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 $W(PCy_3)_2(CO)_3$.[10g] 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 $[Re(H_2)(PCy_3)_2(CO)_3]^+$ (**4c**). This reactivity is similar to that observed for related rhenium dihydrogen complexes with phosphine and carbonyl coligands. Both $[triphosRe(H_2)(CO)_2]^+$ and $[Re(H_2)(PMePh_2)_3(CO)_2]^+$ are deprotonated by NEt_3. 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 $W(H_2)(PCy_3)_2(CO)_3$ and $[Re(H_2)(PCy_3)_2(CN^tBu)_3]^+$ are only weakly acidic and strong bases such as a copper alkoxide[10m] and KO^tBu[16], 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_{1min} data and J_{HD} values. The nature of the ligands also has a dramatic affect upon the acidity of the dihydrogen complex since $[Re(H_2)(PCy_3)_2(CN^tBu)_3]^+$ does not react with 1,8-bis(dimethylamino)napthalene and is deprotonated only using a large excess of KO^tBu. 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 frequences 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_{1min} data or J_{HD} values.

Reactivity of $[Re(PR_3)_2(CO)_3]B(Ar')_4$ (5a,b,c) with O_2 and CO: Formation of $[Re(PR_3)_2(CO)_4]B(Ar')_4$ (PR_3 = PPh_3, 7a; *P*i–$PrPh_2$, 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. $^{31}P\{^1H\}$ NMR spectra indicate the formation of several species, including peaks that correspond to the water complexes. In a scaled up reaction, a solution of $[Re(PPh_3)_2(CO)_3]B(Ar')_4$ in CH_2Cl_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 $^{31}P\{^1H\}$ 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

$^{13}C\{^1H\}$ 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 ^1H or $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ 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. $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ 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_2O was added to a CH_2Cl_2 solution of [Re(P*i*–

$PrPh_2)_2(CO)_3]B(Ar')_4$ 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 $^{31}P\{^1H\}$ 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 H_2O, a triplet at 1.45 ppm is observed for the bound H_2O with a 1.4 Hz coupling to the phosphines. Low temperature ^1H and $^{31}P\{^1H\}$ 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 H_2O with an ν(OH) at 3562(w) cm^{-1} and δ(HOH) at 1608(m) cm^{-1}. **8b** does not react in CD_2Cl_2 with a full atmosphere of H_2, but does react with CO to give $[Re(Pi–PrPh_2)_2(CO)_4]B(Ar')_4$ and free H_2O. The aquo complexes are oxygen sensitive in solution and $[Re(PR_3)_2(CO)_4]B(Ar')_4$ is the main decomposition product. $[Re(OH_2)(PR_3)_2(CO)_3]B(Ar')_4$ (PR_3 = PCy_3, P^iPr_3) have been previously characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR.[45] The coordinated water in these complexes is much more labile compared to complexes **8a** and **8b** and can be partially displaced by H_2 to form the dihydrogen complexes and free water.

Synthesis of $[Re(NH_3)(PCy_3)_2(CO)_3]B(Ar')_4$ (9c). Both $[Re(H_2)(PCy_3)_2(CO)_3]^+$ (**4c**) and $[Re(PCy_3)_2(CO)_3]^+$ (**5c**) will react with NH_3 in the solid state or in solution. The addition of NH_3 (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 $^{31}P\{^1H\}$ NMR spectra indicate the clean formation of a new complex. The resonance for bound NH_3 was not located in the ^1H NMR spectrum and is presumably obscured by the cyclohexyl resonances. The ^2H NMR spectrum of $Re(ND_3)(PCy_3)_2(CO)_3]B(Ar')_4$ in CH_2Cl_2

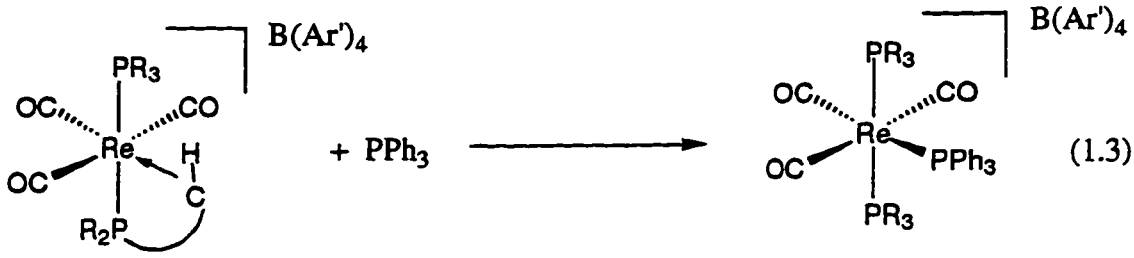
shows a broad resonance at 2.03 ppm. An IR spectrum of **9c** as a Nujol mull shows three bands at 2047(w), 1942(s) and 1934(m) for the carbonyl ligands and bands for the NH_3 ligand for ν(NH) at 3375(w) and 3300(w) cm^{-1} and a bending band, δ(NH_3), at 1612(m) cm^{-1}. When a solution of **9c** in CD_2Cl_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_2H_4. When ethylene (300 torr) was added to a CD_2Cl_2 solution of **5c**, the color changed from a bright orange to pale orange. The $^{31}P\{^1H\}$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, $[Re(C_2H_4)(PCy_3)_2(CO)_3]B(Ar')_4$ (**10c**). By cooling the sample to 10 °C only the $^{31}P\{^1H\}$ NMR resonance for **10c** remained. Warming to room temperature regenerated the agostic complex, **5c**. The ^1H NMR spectrum shows a broad resonance at 3.3 ppm in addition to free ethylene, the cyclohexyl, and anion resonances. The ^2H NMR spectrum of $[Re(C_2D_4)(PCy_3)_2(CO)_3]B(Ar')_4$ (**10c**-*d*$_4$) in CH_2Cl_2 show resonances for both free C_2D_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 $[H(Et_2O)_2]B(Ar')_4$ 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 $^{31}P\{^1H\}$ NMR spectrum of the compound in CD_2Cl_2 does not show any resonances and presumably the resonance is exchange broadened due to the labile THF. When

$[Re(THF)(PCy_3)_2(CO)_3]B(Ar')_4$ (**11c**) is placed under a H_2 atmosphere in CD_2Cl_2, **4c** is generated quantitatively. Complex **11c** reacts in THF-d_8 to form $[Re(PCy_3)_2(CO)_4]B(Ar')_4$ (**7c**) when pressurized with 400 torr of CO. Heating the solid **11c** at 100 °C for 2 days under dynamic vacuum or recrystallization from CH_2Cl_2/pentane removes the bound THF and a subsequent $^{31}P\{^1H\}$ NMR spectrum shows only **5c**.

Reactivity of $[Re(PPh_3)_2(CO)_3]B(Ar')_4$ (5a) with PPh_3. **5a** reacts with excess PPh_3 to generate [*mer*-$Re(PPh_3)_3(CO)_3]B(Ar')_4$ (**12a**). The $^{31}P\{^1H\}$ 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 J_{PP} = 18.5 Hz is consistent with a cis phosphorus coupling.



5a **12a** (1.3)

Conclusions

The thermolysis of toluene solutions of $ReX(CO)_5$ (X = CH_3 or H) in the presence of PPh_3 or P^iPrPh_2 generates *trans-mer*-$Re(X)(PR_3)_2(CO)_3$ complexes. Protonation of the neutral methyl or hydride complexes with $[H(Et_2O)]B(Ar')_4$ under an H_2 atmosphere generates stable dihydrogen complexes, $[Re(H_2)(PR_3)_2(CO)_3]B(Ar')_4$, which have been characterized by ^1H NMR spectroscopy. Large HD coupling constants

and short T_{1min} values are consistent with a dihydrogen formulation. These dihydrogen complexes are similar to their PCy_3 and P^iPr_3 analogs and there is no evidence that changing the sterics 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 $W(PR_3)_2(CO)_3$ ($PR_3 = P^iPr_3$, PCy_3). The dihydrogen ligand or agostic bond is easily displaced in the presence of small molecules to form $[ReL(PR_3)_2(CO)_3]^+$ ($L = H_2O$, NH_3, C_2H_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_2O_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. $Re(CH_3)(CO)_5$ and $ReH(CO)_5$ were prepared from $Re_2(CO)_{10}$ (Strem) using literature methods.[46,47] PCy_3 (Strem) was recrystallized from ethanol, P*i*-$PrPh_2$ (Aldrich) and PPh_3 (Aldrich) were used as received, and P*i*-Pr_3 and PMe_3 (Strem) were degassed and stored under argon. $[H(Et_2O)_2]B(Ar')_4$ (Ar' = 3.5-$(CF_3)_2C_6H_3$) 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-d_3 (Cambridge, 99%), ethylene (Airco, 99.9%), ethylene-d_4 (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, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker AC-200 (200.133 MHz ^1H, 30.7 MHz ^2H, 81.015 MHz ^{31}P), AF-300 (300.117 MHz ^1H, 75.465 MHz ^{13}C) 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 ^{13}C NMR chemical shifts (δ) are referenced to the internal residual proton or natural abundance ^{13}C resonances of the deuterated solvent relative to TMS. $^{31}P\{^1H\}$ NMR chemical shifts (δ) are reported in parts per million relative to 85% H_3PO_4 (external standard). All NMR tube reactions were conducted in flame sealed tubes or J. Young® screw-cap tubes. T_{1min} 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-C*H*$_3$); 7.29 (m, 18H, P*Ph*$_3$ meta and para); 7.49 (m, 12H, P*Ph*$_3$ ortho). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): -22.3 (t, $^{2}J_{PC}$ = 6.3 Hz, Re-*C*H$_3$); 128.0 (vt, J_{PC} = 4.5 Hz, P*Ph*$_3$ ortho or meta); 129.6 (s, P*Ph*$_3$ para); 133.6 (vt, J_{PC} = 5.6 Hz, P*Ph*$_3$ ortho or meta); 135.3 (t, AXX', $J_{PC} + J_{P'C}$ = 23.2 Hz, P*Ph*$_3$ ipso); 195.4 (br,*C*O trans to CH_3); 199.0 (t, $^{2}J_{PC}$ = 9.3 Hz, *C*O cis to CH_3). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): 16.8 (s). IR (cm^{-1}, CH_2Cl_2, ν_{CO}): 2023(w), 1916(s), 1872(m).

***trans-mer*-$Re(CH_3)(Pi\text{-}PrPh_2)_2(CO)_3$ (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 P*i*-$PrPh_2$ (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, $^3J_{PH}$ = 6.6 Hz, 3H, ReCH_3); 1.11 (dd, $^3J_{PH}$ = 14.9 Hz, $^3J_{HH}$ = 7.0 Hz, 12H, P(CH(CH_3)$_2$)Ph$_2$); 2.91 (sept, $^3J_{HH}$ = 7.0 Hz, 2H, P(C*H*(CH$_3$)$_2$)Ph$_2$); 7.38 (m, 12H, P*i*-Pr*Ph*$_2$ meta and para); 7.51 (m, 8H, P*i*-Pr*Ph*$_2$ ortho). ^{13}C{^{1}H} NMR ($CDCl_3$): -25.7 (t, $^2J_{PC}$ = 6.6 Hz, Re*C*H$_3$); 19.5 (s, P(CH(*C*H$_3$)$_2$)Ph$_2$); 28.9 (t, AXX', J_{PC} + $J_{P'C}$ = 14.0 Hz, P(*C*H(CH$_3$)$_2$)Ph$_2$); 129.0 (vt, J_{PC} = 4.3 Hz, P*i*-Pr*Ph*$_2$ ortho or meta); 130.6 (P*i*-Pr*Ph*$_2$para); 134.4 (t, AXX', J_{PC} + $J_{P'C}$ = 20.9 Hz, P*i*-Pr*Ph*$_2$ ipso); 134.7 (vt, J_{PC} = 4.8 Hz, P*i*-Pr*Ph*$_2$ ortho or meta); 197.1 (t, $^2J_{PC}$ = 6.7 Hz, *C*O trans to CH$_3$); 200.4 (t, $^2J_{PC}$ = 9.0 Hz, *C*O cis to CH$_3$). ^{31}P{^{1}H}NMR ($CDCl_3$): 19.7 (s). IR (cm^{-1}, CH_2Cl_2, ν_{CO}): 2023(w), 1916(s), 1872(m).

***mer-trans*-Re(CH3)(PCyPh2)2(CO)3 (1c).** A thick walled glass vessel, equipped with a Kontes valve was charged with Re(CH3)(CO)5 (212mg, 0.621mmol) and PCyPh2 (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, $^3J_{HP}$ = 6.6Hz, Re-C*H*$_3$); 0 to 2.6 (m, RePC*y*Ph$_2$); 7.2 to 7.9 (m, RePCy*Ph*$_2$). ^{31}P{^{1}H} NMR($CDCl_3$): 17.9 (*P*CyPh$_2$). Approx. 67% pure.

***trans-mer*-Re(H)(PPh3)2(CO)3 (2a).** A thick walled glass vessel, equipped with a Kontes valve was charged with PPh3 (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. ^1H NMR (C_6D_6): -4.45 (t, $^2J_{PH}$ = 17.8 Hz, Re-*H*); 7.03 (m, P*Ph*$_3$ meta and para); 7.84 (m, P*Ph*$_3$ ortho). $^{31}P\{^1H\}$ NMR (C_6D_6): 22.8 (s). IR (cm^{-1}, CH_2Cl_2, ν_{CO}): 2020(w), 1925(s).

***trans-mer*-Re(H)(P*i*-PrPh$_2$)$_2$(CO)$_3$ (2b).** A thick walled glass vessel, equipped with a Kontes valve was charged with P*i*-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. ^1H NMR (C_6D_6): -5.55 (t, $^2J_{HP}$ = 18.8 Hz, Re-*H*); 1.08 (dd, $^3J_{PH}$ = 16.2 Hz, $^3J_{HH}$ = 6.9 Hz, P(CH(C*H*$_3$)$_2$)Ph$_2$); 2.61 (m, P(C*H*(CH$_3$)$_2$Ph$_2$); 6.94 (m, PiPr*Ph*$_2$ meta and para); 7.74 (m, PiPr*Ph*$_2$ ortho). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 18.6 (s, P(CH(*C*H$_3$)$_2$)Ph$_2$); 29.4 (t, AXX', $J_{PC} + J_{P'C}$ = 15.6 Hz, P(*C*H(CH$_3$)$_2$)Ph$_2$); 128.2 (s, PiPr*Ph*$_2$ ortho or meta); 129.7 (s, PiPr*Ph*$_2$ para); 133.3 (s, PiPr*Ph*$_2$ ortho or meta); 137.0 (t, AXX', $J_{PC} + J_{P'C}$ = 20.8 Hz, PiPr*Ph*$_2$ ipso); 177.8 (m, CO trans to H); 179.1 (m, CO cis to H). $^{31}P\{^1H\}$ NMR (C_6D_6): 29.6 (s). IR (cm^{-1}, CH_2Cl_2, ν_{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,

0.137mmol) and 10 mL of toluene. Under an argon flow, D_2O (0.25mL, 13.90mmol) was added via syringe. The solution was heated for two weeks at 120°C. An aliquot of the solution was removed for ^1H and $^{31}P\{^1H\}$ NMR. The ^1H NMR did show some evidence of decomposition, but there were no peaks in the hydride region. $^{31}P\{^1H\}$ NMR($CDCl_3$): 28.9(*P*iPrPPh$_2$) and a small peak at 1.54.

Reaction of $Re(CH_3)(CO)_5$ with PMe_3. A screw cap NMR tube was charged with $Re(CH)_3(CO)_5$ (19.2 mg, 0.06 mmol) and 0.5 mL C_7D_8 was vacuum transferred to the tube. Under an argon flow a septum was placed on the tube and PMe_3 (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 $^{31}P\{^1H\}$ NMR. $Re(CH_3)(PMe_3)(CO)_4$ is formed after two days without protection from light. No further reaction was observered 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*-$Re(CH_3)(PMe_3)(CO)_4$.** A thick walled glass vessel, equipped with a Kontes valve was charged with $Re(CH_3)(CO)_5$ (501mg, 1.46mmol) and toluene(15 mL). Under an argon flow PMe_3 (0.25mL, 2.78mmol) 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(C_7D_8): -0.28 (d, $^3J_{PH}$ = 9.1 Hz, ReC*H*$_3$); 0.90 (d, $^2J_{PH}$ = 8.8 Hz, ReP*Me*$_3$). $^{31}P\{^1H\}$ NMR(C_7D_8): -46.4 (Re*P*Me$_3$). IR (nujol mull): υ_{CO} 2073(w), 1983(s), 1967(vs), 1932(s) cm^{-1}.

***fac*-Re(CH_3)(PMe_3)(CH_3CN)(CO)$_3$.** A small glass vessel, equipped with a Kontes valve was charged with Re(CH_3)(PMe_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 $(CH_3)_3NO$ (58mg, 0.772mmol) and degassed with one freeze-pump-thaw cycle. Under an argon flow the solution of $(CH_3)_3NO$ was transferred via cannula to the solution of Re(CH_3)(PMe_3)(CO)$_4$. The solution was allowed to stir overnight under an argon flow to facilitate the removal of $(CH_3)_3N$ gas produced during the reaction. An aliquot of this solution was used for IR, ^1H, and $^{31}P\{^1H\}$ NMR. ^1H NMR($CDCl_3$): -0.56 (d, $^3J_{HP}$ = 9.9 Hz, 3H, ReCH_3); 1.47 (d, $^2J_{HP}$ = 8.4 Hz, 9H, RePMe_3); 2.34 (d, $^5J_{HP}$ = 1.6 Hz, 3H, ReNCCH_3). $^{31}P\{^1H\}$ NMR($CDCl_3$): -34.6 (PMe_3). IR (CH_2Cl_2): υCO 1999(s), 1902(s), 1874(s) cm^{-1}.

***fac-cis*-Re(CH_3)(PMe_3)$_2$(CO)$_3$ (3a).** The CH_3CN was removed *in vacuo* from the solution of Re(CH_3)(PMe_3)(CH_3CN)(CO)$_3$ and 10 mL of C_6H_6 was vacuum transferred to the flask and degassed by three freeze-pump-thaw cycles. Under an argon flow PMe_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. ^1H NMR($CDCl_3$): -0.82 (t, $^3J_{PH}$ = 10.0 Hz, ReCH_3), 1.40 (vt, J_{PH} = 7.6 Hz, RePMe_3). $^{31}P\{^1H\}$ NMR($CDCl_3$): -45.7 (PMe_3). IR (nujol mull): υ_{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 $[H(Et_2O)_2]B(Ar')_4$ (13 mg, 0.013 mmol). CD_2Cl_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_2Cl_2): -3.8 (br s, Re*H*$_2$); 6.7 to 8.0 (m, P*Ph*$_3$ and B(Ar')$_4$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 8.1 (s).

[*trans-mer*-Re(H$_2$)(P*i*-PrPh$_2$)$_2$(CO)$_3$]B(Ar')$_4$ (4b). A screw cap NMR tube was charged with Re(CH$_3$)(P*i*-PrPh$_2$)(CO)$_3$ (10 mg, 0.013 mmol) and [H(Et$_2$O)$_2$]B(Ar')$_4$ (13 mg, 0.013 mmol). CD_2Cl_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_2Cl_2): -4.26 (Re*H*$_2$); 1.17(m, P(CH(C*H*$_3$)$_2$)Ph$_2$); 3.04 (m, P(C*H*(CH$_3$)$_2$)Ph$_2$); 7.55 and 7.73 (m, PiPr*Ph*$_2$ and B(Ar')$_4$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 14.7 (s).

Reactivity of [Re(H$_2$)(PCy$_3$)$_2$(CO)$_3$]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_2Cl_2): -6.66 (t, J_{PH} = 20.5 Hz, 2H); 1.1-2.1 (br, 66H). ^{31}P{^{1}H} NMR (CD_2Cl_2): 30.6 (s).

[*trans-mer*-Re(PPh$_3$)$_2$(CO)$_3$]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_2Cl_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_2Cl_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_2Cl_2): 6.7 to 8.0 (m, P*Ph*$_3$ and B(Ar')$_4$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 14.6 (s).

[*trans-mer*-Re(P*i*-PrPh$_2$)$_2$(CO)$_3$]B(Ar')$_4$ (5b). A sealable NMR tube was charged with Re(CH_3)(P*i*-PrPh$_2$)$_2$(CO)$_3$ (15 mg, 0.020 mmol) and [H(Et_2O)$_2$]B(Ar')$_4$ (20 mg, 0.020 mmol). A 1 mL portion of CH_2Cl_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_2Cl_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_2Cl_2): 1.17 (m, P(CH(C*H*$_3$)$_2$)Ph$_2$); 3.04 (m, P(C*H*(CH_3)$_2$)Ph$_2$); 7.55 and 7.73 (m, PiPr*Ph*$_2$ and B(Ar')$_4$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 20.9 (s).

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)$_3$ (15mg, 0.018mmol) and HB(Ar')$_4$ (19mg, 0.019mmol). A 1 mL portion of CH_2Cl_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_2Cl_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_2Cl_2): 0.08 to 2.72 (m, PC*y*Ph$_2$); 7.53 and 7.73 (m, PCy*Ph*$_2$ and B(Ar')$_4$). ^{31}P{^{1}H} NMR(CD_2Cl_2): 19.0 (*P*CyPh$_2$). Approx. 44% pure.

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)$_3$ (6mg, 0.014mmol) and HB(Ar')$_4$ (14mg, 0.014mmol). 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, P*Me*$_3$); 7.5(m, p-B(Ar')$_4$); 7.7 (m, o-B(Ar')$_4$). ^{31}P{^{1}H}

NMR($CDCl_3$): -38.1; -35.8; -32.0; -31.0. After 1 day at room temperature the $^{31}P\{^1H\}$ 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_2O, 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). ^1H NMR (CD_2Cl_2): 7.35 (m, 18H, P*Ph*$_3$ meta and para); 7.58 (m, 12H, P*Ph*$_3$ ortho). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 9.7 (s). IR (cm^{-1}, Nujol, ν_{CO}): 2045 (w), 1940 (s), 1892 (m).

***trans-mer*-ReCl(P*i*-PrPh$_2$)$_2$(CO)$_3$ (6b).** A screw cap NMR tube was charged with Re(CH_3)(P*i*-PrPh$_2$)$_2$(CO)$_3$ (10 mg, 0.013 mmol) and 0.5 mL of CD_2Cl_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. ^1H NMR (CD_2Cl_2): 1.10 (dd, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 7.0 Hz, 12H, P(CH(C*H*$_3$)$_2$)Ph$_2$); 3.27 (sept of trip, AXX', $J_{PH} + J_{P'H}$ = 2.4 Hz, $^3J_{HH}$ = 7.0 Hz, 2H, P(C*H*(CH$_3$)$_2$)Ph$_2$); 7.43 (m, 12H, P*i*-Pr*Ph*$_2$ meta and para); 7.65 (m, 8H, P*i*-Pr*Ph*$_2$ ortho). $^{31}P\{^1H\}$ NMR (CD_2Cl_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 agron flow excess HCl (1 M in Et_2O, 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}H NMR (CD_2Cl_2): 0.9 to 2.5 (m, ReP*Cy*$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): 29.59 (P-γ-*C*); 30.86 (t, J_{PC} = 3 Hz, P-β-*C*) 32.68 (P-δ-*C*); 38.82 (t, J_{PC} = 11.2 Hz, P-α-*C*); 196.9 (br, *C*O); 200.8 (t, J_{PC} = 9.2 Hz, *C*O). ^{31}P{^{1}H} NMR (CD_2Cl_2): 13.87 (s). IR (cm^{-1}, Nujol, ν_{CO}): 2025 (w), 1914 (s), 1869 (m).

[*trans*-Re(PPh$_3$)$_2$(CO)$_4$]B(Ar')$_4$ (7a). A screw cap NMR tube was charged with Re(CH$_3$)(PPh$_3$)$_2$(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}H NMR ($CDCl_3$): 7.20 and 7.44 (m, B(Ar')$_4$ and P*Ph*$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$): 3.7 (s). IR (cm^{-1}, CH_2Cl_2, ν_{CO}): 2003.

Reaction of Re(CH$_3$)(PPh$_3$)$_2$(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)$_3$(PPh$_3$)$_2$ (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_2Cl_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}H NMR ($CDCl_3$): 7.48 and 7.70 (m, B(Ar')$_4$ and P*Ph*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): 129.6 (vt, J_{PC} = 5.3 Hz, P*Ph*$_3$ ortho or meta); 131.5 (t, AXX', $J_{PC} + J_{P'C}$ = 26.9 Hz, P*Ph*$_3$ ipso); 132.4 (vt, J_{PC} = 6.1 Hz, P*Ph*$_3$ ortho or meta); 185.5 (t, $^2J_{PC}$ = 7.4 Hz, Re-*C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): 3.7 (s). IR (cm^{-1}, CH_2Cl_2, ν_{CO}): 2002 (s).

[*trans*-Re(P*i*-PrPh$_2$)$_2$(CO)$_4$]B(Ar')$_4$ (7b). A screw cap NMR tube was charged with Re(H)(P*i*-PrPh$_2$)$_2$(CO)$_3$ (10 mg, 0.014 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. ^1H NMR ($CDCl_3$): 0.93 (dd, $^3J_{PH}$ = 17.3 Hz, $^3J_{HH}$ = 6.9 Hz, P(C*H*(CH_3)$_2$)Ph_2); 7.35 and 7.57 (m, B(Ar')$_4$ and P*i*-Pr*Ph*$_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 9.1 (s).

[*trans*-Re(PCy$_3$)$_2$(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 (CD_2Cl_2): 1.3-2.0 (br, 60H); 2.2 (br, 6H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 17.9 (s). IR (cm^{-1}, Nujol, ν_{CO}): 1983 (s).

[*trans-mer*-Re(OH$_2$)(P*i*-PrPh$_2$)$_2$(CO)$_3$]B(Ar')$_4$ (8b). A small glass vessel, equipped with an 8 mm Kontes valve was charged with Re(CH_3)(P*i*-PrPh$_2$)$_2$(CO)$_3$ (101 mg, 0.136 mmol) and [H(Et_2O)$_2$]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 H_2O 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 (CD_2Cl_2): 0.39 (br, ReO*H*$_2$); 1.21 (dd, $^3J_{PH}$ = 16.5Hz, $^3J_{HH}$ = 7.08Hz, P(CH(C*H*$_3$)$_2$Ph$_2$)); 3.05 (quint, $^3J_{HH}$ = 6.9Hz, P(C*H*(CH_3)$_2$)Ph$_2$)); 7.46 and 7.70 (br m, B(Ar')$_4$ and P*i*-Pr*Ph*$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 18.2 (s, P(CH(C*H*$_3$)$_2$Ph$_2$)); 30.0 (t, AXX', J_{PC} + $J_{P'C}$ = 15.3 Hz, P(C*H*(CH_3)$_2$Ph$_2$)); 127.4 (t, AXX', J_{PC} + $J_{P'C}$ = 22.2Hz, P*i*-Pr*Ph*$_2$ ipso); 130.0 (vt, J_{PC} = 4.6 Hz, P*i*-Pr*Ph*$_2$ ortho or meta); 132.4 (s, P*i*-Pr*Ph*$_2$ para); 133.6 (vt, J_{PC} = 4.7Hz, P*i*-Pr*Ph*$_2$ ortho or meta); 193.4 (t, $^2J_{PC}$ = 8.2Hz, *C*O cis to CH_3); 194.5 (t, $^2J_{PC}$ = 6.7Hz, *C*O trans to CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2):

27.7 (s). IR (cm^{-1}, Nujol): ν(CO) 1972(s), 1921(m); ν(OH) 3562(w); δ(HOH) 1608(m).

[*trans-mer*-Re(NH$_3$)(PCy$_3$)$_2$(CO)$_3$]B(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. ^1H NMR (CD_2Cl_2): 1.3-2.0 (br, 60H); 2.2 (br, 6H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 13.6 (s). IR (cm^{-1}, Nujol): ν(CO) 2047 (w), 1942(s), 1934(m); ν(NH) 3375 (w), 3300 (w); δ(NH_3) 1612 (m).

[*trans-mer*-Re(ND$_3$)(PCy$_3$)$_2$(CO)$_3$]B(Ar')$_4$ (9c-d$_3$). 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_2Cl_2 was added by vacuum transferred and the tube was sealed. ^2H NMR (CH_2Cl_2): 2.03 (s, N*D*$_3$).

[*trans-mer*-Re(C$_2$H$_4$)(PCy$_3$)$_2$(CO)$_3$]B(Ar')$_4$ (10c). An NMR tube affixed to a 4 mm Kontes valve was charged with **5c** (6 mg, 0.0035 mmol). CD_2Cl_2 (0.5 mL) was vacuum transferred to the tube and pressurized with 300 torr C_2H_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. ^1H NMR (CD_2Cl_2): 1.2-2.0 (br, 60H); 2.3 (br, 6H); 3.29 (br, 4H, C$_2$*H*$_4$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 1.8 (s).

[*trans-mer*-Re(C$_2$D$_4$)(PCy$_3$)$_2$(CO)$_3$]B(Ar')$_4$ (10c-d$_3$). An NMR tube affixed to a 4 mm Kontes valve was charged with **3b** (6 mg, 0.0035 mmol). CH_2Cl_2

(0.5 mL) was vacuum transferred to the tube and pressurized with 300 torr C_2D_4 and sealed. ^2H NMR (CH_2Cl_2): 3.29 (br, C_2D_4).

[Re(N$_2$)(PCy$_3$)$_2$(CO)$_3$]B(Ar')$_4$. A screw cap NMR tube was charged with **5c** (8 mg, 0.0047 mmol). CD_2Cl_2 was vacuum transferred to the tube and place under N_2 (760 torr). The solution turned colorless at low temperature. ^1H NMR (190 K, CD_2Cl_2): 1.2-2.0 (br, 60H); 2.4 (br, 6H). $^{31}P\{^1H\}$ NMR (190 K, CD_2Cl_2): 17.1 (s).

[Re(N$_2$)(P*i*-Pr$_3$)$_2$(CO)$_3$]B(Ar')$_4$. A screw cap NMR tube was charged with **5d** (7 mg, 0.0048 mmol). CD_2Cl_2 was vacuum transferred to the tube and place under N_2 (760 torr). The solution turned colorless at low temperature. ^1H NMR (240 K, CD_2Cl_2): 1.3 (m, 36H, P(CH(C*H*$_3$)$_2$)$_3$); 2.7 (m, 6H, P(C*H*(CH$_3$)$_2$)$_3$). $^{31}P\{^1H\}$ NMR (240 K, CD_2Cl_2): 25.0 (s).

[*trans-mer*-Re(THF)(PCy$_3$)$_2$(CO)$_3$]B(Ar')$_4$ (11c). A 10 mL round bottom flask was charged with *trans-mer*-$Re(CH_3)(PCy_3)_2(CO)_3$ (50 mg, 0.059 mmol), $[H(Et_2O)_2]B(Ar')_4$ (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^{-1}, Nujol, ν_{CO}): 2043(w), 1937(s), 1913(m).

[*mer*-Re(PPh$_3$)$_3$(CO)$_3$]B(Ar')$_4$ (12a). A screw cap NMR tube was charged with PPh_3 (5 mg, 0.019 mmol), $ReCH_3(PPh_3)_2(CO)_3$ (10 mg, 0.012 mmol), and $[H(Et_2O)_2]B(Ar')_4$ (13 mg, 0.013 mmol). $CDCl_3$ (0.5 mL) was vacuum transferred and the solution was degassed by three freeze-pump-thaw cycles. ^1H NMR ($CDCl_3$):

6.6 to 7.8 (m, $B(Ar')_4$ and PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 0.2 (t, $^2J_{PP}$ = 18.3 Hz, PPh_3 trans to CO); 3.8 (d, $^2J_{PP}$ = 18.7 Hz, PPh_3 cis to CO).

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CHAPTER 2

REACTIVITY OF $(\eta^5\text{-}C_5H_5)_2Re\text{-}X$ 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, metallocene structures have been discovered for all metals in the titanium through iron triads.[1] The first metallocene complex of rhenium, Cp_2ReH, was initially reported by Wilkinson and Birmingham in 1955.[2] During initial reactivity studies it was reported that Cp_2ReH reacts with acids to form $[Cp_2ReH_2]^+$ without loss of hydrogen.[2,3] The study of rhenocene complexes has received relatively little attention compared to other metallocene complexes. Complexes of the type Cp_2ReX (X = H, alkyl, Cl), are electron rich and previous investigations have documented the reactivity of rhenocene complexes with H^+, Me^+, Ph_3C^+, 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.

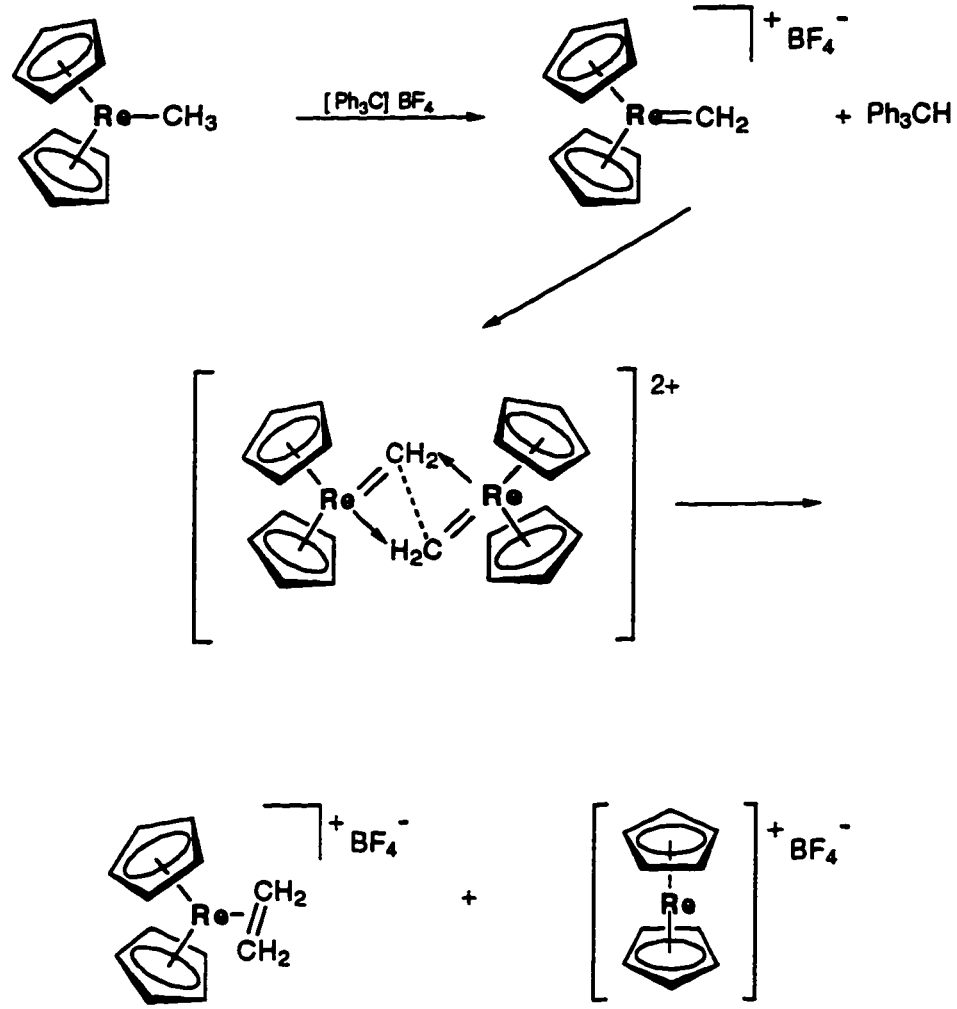
Rhenocene chemistry has been relatively underexplored compared to the group 6 metallocene complexes of molybdenum and tungsten. Several authors have alluded to the lack of research of rhenocene complexes due to the difficulties in the synthesis of Cp_2ReH.[15-17] The synthesis of Cp_2ReH reported by Wilkinson and Birmingham is accomplished by the reduction of $ReCl_5$ with excess NaCp in THF followed by the addition of $NaBH_4$.[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.[12,13] Recovery of pure material is facilitated by sublimation of the Cp_2ReH directly from the reaction mixture. The conversion of Cp_2ReH to simple derivatives, such as a variety of alkyl complexes and Cp_2ReCl, has also proven to be difficult. Initial attempts to synthesize Cp_2ReR ($R = CH_3$, CH_2CH_3, $CH_2CH_2CH_3$, $CH_2CH{=}CH_2$) by alkylation of $Cp_2ReLi{\bullet}PMDT$ with RX (X = Cl, Br) in hydrocarbon solvents led to samples contaminated with Cp_2ReH.[18] The target alkyl complexes are difficult to separate from Cp_2ReH 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.[18] Mink and Stucky also observed that the use of alkyl bromide reagents in the synthesis of $Cp_2Re(CH_2CH{=}CH_2)$ and $Cp_2ReCH_2CH_2CH_3$ significantly reduced the amount of Cp_2ReH.[18] The explanation for this observation was that the alkyl chlorides are likely to have more acidic protons and will then protonate Cp_2ReLi. 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 $Cp_2Re(CH_3)_2^+$ which could then protonate any Cp_2ReLi in solution.[12,19]

The synthesis of pure alkyl complexes has been described in detail by Gould and Heinekey.[12] Cp_2ReLi is generated by addition of a slight excess of ^nBuLi to Cp_2ReH in THF at -78 °C. Addition of excess CH_3Cl by vacuum transfer followed by slowly warming the solution to room temperature generates Cp_2ReCH_3. Their procedure leads to alkyl complexes which are free from Cp_2ReH and the yields are very reproducible (> 90% for Cp_2ReCH_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_2ReX 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 $[Ph_3C]BF_4$ with Cp_2ReCH_3 and $Cp_2ReCH_2CH_3$.[6,14] The reaction of Cp_2ReCH_3 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, $[Cp_2Re(C_2H_4)]^+$. The proposed mechanism for this reaction is shown in Scheme 2.1.[14]



Scheme 2.1

The other required product, $[Cp_2Re]^+$, was not observed and presumably it decomposed to several different products. The reaction of $Cp_2ReCH_2CH_3$ with $[Ph_3C]BF_4$ also results in the production of $Cp_2Re(C_2H_4)^+$, but was proposed to be generated by a β-hydride abstraction from the ethyl group.[14]

Due to the contamination of the alkyl complexes by Cp_2ReH, the reactivity of this complex with $[Ph_3C]BF_4$ was also investigated.[14] Welter and Stucky claim to have isolated a complex formulated as Cp_2ReBF_4 from reaction of Cp_2ReH with $[Ph_3C]BF_4$. 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 $[Cp_2ReH_2]BF_4$. The ^1H NMR spectrum of Cp_2ReBF_4, when dissolved in acetone, indicated the formation $[Cp_2ReH_2]BF_4$. A related complex was reported by the reaction of Cp_2ReH with $CuCl_2$ to form $[Cp_2Re]CuCl_2$ and includes a crystal structure with the cyclopentadienyl rings in a *bent* conformation.[9] The addition of $[Cp_2Re]CuCl_2$ to CCl_4 produces $CHCl_3$ 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 Cp_2ReH with potential oxidizing reagents such as $[Ph_3C]^+$ and $[Cp_2Fe]^+$.

Welter and Stucky have also investigated the reactivity of the alkyl complexes, Cp_2ReCH_3 and $Cp_2ReCH_2CH_3$, with $[H(Et_2O)]BF_4$.[14] Analysis of the products by gas chromatography after the reaction indicate the formation of CH_4 and C_2H_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.

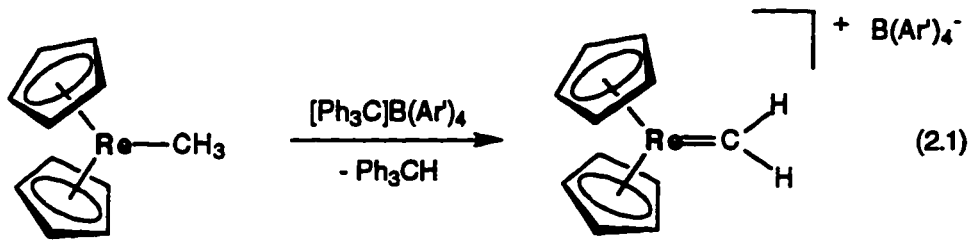
Baudry and Ephritikhine have reported the synthesis of Cp_2ReCl by reaction of Cp_2ReH with halogenated solvents such as chloroform although this results in very poor yields.[7] Cp_2ReCl is reported to react with donor ligands such as PPh_3 and pyridine in

the presence of silver salts to form $[Cp_2ReL]^+$ (L = PPh_3, NC_5H_5) complexes. We have observed that Cp_2ReH is easily oxidized by chlorinated solvents to form $[Cp_2ReH_2]Cl$ as a major product which may account for the low yields of Cp_2ReCl. We report a scaled up synthesis of analytically pure Cp_2ReCl 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 ($[Na]B(Ar')_4$, Ar' = $3,5(CF_3)_2C_6H_3$) has been useful in organometallic chemistry.[21] The trifluoro groups increase the solubility of these complexes in common solvents such as CH_2Cl_2 and disperse the anionic charge throughout the anion volume rendering it non-nucleophilic. Several convenient reagents of $B(Ar')_4^-$ have been reported by various groups: $[Na]B(Ar')_4$ and $[H(Et_2O)_2]B(Ar')_4$ have been reported by Brookhart and coworkers, Boudjok and Bahr have reported the synthesis of $[Ph_3C]B(Ar')_4$,[22] Golden and coworkers have reported $[Li(H_2O)_4]B(Ar')_4$ and $[Ag(Et_2O)_x]B(Ar')_4$,[23] Hughes and coworkers have developed a synthesis for $[Tl]B(Ar')_4$,[24] and the synthesis of $[Cp_2Fe]B(Ar')_4$ is reported in this chapter.

Results and Discussion

Preparation and Characterization of $[Cp_2Re{=}CH_2]^+$ (1–$B(Ar')_4$; 1–BPh_4). A solution of Cp_2ReCH_3 in methylene chloride reacts rapidly with $[Ph_3C]B(Ar')_4$ to form $[Cp_2Re{=}CH_2]B(Ar')_4$ (**1**) and Ph_3CH (eq 2.1).



(2.1)

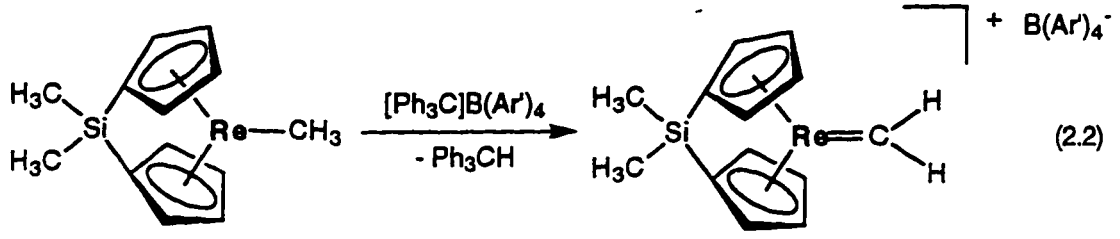
1

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_2Cl_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_2ReX (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

CD_2Cl_2 when stored at -28 °C. Complex **1** can also be formed as a tetraphenylborate salt upon reaction of Cp_2ReCH_3 with $[Ph_3C]BPh_4$ in CH_2Cl_2. Complex **1**-BPh_4 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**-BPh_4 is thermally stable but the low solubility in CH_2Cl_2 makes it inconvenient for synthesis of further derivatives. It was hoped that **1**-BPh_4 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 Et_2O or CH_2Cl_2 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 Cp_2ReCH_3. The reaction of $Me_2SiCp_2ReCH_3$ with $[Ph_3C]B(Ar')_4$ in CH_2Cl_2 immediately forms $[Me_2SiCp_2Re{=}CH_2]B(Ar')_4$ (**2**) and Ph_3CH (eq 2.2).



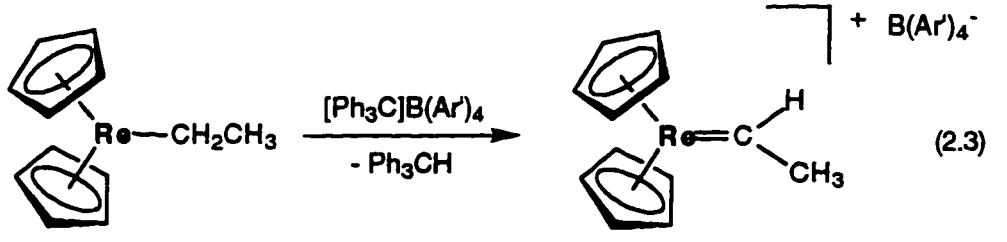
(2.2)

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 $Re{=}CH_2$ protons and two pseudotriplet resonances (J_{CH} = 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 ^{13}C NMR resonance for $Re{=}CH_2$ (δ 246.1) is a triplet with J_{CH} = 150

Hz. Large orange crystals of **2** can be grown by the slow diffusion of pentane into a concentrated CH_2Cl_2 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 $[Cp_2Re{=}CH(CH_3)]B(Ar')_4$ (3). $Cp_2ReCH_2CH_3$ reacts rapidly with $[Ph_3C]B(Ar')_4$ in methylene chloride to form $[Cp_2Re{=}CH(CH_3)]B(Ar')_4$ (**3**) and Ph_3CH (eq 2.3).



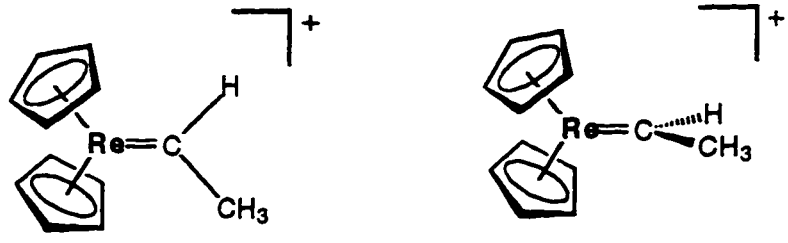
(2.3)

3

Complex **3** is isolated by precipitation with pentane followed by filtration to give a pale orange solid in 94% yield. ^1H and ^{13}C 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 CD_2Cl_2 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 (J_{HH} = 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 ^{13}C 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 $[Cp_2Re(C_2H_4)]B(Ar')_4$ (δ 5.2, Cp and 2.23, C_2H_4) is observed to form initially. This indicates that while the reaction of $Cp_2ReCH_2CH_3$ with Ph_3C^+ 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 $[Ph_3C]BF_4$ with $CpRe(NO)(PPh_3)R$ (R = CH_2CH_3, $CH_2CH_2CH_3$) was initially reported to proceed exclusively by α-hydride abstraction.[33] 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.[35]

The observation of two inequivalent cyclopentadienyl resonances in the ^1H and ^{13}C NMR spectra for $[Cp_2Re{=}CH(CH_3)]B(Ar')_4$ 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

The rotation of the carbene ligand must be slow on the NMR timescale in order to observe this inequivalence. A sample of $[Cp_2Re{=}CH(CH_3)]B(Ar')_4$ in CD_3NO_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 $\Delta G^{\ddagger}_{rot} \geq 17.7$ 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 π bond.[25]

This alignment of the carbene ligand is not what would be predicted by sterics, 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 $Cp_2W{=}CH(CH_3)$ which also shows inequivelant cyclopentadienyl rings by ^1H NMR spectroscopy and have confirmed this arrangement with a crystal structure of $Cp_2W{=}CH(Ph)$.[26]

The carbene ligand in this system will be considered a neutral 2 electron donor and a π acceptor.[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 metallocene complex.[29] The π 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.

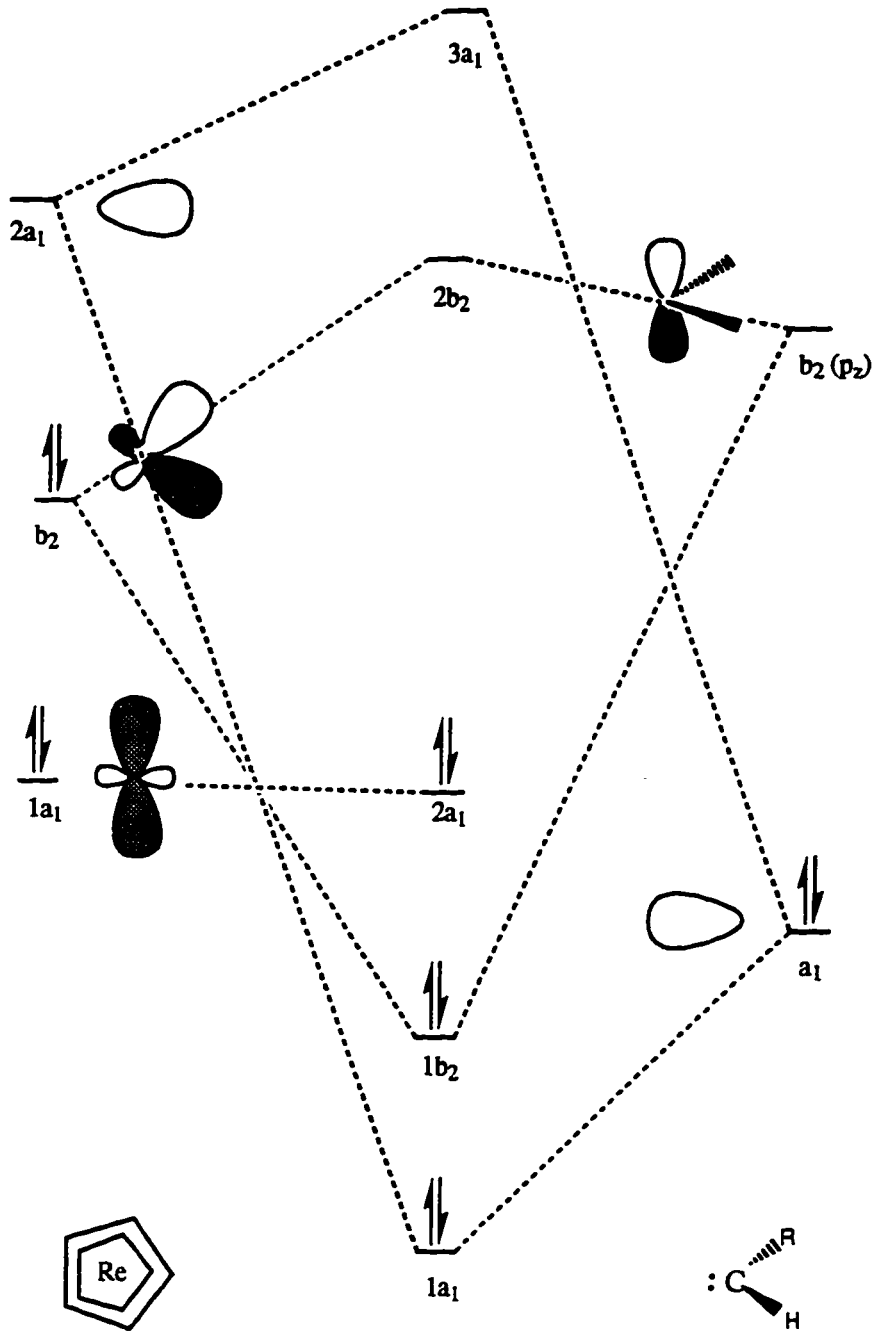
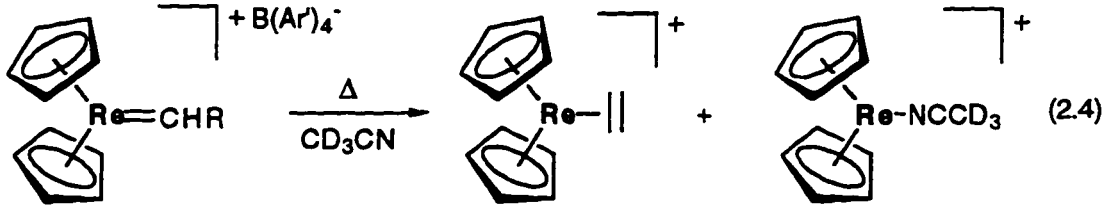


Figure 2.1. Molecular orbital interaction diagram between valence orbitals of the 16 electron fragment, "Cp_2Re^+", and a carbene fragment, :CHR. Adapted from references 28 and 29.

Thermolysis of 1-B(Ar')$_4$ and 3-B(Ar')$_4$. The carbene complexes were heated in CD_2Cl_2 at 40 °C and monitored periodically by ^1H 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(Ar')$_4$ and 3-B(Ar')$_4$ in CD_3CN 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 ^1H NMR chemical shifts were $[Cp_2Re(C_2H_4)]B(Ar')_4$[6] and $[Cp_2Re(NCCD_3)]B(Ar')_4$[13] (eq 2.4). Other minor products were also formed which could not be identified.



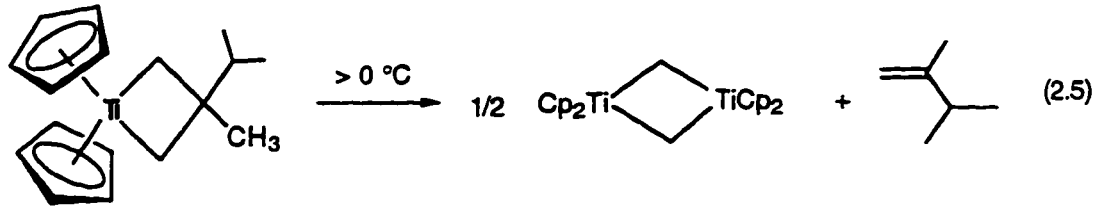
Reactions of Cp_2ReCH_3 and $Cp_2ReCH_2CH_3$ with $[Ph_3C]BF_4$. Welter and Stucky have previously described the reactivity of Cp_2ReCH_3 and $Cp_2ReCH_2CH_3$ with $[Ph_3C]BF_4$.[6,14] They report that a thermally unstable methylene complex is formed by α-hydride abstraction from Cp_2ReCH_3 and a stable ethylene complex is formed by β-hydride abstraction from $Cp_2ReCH_2CH_3$. The results that we have obtained with $[Ph_3C]B(Ar')_4$ contrast with these observations and so we have reinvestigated the reactions with $[Ph_3C]BF_4$. The reaction of Cp_2ReCH_3 with $[Ph_3C]BF_4$ in CD_2Cl_2 forms several unidentifiable products and no evidence for the carbene complex was observed. The reaction is much cleaner in CD_3CN and shows almost exclusive formation of $[Cp_2Re{=}CH_2]BF_4$ as well as a small amount of $[Cp_2Re(NCCD_3)]BF_4$.[30] The carbene complex is reasonably stable and decomposes

after 24 hours at room temperature. The two major products indicated by ^1H NMR spectroscopy are $[Cp_2Re(C_2H_4)]BF_4$ and $[Cp_2Re(NCCD_3)]BF_4$. Several other minor products are formed as well.

The reaction of $Cp_2ReCH_2CH_3$ with $[Ph_3C]BF_4$ gives $[Cp_2Re(C_2H_4)]^+$ immediately when the reaction proceeds in either CD_2Cl_2 or CD_3CN. A minor formation of the carbene complex, **3**, is observed in the initial ^1H NMR spectrum. The reaction in CD_3CN leads to fewer side products and $[Cp_2Re(NCCD_3)]^+$ is also formed as a major product. Gould has observed that $[Cp_2Re{=}CH(CH_3)]BF_4$ 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 $[Cp_2Re{=}CH_2]B(Ar')_4$ (1) and $[Cp_2Re{=}CH(CH_3)]B(Ar')_4$ (3) with BF_4^- and PF_6^-. Addition of BF_4^- salts to CD_3CN solutions of **1**–$B(Ar')_4$ and **3**–$B(Ar')_4$ does slowly lead to decomposition which is similar to the $[Ph_3C]BF_4$ reactions. Complex **1** was allowed to react with either excess $[NH_4]BF_4$, $[NH_4]PF_6$, or $NaBF_4$ in CD_3CN. The reactions with the ammonium salts were much quicker presumably due to greater solubility in CD_3CN. The reactions proceeded to give very clean formation of $[Cp_2Re(C_2H_4)]BF_4$ and $[Cp_2Re(NCCD_3)]BF_4$ as well as a small amount of free ethylene (δ 5.4). The reaction with $[NH_4]BF_4$ 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 $[Cp_2Re{=}CH_2]^+$ and $[Cp_2Re{=}CH(CH_3)]^+$ presumably proceeds to $[Cp_2Re(C_2H_4)]^+$ by different mechanisms. Complexes of the type $L_nM{=}CH_2$ 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 $[CpRe(NO)(PPh_3)(=CH_2)]BF_4$ 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, $[Cp^*Re(NO)(PPh_3)(=CH_2)]BF_4$, 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-dimetalllacyclobutane complex by Grubbs and Ott, from a reaction which is thought to produce "$Cp_2Ti{=}CH_2$" (eq 2.5).[34]



(2.5)

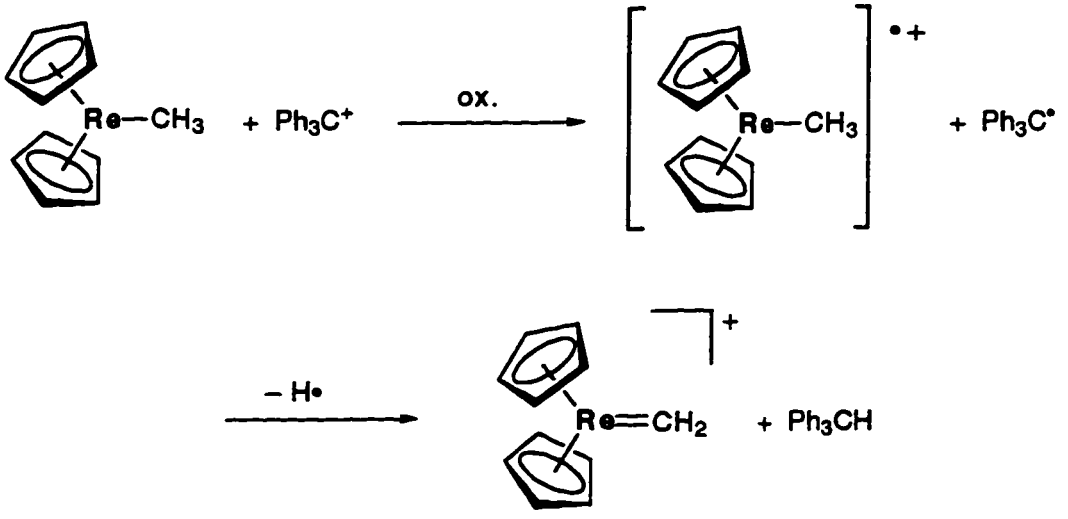
Several complexes of the form $LnM{=}CH(CH_3)$ have also been observed to form corresponding ethylene complexes upon decomposition. This reaction has been proposed to proceed via a [1,2]hydrogen shift. A bimolecular coupling reaction similar to those observed from methylene complexes would produce 2-butene. Gladysz and coworkers have explored the conversion of $[CpRe(NO)(PPh_3)(=CHR)]BF_4$ 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 α 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 $[Cp_2Re{=}CH(CH_3)]B(Ar')_4$ 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 ($PHPh_2$) caused the isomerization of a low valent, neutral ethylene complex, $[N_3N]Ta(C_2H_4)$ (N_3N^{3-} = $(Me_3SiNCH_2CH_2)_3N^{3-}$), to the more stable ethylidene complex, $[N_3N]Ta{=}CH(CH_3)$.[38] Gladysz and coworkers have proposed that similar mechanisms are unlikely to proceed for electrophilic carbene complexes of high valent metal centers.[32] $[CpRe(NO)(PPh_3)(=CHCH_2R)]PF_6$ 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 KO^tBu.[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 BF_4^- 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 BF_4^-, as compared to the intensity of the $B(Ar')_4^-$ resonances in the ^1H NMR spectra. How BF_4^- promotes the isomerization of **3** to the ethylene complex and the bimolecular coupling of complex **1** is currently unknown.

Reactivity of Cp_2ReCH_3 and $Cp_2ReCH_2CH_3$ with $[Cp_2Fe]B(Ar')_4$. Hydride abstraction by Ph_3C^+ 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_2ReCH_3.



Scheme 2.3

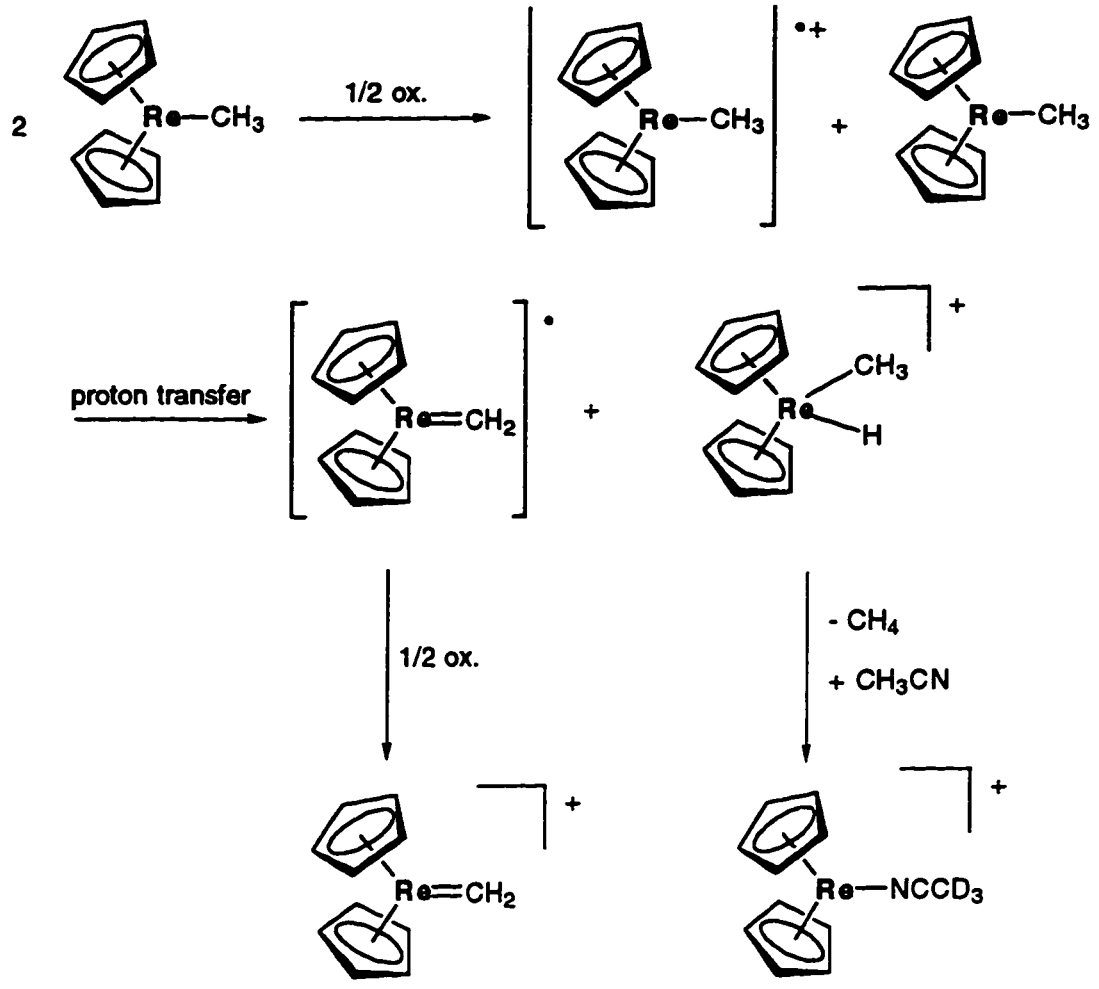
Cooper and Gladysz have both proposed an electron transfer mechanism for their studies of the reactivity of transition metal alkyl complexes with trityl cation. To date, Cooper has provided the best evidence for this mechanism by the isolation and characterization of stable radical cations, $[Cp_2W(CH_3)(C_2H_5)]^{+\bullet}$, which react with $Ph_3C^\bullet$ 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_2ReR complexes with an oxidizing reagent (*i.e.* a

reagent which will initially react by electron transfer) such as Cp_2Fe^+.[43] Based on the results of the Ph_3C^+ reactions, the stability of the carbene complexes generated would be sensitive to the anion. $[Cp_2Fe]B(Ar')_4$ was prepared by a similar method to that reported for $[Cp_2Fe]BPh_4$ by Jordan and coworkers.[44] $NaB(Ar')_4$ is added to an aqueous solution of $[Cp_2Fe]_2SO_4$[45] and precipitation of $[Cp_2Fe]B(Ar')_4$ occurs after stirring overnight (eq 2.6).

$$Cp_2Fe + H_2SO_4 \longrightarrow [Cp_2Fe]_2SO_4 + NaB(Ar')_4 \xrightarrow{H_2O} [Cp_2Fe]B(Ar')_4 \quad (2.6)$$

The reactivity of Cp_2ReCH_3 and $Cp_2ReCH_2CH_3$ with $[Cp_2Fe]B(Ar')_4$ in CD_2Cl_2 led to many different products which could not be identified. In CD_3CN, $[Cp_2Fe]B(Ar')_4$ reacts with Cp_2ReCH_3 to give $[Cp_2Re(NCCD_3)]^+$ and $[Cp_2Re{=}CH_2]B(Ar')_4$. $[Cp_2Re(NCCD_3)]^+$ is proposed to be formed from an intermediate methyl hydride complex which loses methane and coordinates acetonitrile (Scheme 2.4).[46] The reaction of $[Cp_2Fe]B(Ar')_4$ and $Cp_2ReCH_2CH_3$ affords $[Cp_2Re(NCCD_3)]^+$ and the ethylene complex with no evidence of the ethylidene complex.



Scheme 2.4

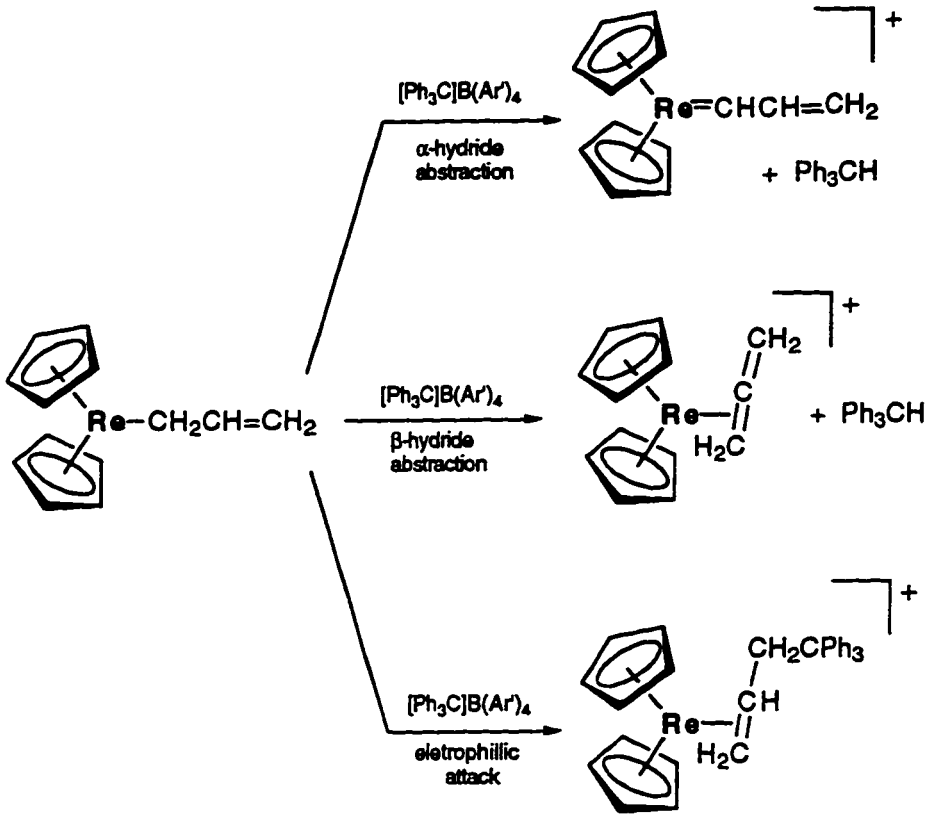
Recent work by Tilset and coworkers has shown that oxidation of metal hydride complexes can generate acidic radical cation species which can then react by proton transfer with a neutral hydride complex and form a dihydride or dihydrogen product.[47] It is unknown if a similar radical cationic alkyl complex is capable of proton transfer. When the reaction of $[Cp_2Fe]^+$ with $Cp_2ReCH_2CH_3$ 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 ^1H NMR spectroscopy at lower

temperatures might confirm the presence of the unstable alkyl hydride complex which reacts further to generate the acetonitrile complex. The $[Cp_2Fe]^+$ experiments seem to confirm that the carbene complexes can be formed via an electron transfer mechanism.

Reactions of $[Ph_3C]B(Ar')_4$ with other Cp_2ReR Compounds. The isolation of two new carbene complexes in this system, led us to further investigate the reactivity of $[Ph_3C]^+$ with known alkyl complexes of rhenocene. Unfortunately, this series is currently limited to complexes where R = $CH_2CH_2CH_3$, $CH_2CH{=}CH_2$, CH_2SiMe_3, and CH_2Ph.[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 ^{n}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 $Cp_2ReCH_2CH{=}CH_2$ and $Cp_2ReCH_2SiMe_3$.

The reaction of $Cp_2Re(CH_2CH{=}CH_2)$ with $[Ph_3C]B(Ar')_4$ in CH_2Cl_2 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

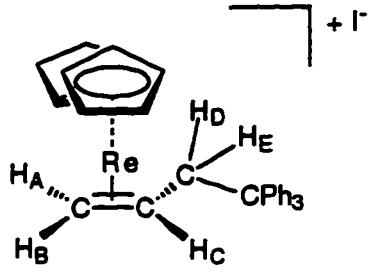
low temperature. Scheme 2.5 shows the possible reaction pathways for the reaction of $Cp_2ReCH_2CH{=}CH_2$ with $[Ph_3C]^+$. The first two possibilities are simply hydride abstraction from either the α or the β carbon. The last reaction is electrophilic attack of the Ph_3C^+ at the γ carbon of the allyl 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 $[Cp_2Re(\eta^2\text{-}CH_2CHCH_2CPh_3)]I$ (**4**) was precipitated from acetone. The

^{1}H NMR spectrum of the isolated product confirmed that electrophilic attack at the γ-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).



4

Scheme 2.6

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

Proton	Chemical Shift (ppm)	Coupling Constant (Hz)
A	3.77	C (13.7) & B (1)
B	2.72	multiplet
C	2.34	A (13.7) & B (9.1)
D	2.01	B (9.4) & E (5.0)
E	1.72	B (13.2) & D (5.0)

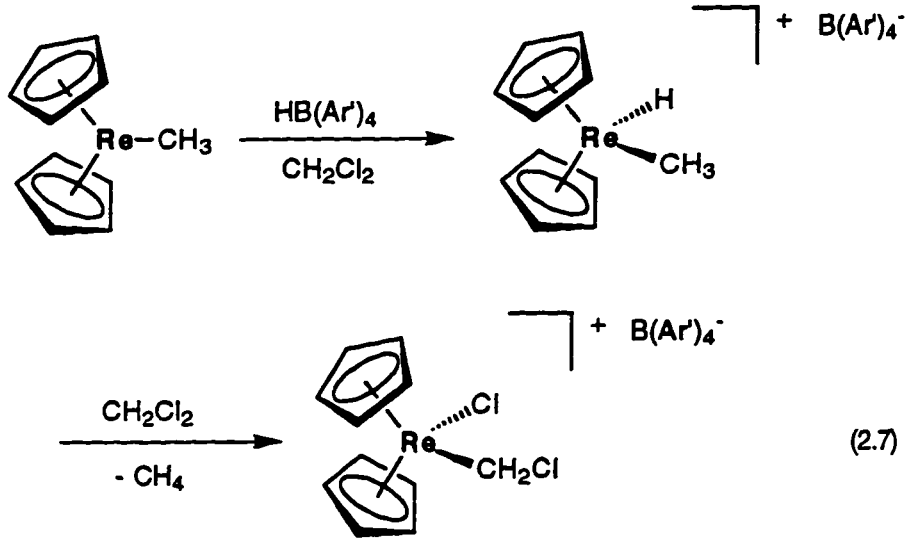
Electrophilic attack on the γ-carbon of η^1-allyl complexes is well precedented and has been reviewed by Rosenblum.[50] The only known reactivity of $Cp_2Re(CH_2CH{=}CH_2)$ is the protonation with $[H(Et_2O)]BF_4$ reported by Gould.[13] At low temperatures a cationic allyl hydride complex is formed although it was observed that even at -70 °C it was slowly isomerizing to an η^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 η^1-propene σ-complex which then undergoes a hydride shift or a rearrangement to the η^2 structure. Reductive elimination of propene followed by attachment in the η^2 configuration could occur assuming that "Cp_2Re^+" 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 γ-C of the allyl ligand. The bulky electrophile, $[Ph_3C]^+$, would likely attack only at the γ-C. The η^2-propene complex has been observed to have only one cyclopentadienyl resonance in the ^1H NMR suggesting that the olefin is spinning rapidly on the NMR timescale or a coincidental chemical shift for the two Cp ligands. $[Cp_2Re(\eta^2\text{-}CH_2CH{=}CH_2CPh_3)]I$ has inequivalent cyclopentadienyl ligands presumably due to the sterics of the CPh_3 group which hinders the rotation. High temperature ^1H 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 ($[Me_3O]BF_4$, $SiMe_3OTf$) to $Cp_2ReCH_2CH{=}CH_2$.

The addition of $[Ph_3C]B(Ar')_4$ to $Cp_2ReCH_2SiMe_3$ in CD_2Cl_2 results in decomposition and the only identifiable species in solution is $[Cp_2ReH_2]B(Ar')_4$. Gladysz and coworkers have investigated the reaction of $[Ph_3C]BF_4$ with $CpRe(NO)(PPh_3)(CH_2CMe_3)$ and could not identify any organometallic products.[39] The trimethylsilylmethyl and neopentyl ligands lack β-hydrides, but the steric bulk of the alkyl ligands should discourage α-hydride abstraction based on the trends reported by Gladysz and coworkers.

Reactivity of Cp_2ReCH_3 with $[H(Et_2O)_2]B(Ar')_4$ and HCl. Previous investigations from this group have reported the protonation of Cp_2ReCH_3 to generate

Re(V) alkyl hydride complexes of the form, $[Cp_2Re(CH_3)H]^+$.[5] 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, Cp_2ReCl is formed from $[Cp_2Re(CH_3)H]Cl$ while methane elimination from $[Cp_2Re(CH_3)H]BF_4$ results in decomposition. The protonation of Cp_2ReCH_3 with $[H(Et_2O)_2]B(Ar')_4$ results in the formation of $[Cp_2Re(CH_3)H]B(Ar')_4$ 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 "Cp_2Re^+" (eq 2.7).



(2.7)

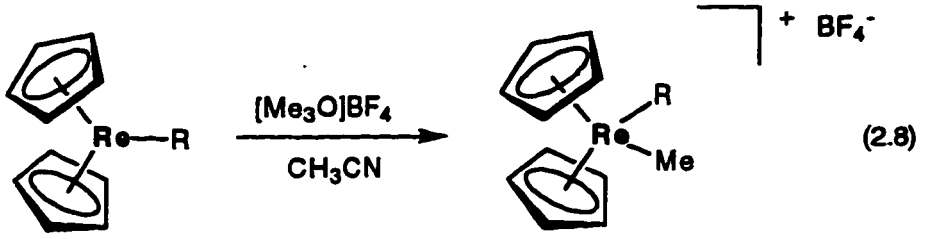
5

There was no evidence for the intermediacy of an η^1–CH_2Cl_2 type complex which has been observed in some systems either as an intermediate prior to oxidative addition[51,52] or as a stable complex.[53,54] Confirmation of the structure of **5**, depicted above, was obtained by ^1H and ^{13}C NMR spectroscopy. The ^1H 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_2Cl appears as a triplet at δ 11.5 (J_{CH} = 163 Hz). Complex **5** can also be formed by the reaction of $[Cp_2Re{=}CH_2]B(Ar')_4$ (**1**) with Cl_2 in CH_2Cl_2 (see Chapter 3).

A synthetic prep for Cp_2ReCl in good yield and purity has remained elusive. Cp_2ReCl can be prepared directly from $ReCl_5$ with KCp (4 equiv.) in 10% yield and has been structurally characterized.[55] The preparation of Cp_2ReCl from Cp_2ReH has been previously reported by two groups.[4,6] Baudry and Ephritikine reported that Cp_2ReCl is formed by addition of CCl_4 to an acetone solution of Cp_2ReH. In a similar preparation, Mink and Stucky isolate Cp_2ReCl by refluxing Cp_2ReH in $CHCl_3$. Both reported yields are quite low although possible side reactions are not investigated. We have observed that Cp_2ReH reacts in $CDCl_3$ at room temperature to readily form $[Cp_2ReH_2]Cl$. This product presumably forms from the oxidation of Cp_2ReH which will be discussed later. The ^1H NMR investigations of $[Cp_2Re(CH_3)H]^+$ by Gould has found that when the anion is chloride, Cp_2ReCl will be formed quantitatively upon methane elimination.[5] The protonation of Cp_2ReCH_3 with HCl followed by stirring in CH_2Cl_2 gives a dark orange solution with brown precipitate. The solvent was removed *in vacuo* and Cp_2ReCl was isolated in 91% yield as an analytically pure solid with a single resonance in the ^1H NMR spectrum in CD_2Cl_2 (δ 4.54). Although this route involves the added step of preparing Cp_2ReCH_3, the benefits of isolating a clean product in near quantitative yield outweigh the drawbacks.

Synthesis of $Cp_2Re(R)CH_3^+$. The synthesis of the dialkyl, $[Cp_2Re(CH_3)_2]PF_6$, has been previously reported by the reaction of Cp_2ReH with excess methyl iodide in the presence of base. We have found that a series of dialkyl complexes can be synthesized by reacting Cp_2ReR (R = CH_3, CH_2CH_3, CH_2SiMe_3) compounds with $[Me_3O]BF_4$ in CH_3CN (eq 2.8).



(2.8)

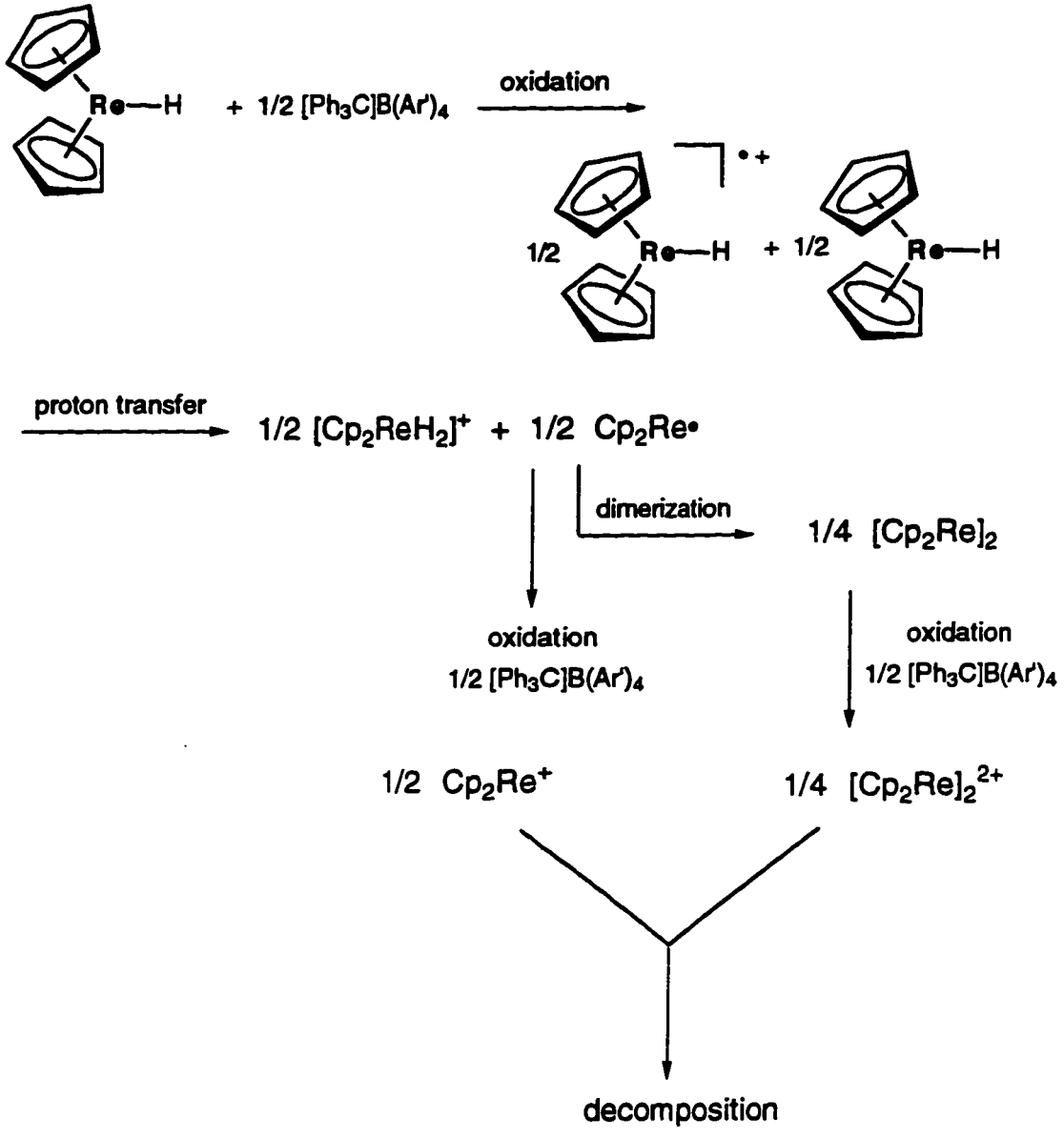
R = CH_3 (6), CH_2CH_3 (7), CH_2SiMe_3 (8)

The spectroscopic data for complex **6** was identical to that previously reported. The reactions can be run in CD_2Cl_2 or CD_3CN, 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 $[Cp_2ReH_2]^+$ and $[Cp_2Re(CH_3)_2]^+$ in CD_3CN at 90 °C.[13] 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 β hydrogens of the ethyl group. Reductive elimination of methane from complex **7** might provide a facile route to the ethylene complex, $[Cp_2Re(C_2H_4)]BF_4$. Complex **7** was observed to decompose after heating in CD_3CN 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 β hydrogen would most likely occur to the metal center which for this complex is already electronically saturated.

Reactivity of Cp_2ReH with Electrophiles. Sweet has reported extensive studies of CpRe(NO)(CO)H with trityl cation in which a hydride is abstracted and Ph_3CH is generated.[56] When these reactions are conducted in the presence of donor solvents such as CH_3CN, 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 η^2-Ph_3CH in which a fluxional process interconverts diastereomers. Gladysz and coworkers have demonstrated in a similar system that $CpRe(NO)(PPh_3)H$ reacts with $[Ph_3C]PF_6$ to generate Ph_3CH and $[CpRe(NO)(PPh_3)L]^+$ in the presence of THF or diethyl ether.[57]

Mink and Stucky have previously reported that Cp_2ReH reacts with $[Ph_3C]BF_4$ to generate "Cp_2ReBF_4". It was not reported whether the species is an unsaturated cationic species or if BF_4^- is coordinated to the metal center. We have observed that Cp_2ReH reacts with $[Ph_3C]B(Ar')_4$ in CD_2Cl_2 to generate two species at -78 °C. The first complex has been identified as $[Cp_2ReH_2]B(Ar')_4$ by comparison to the ^1H NMR spectrum of an authentic sample. The second complex exhibits a cyclopentadienyl resonance of equal intensity to $[Cp_2ReH_2]^+$ but no other ^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 $[Cp_2ReH_2]^+$ we began to speculate upon the mechanism of this reaction in order to identify the unknown species (Scheme 2.7).



Scheme 2.7

Attempts were made to trap the unknown species with H_2, CH_4, C_2H_4, and PPh_3 to give previously characterized compounds, but none of these compounds were identified in the ^1H NMR spectra. When the reaction between Cp_2ReH and $[Ph_3C]B(Ar')_4$ was carried out in CD_3CN, $[Cp_2Re(NCCD_3)]^+$ 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 $[Cp_2Re]^+$ was generated based on the previous result that $[Cp_2Re(CH_3)H]^+$ cleanly reacted with CH_2Cl_2 upon methane elimination to form $[Cp_2Re(CH_2Cl)Cl]^+$.

The synthesis of $[Cp_2Re]_2$ 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 $[Cp_2Re]_2$ with $[Ph_3C]B(Ar')_4$, $[Cp_2Fe]B(Ar')_4$ and $[H(Et_2O)_2]B(Ar')_4$ failed to provide any clean products even at low temperature.

Although we could not conclusively identify the second product of the reaction of Cp_2ReH with $[Ph_3C]B(Ar')_4$, it is clear that Cp_2ReH does not react by a simple hydride abstraction mechanism as described for $CpRe(NO)(CO)H$ and $CpRe(NO)(PPh_3)H$. Cp_2ReH is more electron rich than either of these complexes and is oxidized by $[Ph_3C]^+$. The previous reports of Cp_2ReBF_4[14] and $[Cp_2Re]CuCl_2$[11] are more likely to be characterized as $[Cp_2ReH_2]^+$ based on the reactivity reported here as well as the suspect characterization of these complexes.

The synthesis of $[Cp_2ReH_2]^+$ has been reported by several groups with a variety of anions by the direct protonation of Cp_2ReH.[2,3,4,6,13] We have prepared $[Cp_2ReH_2]B(Ar')_4$ by the reaction of Cp_2ReH with $[H(Et_2O)_2]B(Ar')_4$ in Et_2O. The dihydride was isolated as a white solid in 95 % yield. The ^1H 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. $[Cp_2ReH_2]B(Ar')_4$ has resonances at δ 5.30 (Cp) and - 13.83 (H) while the resonances for $[Cp_2ReH_2]Cl$ are observed at δ 5.68 (Cp) and - 14.04 (H).

Due to the recent interest in synthesizing dicationic dihydrogen complexes we prepared and isolated $[Cp_2ReH_2]OTf$. Attempts to react this complex with a large excess of triflic acid did not produce any observable change in the ^1H NMR spectrum.

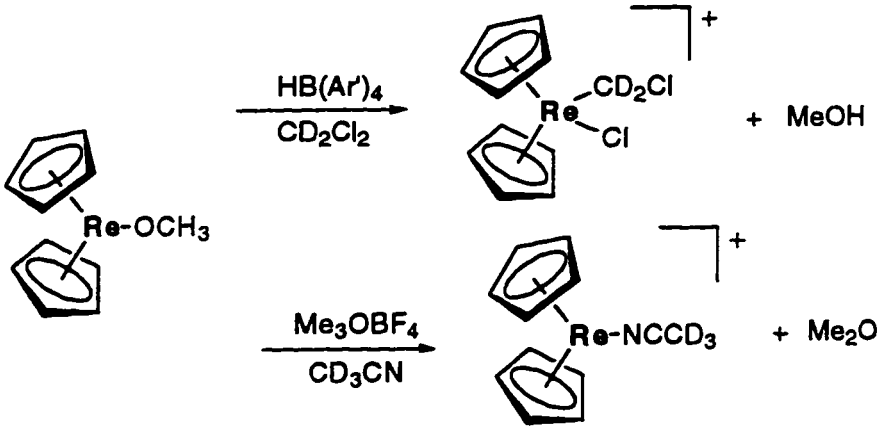
Reactivity of Cp_2ReCl with Electrophiles. As described above, Cp_2ReCl can now be synthesized in excellent yield and purity. It was anticipated that this compound would be a useful starting material for preparation of a variety of new compounds. $[H(Et_2O)_2]B(Ar')_4$ reacts cleanly with Cp_2ReCl in CD_2Cl_2 to form $[Cp_2Re(H)Cl]B(Ar')_4$ (**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 LiNHPh* (Ph* = 2,6-diisopropylphenyl) to regenerate Cp_2ReCl and NH_2Ph*.

Attempts to react Cp_2ReCl with halide abstraction reagents such as AgOTf and $AgBF_4$ led to several products even when conducted in CD_3CN. Complex **9** was often the major product which could be identified from these reactions which is formed by the oxidation of Cp_2ReCl. Thallium reagents are considered to be useful for halide abstraction reagents and are less oxidizing than silver reagents. $TlB(Ar')_4$ was synthesized by addition of TlOEt to an ether solution of $[H(Et_2O)_2]B(Ar')_4$ and isolated as a white solid.[24] The addition of $TlB(Ar')_4$ to Cp_2ReCl again lead to oxidized products including $[Cp_2ReH(Cl)]^+$ as the major product. The reaction of $[Me_3O]BF_4$ with Cp_2ReCl also produced **9** and the thermolysis of Cp_2ReCl with LiNHPh* or KOH in THF failed to produce any reaction.

Reactivity of Cp_2ReOCH_3 with Electrophiles. The synthesis of Cp_2ReOCH_3 from Cp_2ReCH_3 and CH_3OH was reported by Gould.[13] The reaction was proposed to proceed by protonation to $[Cp_2Re(CH_3)H]OCH_3$ followed by reductive elimination of methane and coordination of OCH_3^-. 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 Cp_2ReOCH_3 with $[Ph_3C]B(Ar')_4$ in CD_2Cl_2 led to many products. The only product which was identified from the mixture was Ph_3COCH_3, indicating that some of the methoxide complex had reacted by abstraction of 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 $[H(Et_2O)_2]B(Ar')_4$ with Cp_2ReOCH_3 in CD_2Cl_2 led to clean formation of CH_3OH and $[Cp_2Re(CD_2Cl)Cl]B(Ar')_4$. Similarly, $[Me_3O]BF_4$ was observed to react with Cp_2ReOCH_3 in CD_3CN to cleanly form $(CH_3)_2O$ and $Cp_2ReNCCD_3^+$.



Scheme 2.8

These reactions were closely monitored by low temperature ^1H 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(CH_3)(OCH_3).[59] Apparently coordinated alcohols or ethers are unstable in the presence of coordinating solvents such as CD_2Cl_2 and CD_3CN.

Conclusions

This chapter details the reactivity of electron rich Cp_2ReX (X = H, alkyl, Cl, OCH_3) complexes with electrophilic reagents (H^+, Me^+, Ph_3C^+, Cp_2Fe^+). $[Ph_3C]B(Ar')_4$ reacts with Cp_2ReCH_3 and $Cp_2ReCH_2CH_3$ to abstract an α-hydride from the alkyl ligand to generate carbene complexes, $[Cp_2Re{=}CH_2]B(Ar')_4$ (**1**) and $[Cp_2Re{=}CH(CH_3)]B(Ar')_4$ (**3**). The thermal stability of these complexes is dependent upon the anion and a more reactive anion such as BF_4^- leads to unstable carbene complexes either by reaction of Cp_2Re(alkyl) with $[Ph_3C]BF_4$ or by addition of BF_4^- salts to solutions of **1** and **3**. Both complexes **1** and **3** decompose to $[Cp_2Re(C_2H_4)]^+$ and $[Cp_2Re(NCCD_3)]^+$ in acetonitrile upon addition of BF_4^- salts or thermolysis of solutions. The hydride abstraction from Cp_2Re(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, $[Cp_2Fe]B(Ar')_4$.

Addition of $[H(Et_2O)_2]B(Ar')_4$ to Cp_2ReCH_3 in CH_2Cl_2 forms a thermally unstable alkyl hydride complex, $[Cp_2Re(CH_3)H]B(Ar')_4$. Methane elimination occurs at 0 °C followed by reaction with the solvent to form a stable chloromethyl chloride complex, $[Cp_2Re(CH_2Cl)Cl]B(Ar')_4$. Addition of $[Me_3O]BF_4$ to Cp_2ReR (R = CH_3, CH_2CH_3, CH_2SiMe_3) in acetonitrile forms stable bis-alkyl complexes, $[Cp_2Re(CH_3)R]BF_4$.

Cp_2ReH reacts with acids such as $[H(Et_2O)_2]B(Ar')_4$ and HOTf to form the stable dihydride cation, $[Cp_2ReH_2]^+$. $[Cp_2ReH_2]^+$ is formed by reaction of Cp_2ReH with oxidizing reagents, $[Ph_3C]B(Ar')_4$, $[Cp_2Fe]B(Ar')_4$ and $[Me_3O]BF_4$.

Experimental Section

General Considerations. General experimental techniques have been described in Chapter 1. Several of the starting materials (Cp_2ReH and Cp_2Re-alkyl) react rapidly with oxygen and rigorous Schlenk, glove-box, and vac-line procedures were followed. Cp_2ReH,[12] Cp_2ReCH_3,[12] Cp_2ReOCH_3,[13] $Cp_2ReCH_2CH_3$,[12] $Cp_2ReCH_2SiMe_3$,[12] $Cp_2ReCH_2CH{=}CH_2$,[12] $[Cp_2Re]_2$,[58] $Me_2SiCp_2ReCH_3$,[60] $[Ph_3C]BPh_4$,[61] $[Ph_3C]B(Ar')_4$,[22] $NaB(Ar')_4$,[21] and $[H(Et_2O)_2]B(Ar')_4$[21] were all prepared by reported procedures. All other reagents were purchased from Aldrich. The ^1H and ^{13}C resonances for $B(Ar')_4^-$ are identical with those reported for complex 1-$B(Ar')_4$ and have been omitted from subsequent complexes.

Synthesis of Complexes.

$[(\eta^5\text{-}C_5H_5)_2Re{=}CH_2]B(Ar')_4$ (1-$B(Ar')_4$). A 20 mL round bottom flask was charged with $(\eta^5\text{-}C_5H_5)_2ReCH_3$ (250 mg, 0.754 mmol), $[Ph_3C]B(Ar')_4$ (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_2Cl_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_2Cl_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, η^5-C_5H_5). ^{13}C NMR (CD_2Cl_2): 247.7 (t, J_{CH} = 152 Hz, Re-CH_2); 162.2 (quart, $^1J_{CB}$ = 49.8 Hz, B(Ar')$_4$ ipso); 135.2 (d, $^1J_{CH}$ = 158.9 Hz, *o*-B(Ar')$_4$); 129.3 (quart, $^2J_{CF}$ = 30.1 Hz, *m* -B(Ar')$_4$); 125.0 (quart, $^1J_{CF}$ = 272.3 Hz, B(Ar')$_4$ *C*F$_3$); 117.9 (d of t, $^1J_{CH}$ = 165.9 Hz, $^3J_{CF}$ = 3.6 Hz, *p*-B(Ar')$_4$); 86.4 (d of quint, $^1J_{CH}$ = 188 Hz, J_{CH} = 7 Hz, η^5-C_5H_5). Anal. Calcd for $C_{43}H_{24}BF_{24}Re$: C, 43.27; H, 2.03. Found: C, 43.19; H, 2.06.

[(η^5-C_5H_5)$_2$Re=CH_2]BPh$_4$ (1-BPh$_4$). A 20 mL round bottom flask was charged with (η^5-C_5H_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_2Cl_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_2Cl_2): 12.95 (s, 2 H, Re-CH_2); 7.4 - 6.8 (m, BPh$_4$); 5.29 (s, 10 H, η^5-C_5H_5).

[(η^5-C_5H_4-Si(CH_3)$_2$-η^5-C_5H_4)Re=CH_2]B(Ar')$_4$ (2). A 20 mL round bottom flask was charged with (η^5-C_5H_4-Si(CH_3)$_2$-η^5-C_5H_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_2Cl_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_2Cl_2): 12.76 (s, 2 H, Re=C*H*$_2$); 6.02 (t, 4H, J_{HH} = 1.8 Hz, η^5-C_5H_4,); 5.87 (t, 4 H, J_{HH} = 1.8Hz, η^5-C_5H_4); 0.34 (s, 6 H, Si(C*H*$_3$)$_2$). ^{13}C NMR (CD_2Cl_2): 246.1 (t, J_{CH} = 150 Hz, Re=*C*H$_2$); 101.4 (d of quart, $^1J_{CH}$ = 186 Hz, J_{CH} = 6 Hz, η^5-C_5H_4); 86.6 (d of quart, $^1J_{CH}$ = 189 Hz, J_{CH} = 7 Hz, η^5-C_5H_4); -6.5 (quart, J_{CH} = 123 Hz, Si(*C*H$_3$)$_2$). Anal. Calcd for $C_{45}H_{28}BF_{24}ReSi$: C, 43.25; H, 2.26. Found: C, 42.85; H, 2.25.

[(η^5-C_5H_5)$_2$Re=CH(CH$_3$)]B(Ar')$_4$ (3). A 20 mL round bottom flask was charged with (η^5-C_5H_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_2Cl_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_2Cl_2): 13.82 (quart, 1 H, J_{HH} = 7.9 Hz, Re=C*H*(CH$_3$)); 5.56 (s, 5 H, η^5-C_5H_5); 5.51 (s, 5 H, η^5-C_5H_5); 1.53 (d, 3 H, J_{HH} = 8.1 Hz, Re=CH(C*H*$_3$)). ^{13}C NMR (CD_2Cl_2): 266.0 (d, J_{CH} = 143 Hz, Re=*C*H(CH$_3$)); 86.0 (d of quint, J_{CH} = 187 Hz, J_{CH} = 6 Hz, η^5-C_5H_5); 85.6 (d of quint, J_{CH} = 187Hz, J_{CH} = 6 Hz, η^5-C_5H_5); 45.0 (quart, J_{CH} = 128 Hz, Re=CH(*C*H$_3$). Anal. Calcd for $C_{44}H_{26}BF_{24}Re$: C, 43.76; H, 2.17. Found: C, 43.70; H, 2.16.

$[(\eta^5\text{-}C_5H_5)_2Re(\eta^2\text{-}H_2C{=}CHCHCPh_3)]I$ (4). A 20 mL round bottom flask was charged with $(\eta^5\text{-}C_5H_5)_2Re(CH_2CH{=}CH_2)$ (74.5 mg, 0.21 mmol), $[Ph_3C]B(Ar')_4$ (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 CH_2Cl_2 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 $CHCl_3$/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 Et_2O. ^1H NMR (CD_2Cl_2): 7.4 to 7.2 (m, CPh_3); 5.43 (s,η^5-C_5H_5); 5.11 (s, η^5-C_5H_5); 3.77 (d of d, J_{HH} = 13.72 and 1 Hz, η^2-CH_2=$CHCH_2CPh_3$); 2.72 (m, η^2-CH_2=$CHCH_2CPh_3$); 2.34 (d of d, J_{HH} = 13.65 and 9.08 Hz, η^2-CH_2=$CHCH_2CPh_3$); 2.01 (d of d, J_{HH} = 9.42 and 5.05 Hz, η^2-CH_2=$CHCH_2CPh_3$); 1.72 (d of d, J_{HH} = 13.22 and 5.06 Hz, η^2-CH_2=$CHCH_2CPh_3$).

$[(\eta^5\text{-}C_5H_5)_2Fe]B(Ar')_4$ Ferrocene (0.625 g, 3.36 mmol) was placed in a small beaker followed by 12.5 mL of H_2SO_4. The dark blue solution was stirred for two hours then added to 185 mL of H_2O 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 H_2O, and dried overnight under dynamic vacuum. Yield 0.892 g (76 %). ^1H NMR (acetone-d_6): 28 (s, 10H, Cp_2Fe^+); 7.8 (s, 4H, *p*-$B(Ar')_4$); 7.7 (s, 8H, *o*-$B(Ar')_4$).

$[(\eta^5\text{-}C_5H_5)_2Re(CH_2Cl)Cl]B(Ar')_4$ (5). A small glass vessel with an 8 mm Kontes valve was charged with $(\eta^5\text{-}C_5H_5)_2ReCH_3$ (50 mg, 0.151 mmol) and $[H(Et_2O)_2]B(Ar')_4$ (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 (CD_2Cl_2): 6.02 (s, 10 H, η^5-C_5H_5); 4.40 (s, 2 H, Re-CH_2Cl). ^{13}C NMR (CD_2Cl_2): 98.6 (d of quint, $^1J_{CH}$ = 191.4 Hz, J_{CH} = 6.3 Hz, η^5-C_5H_5); 11.5 (t, J_{CH} = 163.1 Hz, Re-CH_2Cl). Anal. Calcd for $C_{43}H_{24}BCl_2F_{24}Re$: C, 40.84; H, 1.91. Found: C, 40.65; H, 2.02.

$(\eta^5\text{-}C_5H_5)_2ReCl$ A small glass vessel with an 8 mm Kontes valve was charged with $(\eta^5\text{-}C_5H_5)_2ReCH_3$ (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 anyhdrous 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 CH_2Cl_2 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 (CD_2Cl_2): 4.54 (s, η^5-C_5H_5). Anal. Calcd for $C_{10}H_{10}ClRe$: C, 34.14; H, 2.86. Found: C, 33.71; H, 3.06.

$[(\eta^5\text{-}C_5H_5)_2Re(CH_3)_2]BF_4$ (6). A NMR tube was charged with $(\eta^5$-$C_5H_5)_2ReCH_3$ (4 mg, 0.012 mmol) and $[Me_3O]BF_4$ (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_3CN): 5.38 (s, 10 H, η^5-C_5H_5); 0.97 (s, 6 H, Re-CH_3).

[(η^5-C_5H_5)$_2$Re(CH_3)CH_2CH_3]BF_4 (7). A NMR tube was charged with (η^5-C_5H_5)$_2$ReCH_2CH_3 (2 mg, 0.006 mmol) and [Me_3O]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_3CN): 5.37 (s, 10 H, η^5-C_5H_5); 1.69 to 1.46 (m, 5 H, Re-CH_2CH_3); 0.81 (s, 3 H, Re-CH_3).

[(η^5-C_5H_5)$_2$Re(CH_3)($CH_2Si(CH_3)_3$)]BF_4 (8). A small glass vessel with an 8 mm Kontes valve was charged with (η^5-C_5H_5)$_2$Re($CH_2Si(CH_3)_3$) (50 mg, 0.124 mmol) and [Me_3O]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_2Cl_2): 5.43 (s, 10 H, η^5-C_5H_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_2Cl_2): 91.5 (d of quart, $^1J_{CH}$ = 188 Hz, J_{CH} = 6 Hz, η^5-C_5H_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-).

[(η^5-C_5H_5)$_2$ReH_2]B(Ar')$_4$ A small glass vessel with an 8 mm Kontes valve was charged with (η^5-C_5H_5)$_2$ReH (100 mg, 0.315 mmol) and [H(Et_2O)$_2$]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_2Cl_2): 5.34 (s, 10 H, η^5-C_5H_5); -13.80 (s, 2 H, ReH_2).

[(η^5-C_5H_5)$_2$$ReH_2$]OTf A small glass vessel with an 8 mm Kontes valve was charged with (η^5-C_5H_5)$_2$ReH (50 mg, 0.157 mmol). Diethyl ether (5 mL) was vacuum transferred to the vessel and the solutionn was warmed to 0 °C. Under an argon flow, HOTf (14 μL, 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_2O and dried under vacuum. The solid was collected in 72% yield (53 mg). ^{1}H NMR (CD_2Cl_2): 5.48 (s, 10 H, η^5-C_5H_5); -13.98 (s, 2 H, ReH_2).

[(η^5-C_5H_5)$_2$Re(H)Cl]B(Ar')$_4$ A small glass vessel with an 8 mm Kontes valve was charged with (η^5-C_5H_5)$_2$ReCl (17.4 mg, 0.049 mmol) and [H(Et_2O)$_2$]B(Ar')$_4$ (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_2Cl_2): 5.85 (s, 10 H, η^5-C_5H_5); -11.84 (s, 1 H, Re-H).

[Tl]B(Ar')$_4$ A small glass vessel with an 8 mm Kontes valve was charged with [H(Et_2O)$_2$]B(Ar')$_4$ (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 μL, 0.222 mmol) in 5 mL of diethyl ether was slowly cannula transferred to the [H(Et_2O)$_2$]B(Ar')$_4$ 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_3CN): 7.70 (br, $B(Ar')_4$).

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CHAPTER 3

REACTIVITY OF A CATIONIC METHYLENE COMPLEX OF RHENOCENE

Introduction

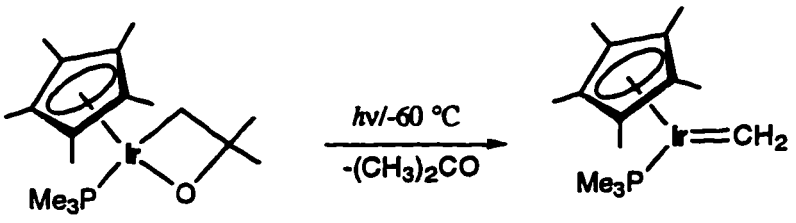
Fischer and Maasbol first reported the direct synthesis of a stable carbene complex in 1964 by reaction of an alkyl lithium reagent with $W(CO)_6$ followed by protonation and addition of diazomethane to give $(CO)_5W{=}CR(OMe)$.[1] "Fischer-type" carbene complexes are electrophilic and are typically 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 alkylidene complex in 1975 by the addition of two equivalents of neopentyl lithium to $Ta(neopentyl)_3Cl_2$ to form $(^tBuCH_2)_3Ta{=}CH^tBu$ and neopentane.[2] Unlike the Fischer carbenes, the alkylidene ligands formally have a 2^- charge and are typically formed on high valent, early transition metals. Typically the Schrock alkylidenes contain only alkyl or H substituents and are nucleophilic.

Schrock alkylidenes 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 $[Cp_2W(=CH_2)H]^+$ 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 $Ru(=CF_2)(PPh_3)(CO)_2$ reacts with both $MeNH_2$ 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 ^{n}alkyl chloride complex as well as deprotonation of the carbene with $KOCMe_3$ 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.

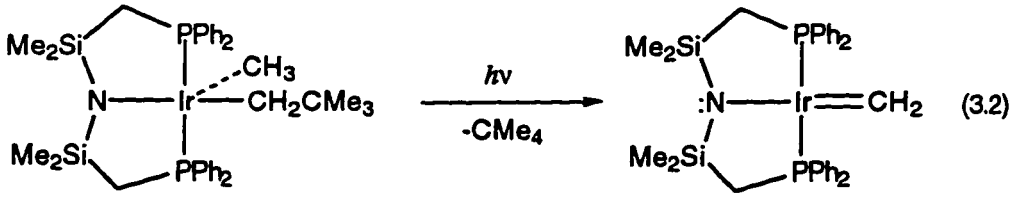
Despite the rapid development of carbene chemistry in the last 33 years,[6-8] few examples have been completely characterized due to their reactivity. The methylene ligand, $L_nM{=}CH_2$, is the simplest type of carbene ligand and the study of methylene ligands still remains quite rare. The first methylene complex was synthesized by deprotonation of $[Cp_2TaMe_2]^+$ to give $Cp_2TaCH_3(=CH_2)$.[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 $[Ph_3C]^+$. Gladysz and coworkers have successfully abstracted an α-hydride from $Cp^*Re(NO)(PPh_3)(CH_3)$ using $[Ph_3C]^+$ to give a stable methylene complex which has been structurally characterized.[10] Despite the usefulness of hydride abstraction by $[Ph_3C]^+$, 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 $L_nM(\eta^2\text{-}C_2H_4)$. A number of unstable iron methylene complexes of the type $[CpFe(=CH_2)L_2]^+$ (L = PR_3 or CO) have been reported by the addition of a Lewis acid to a $CpFe(CH_2OR)L_2$ precursor.[11] Recently a stable complex was isolated in this series, $[Cp^*Fe(dppe)(=CH_2)]BF_4$; apparently the bulkier Cp* ligand and the more basic ligand set increase the stability of this complex.[12] Roper and coworkers have utilized diazomethane as a methylene transfer reagent to several coordinatively unsaturated Ru, Os and Ir complexes.[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 $Cp^*Ir(PMe_3)$(2-oxametallacyclobutane)[14] generates $Cp^*Ir(PMe_3)(=CH_2)$ and eliminates acetone (eq 3.1).[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.



(3.1)

Fryzuk has reported that photolysis of $[N(SiMe_2CH_2PPh_3)_2]Ir(CH_3)(CH_2CMe_3)$ eliminates neopentane to form the stable, 16 electron $[N(SiMe_2CH_2PPh_3)_2]Ir(CH_2)$ (eq 3.2).[16,17]



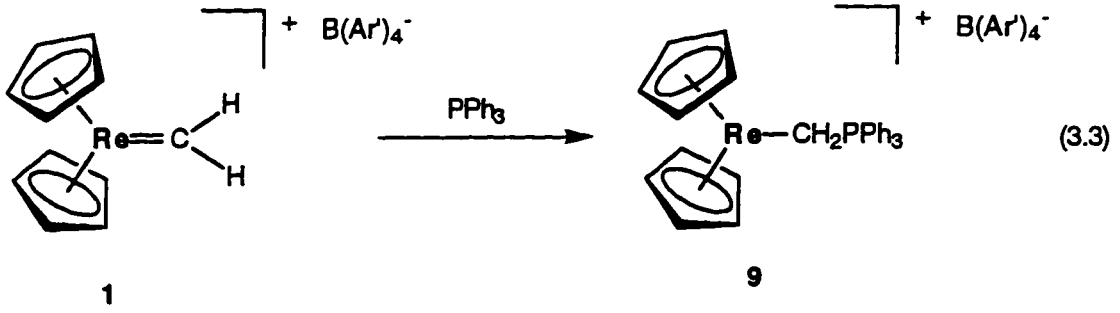
(3.2)

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. $CpFeL_2(CH_2SMe_2)^+$ has been shown to undergo cycloproponation reactions by providing a masked form of the unstable $CpFeL_2(=CH_2)^+$ complex.[19] We

have found that $[Cp_2Re{=}CH_2]B(Ar')_4$ (**1**) reacts with nucleophiles to provide ylide complexes.

Results and Discussion

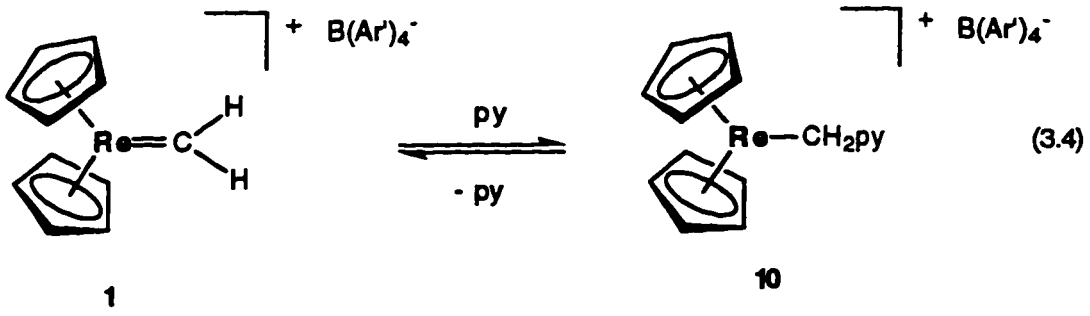
Reaction of $[Cp_2Re{=}CH_2]B(Ar')_4$ (1) with Nucleophiles. Addition of one equivalent of PPh_3 to a solution of **1** in methylene chloride results in an immediate color change from pink to pale orange. A crystalline solid is precipitated in 90% yield by addition of pentane. ^1H, $^{31}P\{$aromatic $^1H\}$, and ^{13}C NMR data are consistent with the formation of the expected phosphine–ylide complex, $[Cp_2Re(CH_2PPh_3)]B(Ar')_4$ (**9**) (eq 3.3).



1 **9** (3.3)

The ^1H and ^{13}C 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 ^{31}P coupling of 10.8 Hz. This is confirmed by the ^{31}P 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 ^{13}C NMR spectrum appears as a doublet of triplets due to ^{31}P and ^1H coupling (J_{CP} = 25.6 Hz, J_{CH} = 26.2 Hz).

Addition of three equivalents of pyridine (py) to **1** in CD_2Cl_2 resulted in the formation of a pyridine-ylide complex, $[Cp_2Re(CH_2NC_5H_5)]B(Ar')_4$ (**10**) (eq 3.4).

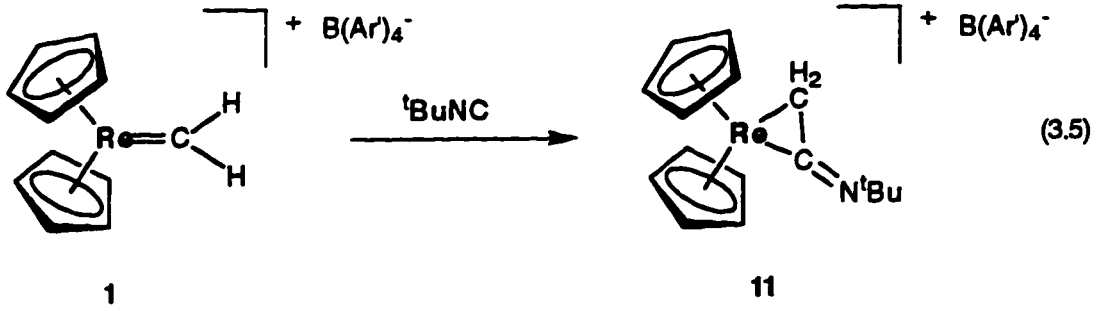


1 10 (3.4)

The ^1H 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 ^1H NMR spectrum of the solid dissolved in CD_2Cl_2 gave broadened resonances for the cyclopentadienyl and the methylene protons which were intermediate between the resonances for **5** and $[Cp_2Re{=}CH_2]^+$ (**1**). Addition of excess pyridine to the solution resulted in conversion back to the sharp ^1H 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_5H_5 and SMe_2.[20,21] The dimethylsulfide is labile in solution and is easily displaced by PPh_3 or NC_5H_5.

Addition of ^{t}BuNC to a CH_2Cl_2 solution of **1** gives a pale orange solution from which $[Cp_2ReCH_2CN^tBu]B(Ar')_4$ (**11**) is isolated in 86% yield (eq 3.5).



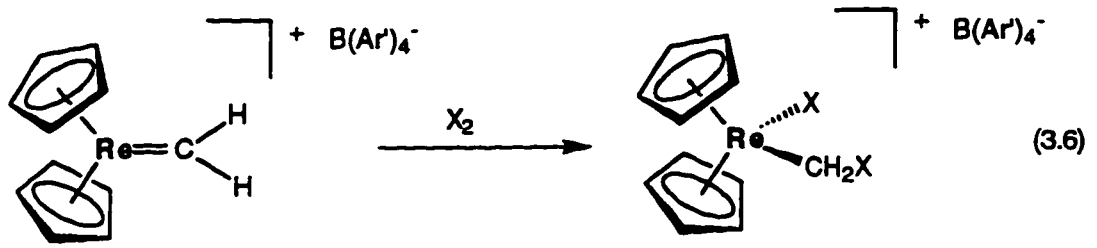
1 11 (3.5)

The ^1H 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 ν_{CN}.[22] 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 ν_{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 CN*p*tolyl 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_3CN, PhNCO, CO_2, or CS_2.

Reaction of 1 with Halogens. Based on our earlier observation of the trapping of "Cp_2Re^+" by CH_2Cl_2 to form $[Cp_2Re(CH_2Cl)Cl]^+$ (**5**), we sought to confirm the identity of the product via another synthetic route. We have observed that $[Cp_2Re{=}CH_2]B(Ar')_4$ (**1**) reacts readily with Cl_2 in CH_2Cl_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 ^1H NMR spectroscopy. The reaction can also be

reversed by sonicating a CD_2Cl_2 solution of **5** for two hours in the presence of Mg to form $[Cp_2Re{=}CH_2]^+$ (**1**). Complex **5** does not react under similar conditions with Hg. The bromine and iodine analogs, $[Cp_2Re(CH_2X)X]B(Ar')_4$ (**12**,Br; **13**,I), have been formed upon addition of Br_2 or I_2 to CH_2Cl_2 solutions of **1** (eq 3.6).

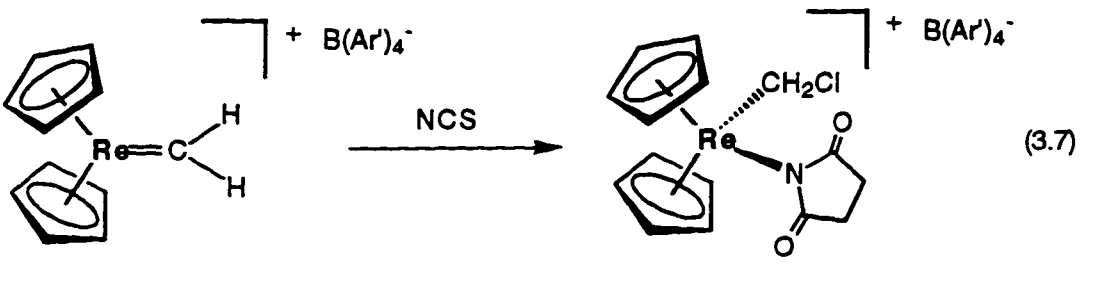


(3.6)

1 X = Cl (**5**), Br (**12**), I (**13**)

Complexes **5**, **12** and **13** have been isolated by recrystallization from CH_2Cl_2/pentane and completely characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. The ^1H and ^{13}C NMR resonances of the methylene group are observed to shift to higher field as the halogens become less electronegative (Cl>Br>I).

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 $[Cp_2Re(CH_2Cl)Cl]^+$ (**5**). NCS is known to be a good chlorine atom donor reagent and the product formed is consistent with $[Cp_2Re(CH_2Cl)$ $[NC(O)CH_2CH_2C(O)]]^+$.



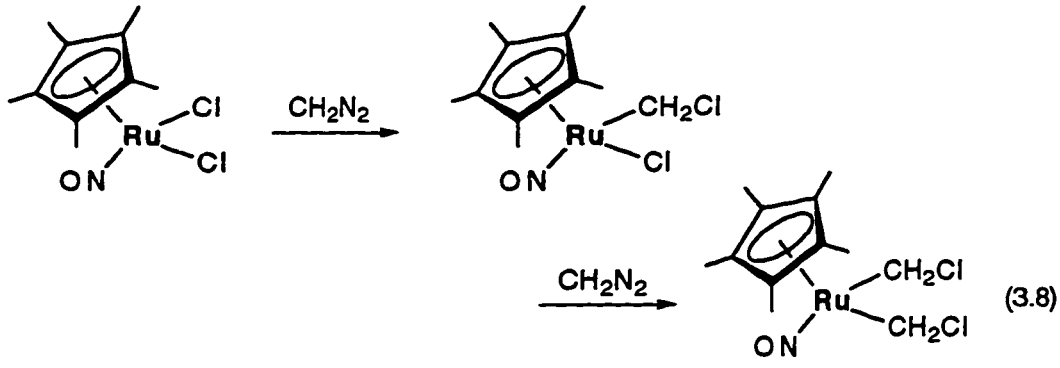
(3.7)

1

Bergman and Klein have reported that $Cp^*Ir(PMe_3)(=CH_2)$ reacts with several Lewis acids including succinimide which forms $Cp^*Ir(PMe_3)[NC(O)CH_2CH_2C(O)](CH_3)$.[15] Complex 1 shows no reactivity with succinimide and decomposes to several products in the presence of *N*-bromosuccinimide and *N*-iodosuccinimide. $Cp^*Ir(PMe_3)(=CH_2)$ was also found to oxidatively add HCl and H_2, neither of which reacted with $[Cp_2Re=CH_2]^+$.

Roper and coworkers have reported that $Os(=CH_2)(PPh_3)_2(NO)(Cl)$ reacts with chlorine to form a chloromethyl-chloride complex, $Os(CH_2Cl)(PPh_3)_2(NO)Cl_2$.[13] This complex undergoes further rearrangement to an ylide complex, $Os(CH_2PPh_3)(PPh_3)(NO)Cl_3$. It is not uncommon for neutral halomethyl complexes to react with phosphines to form cationic ylide complexes, $[L_nMCH_2PR_3]Cl$

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 CH_2Cl_2 to a coordinatively unsaturated metal complex.[23-27] These reactions often proceed by the thermal or photochemical reductive elimination of ligands in CH_2Cl_2 or by the reaction of Pt^0 square planar complexes with CH_2Cl_2. Hubbard and coworkers have reported the stepwise addition of diazomethane to $Cp^*Ru(NO)Cl_2$ (eq 3.8).[28]



(3.8)

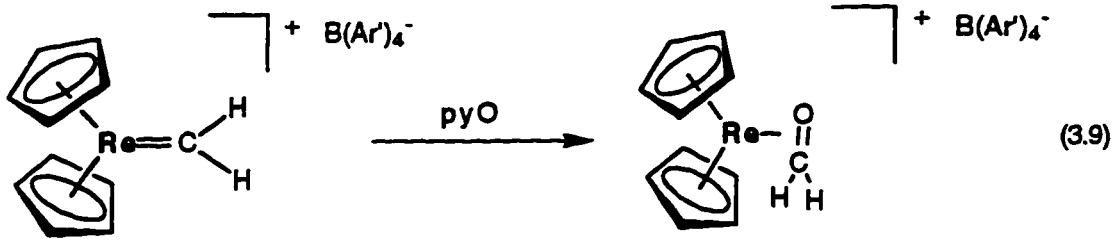
The chloromethyl-chloride complex has been shown to form polymethylene upon thermolysis or photolysis, while the bis(chloromethyl) complex extrudes ethylene. In both cases the dichloride complex is formed. Thermolysis of complex **7** did not result in any conversion to the known $[Cp_2ReCl_2]^+$.[29]

Reaction of 1 with Pyridine *N*–oxide: Formation of an η^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 $Os(\eta^2\text{-}H_2C{=}O)(CO)_2(PPh_3)_2$. 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 η^1 or η^2. Gladysz and Huang have reviewed the field of formaldehyde, aldehyde and ketone complexes from work in their lab and others.[33]

$[Cp_2Re{=}CH_2]B(Ar')_4$ (**1**) reacts cleanly with pyridine *N*-oxide (pyO) to form $[Cp_2Re(\eta^2\text{–}CH_2O)]B(Ar')_4$ (**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.



(3.9)

1 14

The ^1H NMR spectrum shows a single Cp resonance at 5.49 ppm and a resonance at 3.69 ppm for the methylene protons. The highfield ^{13}C NMR resonance of the formaldehyde ligand at 46.2 ppm is consistent with an η^2–CH_2O structure. The IR spectra of $[Cp_2Re{=}CH_2]B(Ar')_4$ and $[Cp_2Re(\eta^2\text{-}H_2C{=}O)]B(Ar')_4$ were compared, but a band for νCO 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 νCO was observed in the IR spectrum for $Cp_2V(\eta^2\text{-}H_2C{=}O)$ at 1160 cm^{-1} and for $Cp_2Mo(\eta^2\text{-}H_2C{=}O)$ 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_3NO. The reaction of Cp_2ReOCH_3 with $[Ph_3C]B(Ar')_4$ led to decomposition, although a resonance in the ^1H NMR spectrum identified Ph_3COCH_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_3CN at 55 °C for several days eventually led to the formation of $[Cp_2ReNCCD_3]^+$. Complex **14** reacts similarly with CD_2Cl_2 to form $[Cp_2Re(CD_2Cl)Cl]^+$ (**5**) after several days at 55 °C. A solution of **14** and PPh_3 in CD_2Cl_2 slowly forms $[Cp_2RePPh_3]^+$ after a week at room temperature. $[Cp_2RePPh_3]^+$ has been previously prepared by thermolysis of $[Cp_2ReH_2]^+$ with PPh_3 at 100 °C in

DMSO.[35] This reactivity suggests that complex **14** may be useful in the synthesis of new complexes by displacement of the relatively weak formaldehyde ligand.

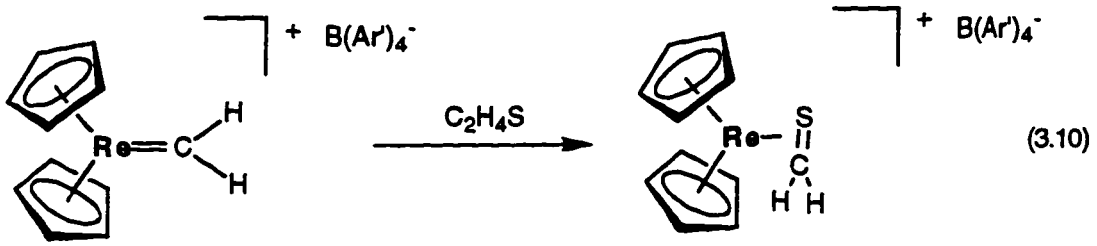
Pyridine *N*-oxide reacts slowly over several days with the phosphine ylide complex, $[Cp_2ReCH_2PPh_3]^+$, to form **14**. Consistent with the above observations of the displacement of the formaldehyde ligand, complex **14** reacts with the free PPh_3 in solution and $[Cp_2RePPh_3]^+$ is the final product. Although pyridine and PPh_3 are present in solution in equal amounts, there is no evidence for the formation of $[Cp_2Re(py)]^+$.[35] $[Cp_2ReCH_2CN^tBu]^+$ does not react with pyO at room temperature in CD_2Cl_2 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 LiNHPh* 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 rhenocene complex. A likely product would be the neutral formyl complex, $Cp_2Re(HCO)$, 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 $CpRe(NO)(PPh_3)(CHO)$ for which the ^1H NMR spectrum reveals a resonance for the formyl ligand at 16.5 ppm.[20] Compound **14** does not react with CS_2, H_2, or H_2O and heating in CD_2Cl_2 at 55 °C eventually leads to $[Cp_2Re(CD_2Cl)Cl]^+$ (**5**) as the only product.

Reaction of 1 with Sulfur-Atom Donors: Formation of an η^2-Thioformaldehyde Complex. The synthesis of a series of chalcogen η^2-H_2C=E (E = S, Se, Te) complexes have been reported by several groups. Roper and coworkers have reported that $Os(=CH_2)(PPh_3)_2(NO)(Cl)$ reacts slowly with elemental S, Se, and Te to form chalcoformaldehyde complexes.[4] Werner and Paul have reported a similar series

by reaction of NaEH (E = S, Se, Te) with $CpRh(PMe_3)(CH_2I)I$.[36] 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, $S{=}PPh_3$, and S_8.[37,38]

Complex **1** reacts with excess sulfur in CD_2Cl_2 for 3 hours at 50 °C and leads to the clean formation of a thioformaldehyde complex. $[Cp_2Re(\eta^2\text{–}CH_2S)]B(Ar')_4$ (**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 CH_2Cl_2/pentane followed by filtration.



(3.10)

1 **15**

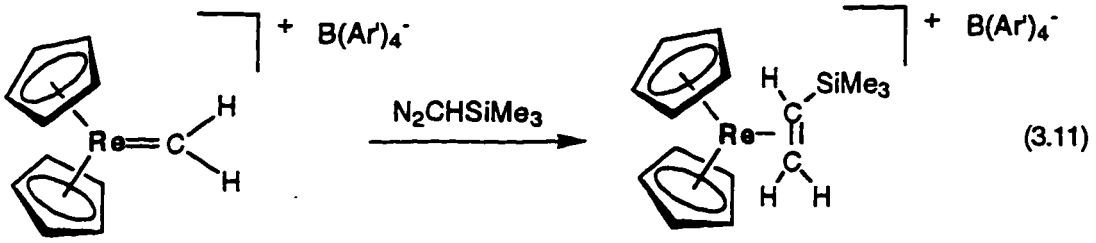
The ^1H NMR spectrum shows a cyclopentadienyl resonance at 5.47 ppm and a methylene resonance for the thioformaldehyde ligand at 3.41 ppm. The ^{13}C NMR spectrum reveals a cyclopentadienyl resonance at 88.2 ppm and a triplet at 13.7 ppm for CH_2S with $^1J_{CH}$ = 168 Hz.

The phosphonium ylide complex, $[Cp_2ReCH_2PPh_3]^+$ (**9**), reacts rapidly with excess ethylene sulfide to form complex **15** and $S{=}PPh_3$. Addition of $S{=}PPh_3$ to complex **1** produces a 50/50 mixture of $[Cp_2ReCH_2PPh_3]^+$ (**9**) and $[Cp_2Re(\eta^2\text{-}H_2C{=}S)]^+$ (**15**). Complex **9** is likely formed by the rapid reaction of **1** with the free PPh_3 after transfer of the sulfur atom since there is no reaction of **15** with $S{=}PPh_3$ to form **9**. Similar results have been observed by Gladysz and coworkers.[33] Also

consistent with the observations of Gladysz and coworkers, the thioformaldehyde ligand is less labile than the formaldehyde ligand. Heating complex **15** in CD_3CN for 2 weeks at 50 °C shows no formation of $[Cp_2Re(NCCD_3)]^+$. The thioformaldehyde ligand is not displaced by PPh_3, but reacts rapidly to form $[Cp_2ReCH_2PPh_3]^+$ 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 $N_2CHSiMe_3$ (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. $[Cp_2Re(CH_2{=}CHSiMe_3)]B(Ar')_4$ (**16**) is isolated in 69% yield by crystallization from a concentrated CH_2Cl_2 solution layered with pentane.



1 **16**

The ^1H 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 $[Cp_2Re{=}CH_2]B(Ar')_4$ (**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 $Cp_2Re(CH_2CH{=}CH_2)$ with electrophiles and the isomerization of the cationic ethylidene complex to $[Cp_2Re(\eta^2\text{-}C_2H_4)]^+$ (see Chapter 2). The isolation of $[Cp_2Re(\eta^2\text{-}C_2H_4)]^+$ 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 $[Cp_2Re{=}CH_2]B(Ar')_4$ (**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, $Cp_2TaCH_3(=CH_2)$, 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 PPh_3 and NC_5H_5 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, $[CpRe(NO)(PPh_3)(=CH_2)]^+$, which has been studied for many years by Gladysz and coworkers.[10,20,21,32,33,37,40] Complex **1** reacts with Cl_2, Br_2, I_2 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 η^2-formaldehyde, η^2-thioformaldehyde and η^2-olefin complexes. The reactivity of $[Cp_2Re{=}CH_2]B(Ar')_4$ (**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 $[Cp_2Re{=}CH_2]B(Ar')_4$ (**1**) is reported in Chapter 2. The ^1H and ^{13}C NMR resonances for $B(Ar')_4^-$ are identical with those reported for complex **1**-$B(Ar')_4$ 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.

$[(\eta^5\text{-}C_5H_5)_2ReCH_2PPh_3]B(Ar')_4$ (9). A small glass vessel with an 8 mm Kontes valve was charged with $[Cp_2Re{=}CH_2]B(Ar')_4$ (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). ^1H NMR (CD_2Cl_2): 7.4 to 7.9 (m, 15 H, PPh_3); 4.16 (s, 10 H, η^5-C_5H_5); 2.58 (d, 2 H, J_{PH} = 10.8 Hz, Re-CH_2). $^{31}P\{$aromatic $^1H\}$ NMR (CD_2Cl_2): 32.6 (t, PPh_3). ^{13}C NMR (CD_2Cl_2): 134.5 (s, *p*-PPh_3): 134.3 (d, J_{CP} = 8.9 Hz, *o*-PPh_3): 129.9 (d, J_{CP} = 163 Hz, *m*-PPh_3); 123.5 (d, J_{CP} = 81.3 Hz, ipso PPh_3); 73.7 (d of quint, $^1J_{CH}$ = 182.2 Hz, J_{CH} = 6.5 Hz, η^5-

C_5H_5); -32.7 (d of t, J_{CP} = 25.6 Hz, J_{CH} = 26.2 Hz, Re-CH_2). Anal. Calcd for $C_{61}H_{39}BF_{24}PRe$: C, 50.32; H, 2.70. Found: C, 49.48; H, 2.68.

$[(\eta^5\text{-}C_5H_5)_2ReCH_2CN^tBu]B(Ar')_4$ (11). A small glass vessel with an 8 mm Kontes valve was charged with $[(\eta^5\text{-}C_5H_5)_2Re{=}CH_2]B(Ar')_4$ (60 mg, 0.0503 mmol). Dichloromethane (15mL) was vacuum transferred to the vessel. Under an argon flow, CN^tBu (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 (CD_2Cl_2): 5.15 (s, 10 H, η^5-C_5H_5); 1.64 (s, 2 H, Re-CH_2); 1.26 (s, 9 H, CN^tBu). ^{13}C NMR (CD_2Cl_2): 158.5 (s, CN^tBu); 84.0 (d of quint, $^1J_{CH}$ = 188 Hz, J_{CH} = 6.4 Hz, η^5-C_5H_5); 28.8 (quart, J_{CH} = 125.9 Hz, CN^tBu); -31.8 (t, J_{CH} = 163.8, Re-CH_2). IR (cm^{-1}, Nujol, νCN): 1780. Anal. Calcd for $C_{48}H_{33}BF_{24}NRe$: C, 45.16; H, 2.60; N, 1.10. Found: C, 44.82; H, 2.55; N, 1.15.

Reaction of $[(\eta^5\text{-}C_5H_5)_2Re(=CH_2)]B(Ar')_4$ with pyridine A sealable NMR tube was charged with $[(\eta^5\text{-}C_5H_5)_2Re(=CH_2)]B(Ar')_4$ (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 (CD_2Cl_2): 8.6 and 7.2 (m, free and coordinated NC_5H_5); 5.86 (br, 2 H, Re-CH_2-); 4.51 (s, 10 H, η^5-C_5H_5).

[(η^5-C_5H_5)$_2$Re(CH_2Cl)Cl]B(Ar')$_4$ (5). A sealable NMR tube was charged with [(η^5-C_5H_5)$_2$Re(=CH_2)]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 (CD_2Cl_2): 6.02 (s, 10H, η^5-C_5H_5); 4.40 (s, Re-CH_2Cl). ^{13}C NMR data and elemental analysis for this complex are reported in Chapter 2.

[(η^5-C_5H_5)$_2$Re(CH_2Br)Br]B(Ar')$_4$ (12). A small glass vessel with an 8 mm Kontes valve was charged with [(η^5-C_5H_5)$_2$Re=CH_2]B(Ar')$_4$ (60 mg, 0.0503 mmol). Dichloromethane (10 mL) was vacuum transferred to the vessel. The solution was titrated with a Br_2/CH_2Cl_2 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 CH_2Cl_2 and pentane and isolated in 81% yield (55 mg). ^{1}H NMR (CD_2Cl_2): 6.06 (s, 10 H, η^5- C_5H_5); 4.26 (s, 2 H, Re-CH_2Br). ^{13}C NMR (CD_2Cl_2): 98.1 (d of quint, $^1J_{CH}$ = 191.8 Hz, J_{CH} = 6.1 Hz, η^5-C_5H_5); -5.58 (t, J_{CH} = 162.4 Hz, Re-CH_2Br). Anal. Calcd for $C_{43}H_{24}BBr_2F_{24}Re$: C, 38.16; H, 1.79. Found: C, 37.95; H, 1.80.

[(η^5-C_5H_5)$_2$Re(CH_2I)I]B(Ar')$_4$ (13). A small glass vessel with an 8 mm Kontes valve was charged with [(η^5-C_5H_5)$_2$Re=CH_2]B(Ar')$_4$ (60 mg, 0.0503 mmol). Dichloromethane (10 mL) was vacuum transferred to the vessel. Under an argon flow I_2 (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 CH_2Cl_2 and pentane. The product was isolated as a light green solid in 86% yield (63 mg). ^{1}H NMR (CD_2Cl_2): 6.06 (s, 10 H, η^5-C_5H_5); 3.84 (s, 2 H, Re-CH_2I). ^{13}C NMR (CD_2Cl_2): 96.18 (d of quint, $^1J_{CH}$ =

191.4 Hz, J_{CH} = 6.2 Hz, η^5-C_5H_5); -44.0 (t, J_{CH} = 158.8 Hz, Re-CH_2I). Anal. Calcd for $C_{43}H_{24}BF_{24}I_2Re$: C, 35.68; H, 1.67. Found: C, 35.57; H, 1.57.

Reaction of $[(\eta^5\text{-}C_5H_5)_2Re(=CH_2)]B(Ar')_4$ with *N*-chlorosuccinimide. A sealable NMR tube was charged with $[(\eta^5\text{-}C_5H_5)_2Re(=CH_2)]B(Ar')_4$ (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. ^1H NMR (CD_2Cl_2): 6.25 (s, 10 H, η^5-C_5H_5); 4.68 (s, 2 H, Re-CH_2Cl); 2.8 (s, 4 H, Re-[NC(O)CH_2CH_2C(O)].

$[(\eta^5\text{-}C_5H_5)_2Re(H_2C=O)]B(Ar')_4$ (14). A 20 mL round bottom flask was charged with $[(\eta^5\text{-}C_5H_5)_2Re{=}CH_2]B(Ar')_4$ (105 mg, 0.088 mmol), C_5H_5NO (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_2Cl_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). ^1H NMR (CD_2Cl_2): 5.49 (s, 10 H, η^5-C_5H_5); 3.69 (s, 2 H, Re(H_2C=O)). ^{13}C NMR (CD_2Cl_2): 88.4 (d of quint, $^1J_{CH}$ = 189 Hz, J_{CH} = 6.7 Hz, η^5-C_5H_5); 46.2 (t, J_{CH} = 178.7 Hz, H_2CO). 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 $[(\eta^5\text{-}C_5H_5)_2Re(H_2C=O)]B(Ar')_4$ with PPh_3 A sealable NMR tube was charged with $[(\eta^5\text{-}C_5H_5)_2Re(H_2C=O)]B(Ar')_4$ (4 mg, 0.003 mmol) and

PPh_3 (1 mg, 0.004 mmol). Methylene chloride-d_2 (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 (CD_2Cl_2): 9.65 (s, free CH_2O), 7.7 to 7.3 (m, Re-PPh_3), 4.53 (d, J_{HP} = 3.83 Hz, η^5-C_5H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 23.1 (s, Re-PPh_3).

Reaction of $[(\eta^5\text{-}C_5H_5)_2Re(=CH_2)]B(Ar')_4$ with S_8 A sealable NMR tube was charged with $(\eta^5\text{-}C_5H_5)_2Re(=CH_2)]B(Ar')_4$ (5 mg, 0.004 mmol) and excess sulfur. Methylene chloride-d_2 (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 (CD_2Cl_2): 5.47 (s, 10 H, η^5-C_5H_5); 3.41 (s, 2 H, Re(H_2C=S)).

$[(\eta^5\text{-}C_5H_5)_2Re(H_2C=S)]B(Ar')_4$ (15). A 20 mL round bottom flask was charged with $[(\eta^5\text{-}C_5H_5)_2Re=CH_2]B(Ar')_4$ (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 CH_2Cl_2 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 (CD_2Cl_2): 5.47 (s, 10 H, η^5-C_5H_5); 3.41 (s, 2 H, Re(H_2C=S)). ^{13}C NMR (CD_2Cl_2): 88.2 (d of quint, $^1J_{CH}$ = 189 Hz, J_{CH} = 6.4 Hz, η^5-C_5H_5); 13.7 (t, J_{CH} = 168.4 Hz, H_2CS). Anal. Calcd for $C_{43}H_{24}BF_{24}ReS$: C, 42.14; H, 1.97. Found: C, 42.19; H, 1.97.

$[(\eta^5\text{-}C_5H_5)_2ReCH_2CH(SiMe_3)]B(Ar')_4$ (16). A small glass vessel with an 8 mm Kontes valve was charged with $[(\eta^5\text{-}C_5H_5)_2Re{=}CH_2]B(Ar')_4$ (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,η^5-C_5H_5); 5.10 (s, η^5-C_5H_5); 2.67 (d of d, J_{HH} = 12.1, 3.8 Hz, CH_ZH_E); 2.24 (d of d, J_{HH} = 15.5, 4.0 Hz, CH_ZH_E); 1.73 (d of d, J_{HH} = 15.1, 12.1 Hz, $CHSiMe_3$); 0.18 (s, $SiMe_3$).

Notes to Chapter 3.

(1) Fischer, E. O.; Maasbol, A.; *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 580.

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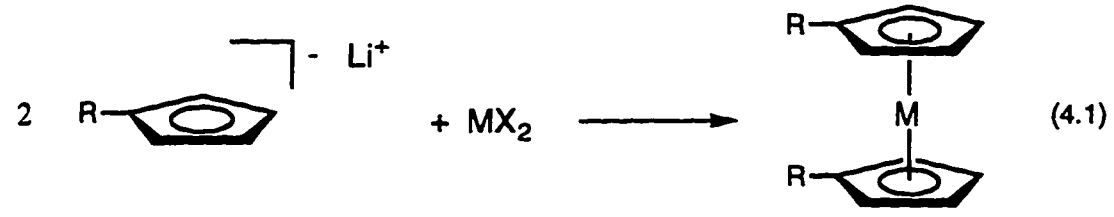
CHAPTER 4

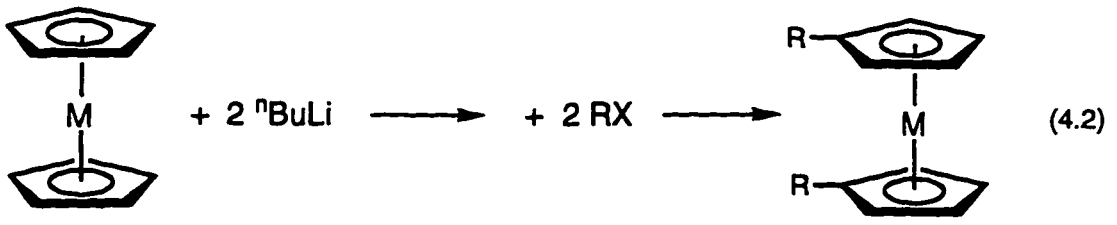
SYNTHESIS, STRUCTURE AND REACTIVITY OF SUBSTITUTED DERIVATIVES OF RHENOCENE

Introduction

The number of metallocene complexes in the organometallic literature is vast, although, there are an even larger number of structural variants which may be synthesized with substituted metallocene 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 metallocene complexes involve the reaction of a substituted cyclopentadianide ligand with a metal halide to generate a metallocene complex (eq 4.1) or the *in situ* substitution of a metallocene complex (eq 4.2).



(4.1)



(4.2)

Other synthetic methods are available and the synthesis and properties of substituted metallocene complexes has recently been reviewed.[1]

Synthesis of Rhenocene Complexes from Substituted Cyclopentadianide. The substitution chemistry of rhenocene complexes has been rather limited. Cloke and coworkers have reported the synthesis of bis(η-pentamethyl cyclopentadienyl)rhenium hydride (Cp_2^*ReH) by the co-condensation of rhenium vapor and 1,2,3,4,5-pentamethylcyclopenta-1,3-diene (Cp*H) at 77 K.[2] Photolysis of Cp_2^*ReH leads to decamethylrhenocene (Cp_2^*Re) which exists as a stable monomeric radical. This provides an interesting contrast in reactivity to the parent rhenocene complexes. When Cp_2ReH is photolyzed in a low temperature matrix, Cp_2Re is generated which is unstable at room temperature.[3] Rhenocene dimer, $[Cp_2Re]_2$, has been generated by conventional methods[4] and is presumably the fate of the unstable Cp_2Re radical. This is consistent with the ability of Cp* to stabilize complexes which are coordinatively or electronically unsaturated.

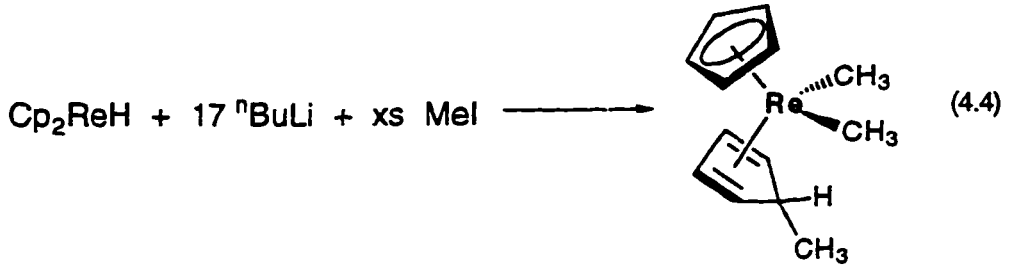
Herrmann and coworkers have used conventional synthetic methods to generate the mixed-ring complexes, Cp*CpReH and (η^5-C_5Me_4Et)CpReH (eq 4.3).[5]

$$Cp^*ReCl_4 + 4\,NaBH_4 + 2\,NaCp \longrightarrow Cp^*CpReH \quad (4.3)$$

Consistent with the increased basicity of the Cp* ligand, Cp*CpReH does not react with ^{n}BuLi or ^{t}BuLi to generate the $[Cp^*CpRe]^-$. Cp_2ReH, however, reacts with ^{n}BuLi•PMDT to generate an isolable Cp_2ReLi•PMDT complex[6] and Cp_2ReLi is often generated *in situ* to synthesize a number of Cp_2ReR derivatives.[7] It was not reported whether Cp_2^*ReH could be deprotonated by strong bases, but $[Cp_2^*Re]^-$ has been generated by the reaction of the 17 electron radical, Cp_2^*Re, with metallic potassium.[2a]

Conventional methods to generate $Cp_2^*WX_2$ (X = H, Cl) complexes have been reported by Parkin and Bercaw.[8] 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.[9,10] 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 Me_3SnCp^* or $TlCp^*$ will be more likely to produce Cp^*_2ReH.

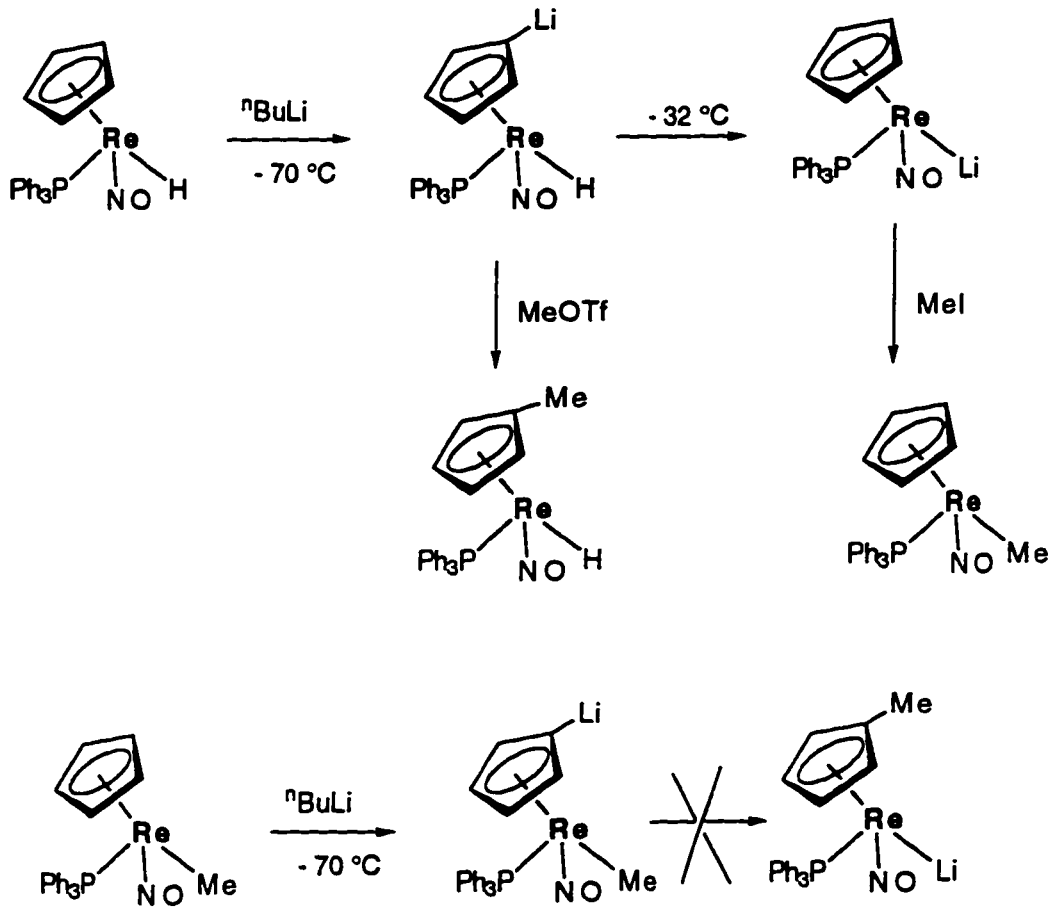
Substitution of Cyclopentadienyl Complexes. Green and coworkers have previously reported two examples of ring substitution by reaction of Cp_2ReH with ^{n}BuLi.[11] Addition of a large excess of ^{n}BuLi (17 equiv.) to Cp_2ReH followed by excess methyl iodide led to a product which was substituted at the metal center and a cyclopentadienyl ring (eq 4.4).[12]



(4.4)

Addition of 2.5 equivalents of ^{n}BuLi to Cp_2ReH followed by $HgCl_2$ is reported to give a disubstituted rhenocene hydride, $(\eta^5\text{-}C_5H_4(HgCl))_2ReH$. This appears to contrast with the results of Ephritikhine,[13] Stucky,[14] and Heinekey[15] which have all reported that Cp_2ReR complexes are readily prepared by the deprotonation of Cp_2ReH followed by the addition of alkyl halides. Gould has reported careful studies of the metallation of Cp_2ReH which suggest that deprotonation of the metal center is kinetically preferred although ring substitution is an accessible pathway.[9]

Gladysz and coworkers have reported that reaction of rhenium hydride complexes with strong bases can lead to reaction at the cylopentadienyl ring.[16] They have found that addition of ^{n}BuLi to $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)H$ 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).



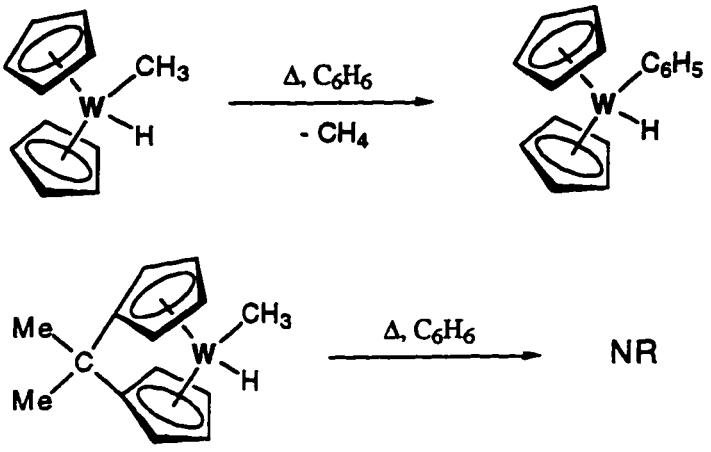
Scheme 4.1

Alkane Elimination from Metallocene Complexes. Previous work in the Heinekey group involved the investigation of alkane elimination from rhenocene alkyl

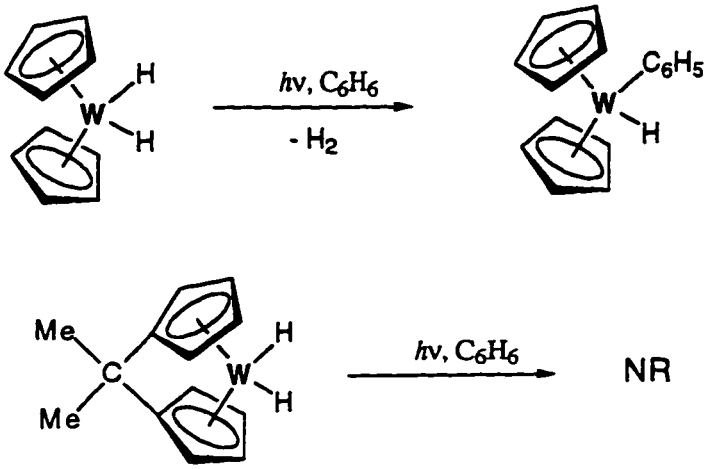
hydride cations, $[Cp_2Re(R)H]^+$.[17] The elimination of methane from $[Cp_2Re(CH_3)H]^+$ with a variety of anions was observed in solution at low temperatures ($t_{1/2}$ ca. 2 hours at 0 °C). Similar reactivity has been reported for related metallocene complexes of group 6. Green and coworkers have reported that $Cp_2W(CH_3)H$ eliminates methane at 40 °C and the intermediate "Cp_2W" complex can then react with various hydrocarbon complexes by oxidative addition of a CH bond.[18] Parkin and Bercaw have also investigated methane elimination from $Cp_2^*W(CH_3)H$.[8b] 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 $Cp^*Ir(PMe_3)(C_6H_{11})H$[19] and $Cp^*Rh(PMe_3)(C_2H_5)H$.[20] 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 (d^0 and d^x) from a mixture of pure isotopomers, showing no intermolecular isotope exchange, and 3) an inverse isotope effect ($k_H/k_D < 0$) 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.[8b,17,21] Until recently, $[Cp_2Re(CH_3)H]^+$ was the only cationic alkyl hydride system which had been reported to result in an intermediate alkane complex upon alkane elimination.[22] 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.[22,23]

Green and coworkers have recently reported on the synthesis, structure and reactivity of *ansa*-metallocene complexes of molybdenum and tungsten.[24,25] The term *ansa* has been popularized by Brintzinger to primarily define an inter-annular bridge between cyclopentadienyl rings in metallocene complexes.[26] Green has found significant reactivity differences between the *ansa* complexes and the well studied parent complexes (Scheme 4.2 and 4.3).



Scheme 4.2



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; $Me_2CCp_2W(CH_3)H$ 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 Cyclopentadianide Salts with $ReCl_4(THF)_2$.

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]

$$(CpH)_2 \xrightarrow{\Delta} 2\ CpH \xrightarrow{2\ ^nBuLi} 2\ LiCp + Me_2SiCl_2$$

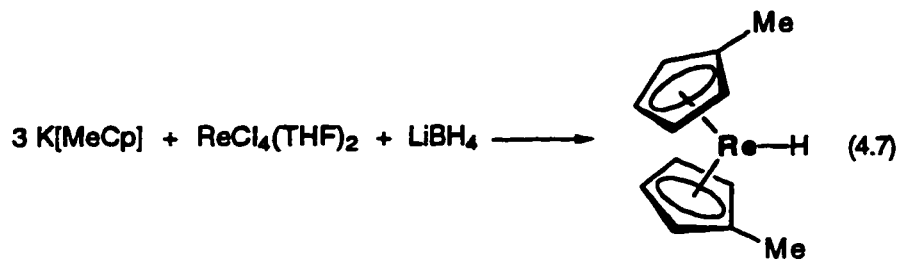
$$\longrightarrow Me_2SiCp_2 \xrightarrow{2\ ^nBuLi} Li_2[Me_2SiCp_2] \quad (4.5)$$

Addition of $Li_2[Me_2SiCp_2]$ 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.

$$Li_2[Me_2SiCp_2] + ReCl_4(THF)_2 + LiBH_4 \longrightarrow \text{decomposition} \quad (4.6)$$

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_2ReH 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_2ReH. 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'_2ReH ($Cp' = MeC_5H_4$) (eq 4.7). The product is isolated as a yellow solid in 33% yield by sublimation under dynamic vacuum.



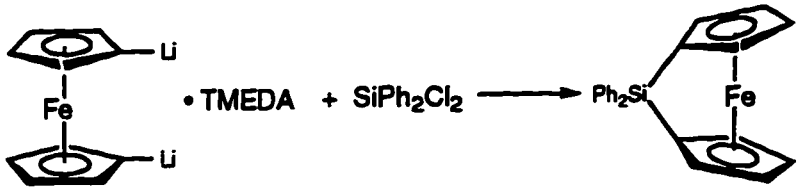
17

Complex **17** has been characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The ^{1}H NMR spectrum of $Cp_2'ReH$ reveals two pseudotriplets for the cyclopentadienyl protons which is consistent with the AA'BB' system. The resonances at δ 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 δ 2.0 integrates for the six protons of the two equivalent methyl groups. The hydride resonance comes at δ -12.64.

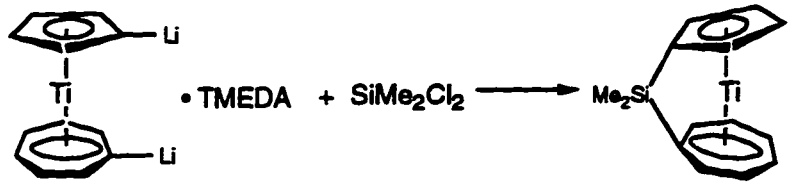
Although the attempt to react $ReCl_4(THF)_2$ with permethylated cyclopentadienide was unsuccessful,[9] it appears that less substituted complexes can still be synthesized by this route in very good yield. As will be discussed later, this route may be particularly useful in the synthesis of Cp_2Re derivatives which are alkyl substituted or disubstituted on the cyclopentadienyl ring. Unfortunately the substituted rings may limit the usefulness of Cp'_2ReH toward further derivitization. The reaction of $(\eta^5\text{-}C_5H_4Me)_2ReH$ with $^{n}BuLi$ followed by excess CH_3Cl led to the methyl complex which was contaminated with the hydride starting material.

Synthesis and Characterization of $(CH_3)_2Si(\eta^5\text{-}C_5H_4)_2ReCH_3$ (18). Due to the lack of a suitable Re(III) starting material for reaction with *ansa*-bridged ligands we have explored the synthesis of *ansa*-metallocene complexes by derivitization of Cp_2ReCH_3 . The metalation of cyclopentadienyl complexes by $^{n}BuLi$ has been

reported by several groups.[31] 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.[32,33]

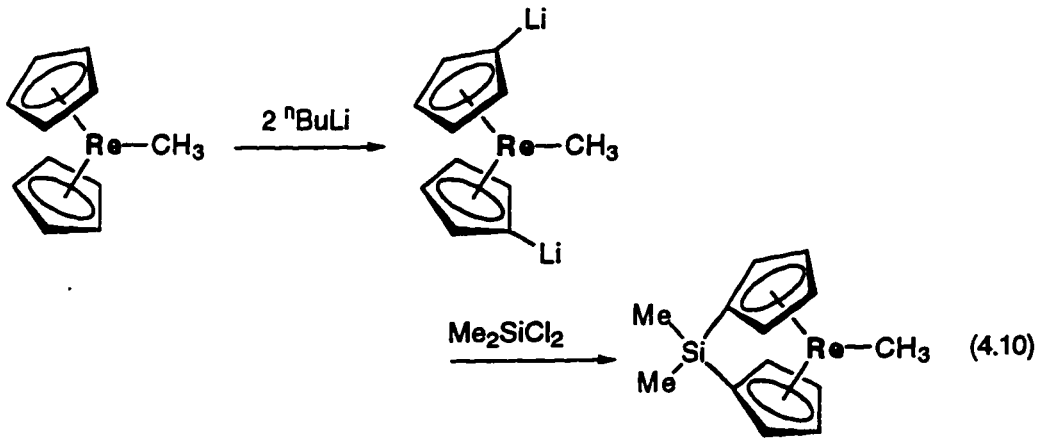


(4.8)



(4.9)

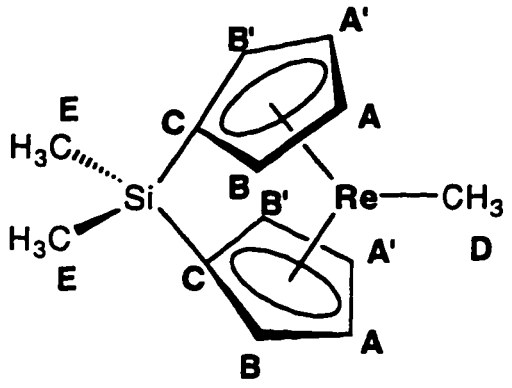
We have observed that Cp_2ReCH_3 can be deprotonated twice by addition of 2 equivalents of ^nBuLi in THF at 0 °C. No change is observed to the bright orange solution and one equivalent of Me_2SiCl_2 is added to the solution and stirred for 15 minutes. Sublimation of the residue gave dark orange crystals of $(CH_3)_2Si(\eta^5\text{-}C_5H_5)_2ReCH_3$ (**18**) in 84% yield (eq 4.10).



(4.10)

18

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 (δ 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 (δ 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

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

	^{1}H	^{13}C
A	4.21	83.7
B	4.82	74.9
C		28.0
D	0.28	-34.0
E	0.18	-5.2

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 δ 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 δ 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 δ 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 $[(\eta^5\text{-}C_5H_4\text{-}Si(CH_3)_2\text{-}\eta^5\text{-}C_5H_4)ReCH_3$ (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.

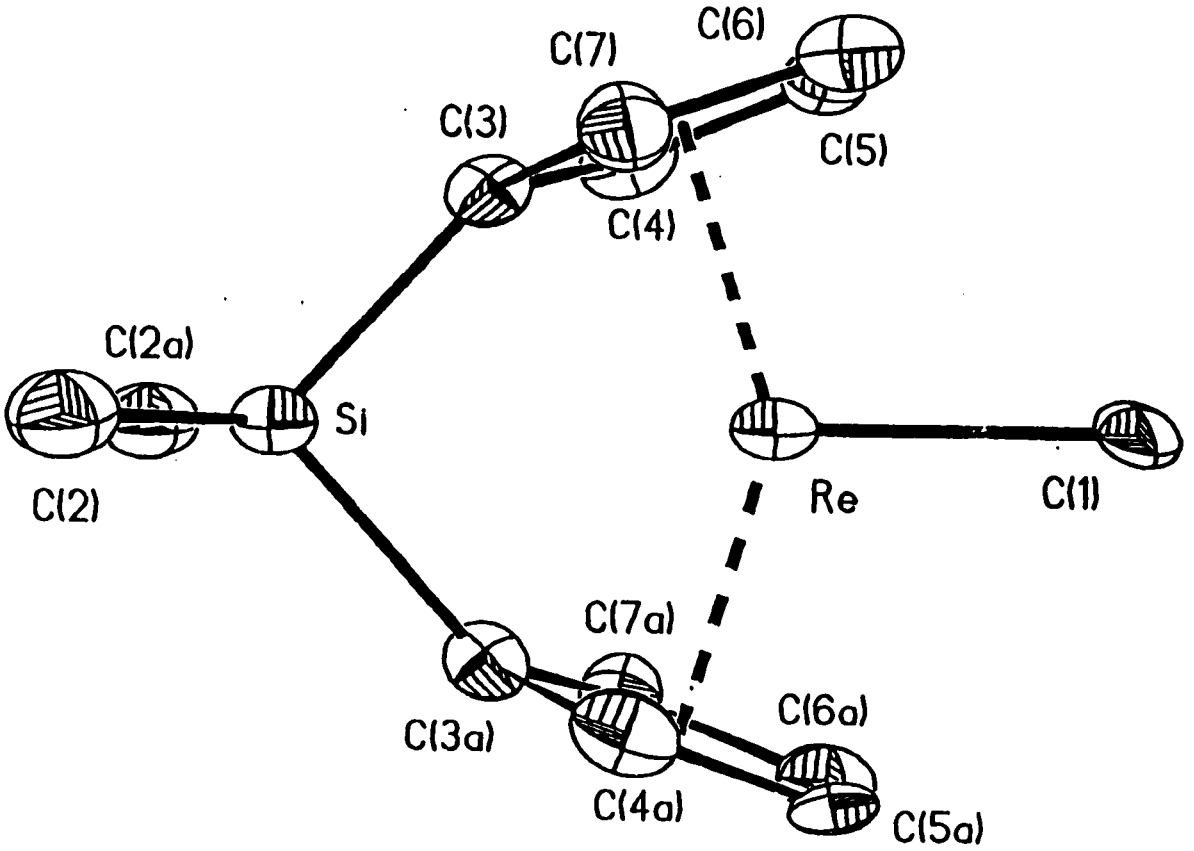


Figure 4.1. ORTEP representation of $[(\eta^5\text{-}C_5H_4\text{-}Si(Me_2)\text{-}\eta^5\text{-}C_5H_4)ReCH_3$ **(18)**. Thermal ellipsoids are shown at 50% probablility. Hydrogen atoms are omitted for clarity.

Table 4.2. Summary of Crystal Data for $[(\eta^5\text{-}C_5H_4\text{-}Si(CH_3)_2\text{-}\eta^5\text{-}C_5H_4)ReCH_3$ **(18).**

Empirical Formula	$C_{13}H_{17}ReSi$
Color; Habit	Orange Needle
Crystal Size (mm)	0.15 x 0.20 x 0.35
Crystal System	Monoclinic
Space Group	C2/c
Unit Cell Dimensions	$\underline{a}$ = 11.242 (2) Å
	$\underline{b}$ = 14.118 (3) Å
	$\underline{c}$ = 7.885 (2) Å
	β = 108.19 (3)°
Volume	1188.9 (4) $Å^3$
Z	4
Formula Weight	387.6
Density (calc.)	2.165 Mg/m^3
Absorption Coefficient	10.285 mm^{-1}
F(000)	736
Radiation	MoKα (λ = 0.71073 Å)
Temperature (K)	183
Monochromater	Highly oriented graphite crystal
2θ Range	2.0 to 50.0 °
Scan Type	2θ-θ
Scan Speed	Variable; 1.50 to 5.50°/min. in ω
Scan Range (ω)	0.80 + 0.35(tan θ)°
Reflections Collected	1203
Independent Reflections	1054 (R_{int} = 10.05%)
Observed Reflections	981 ($F > 4.0\sigma(F)$)
Number of Parameters Refined	71
Final R Indices (obs. data)	R = 6.57 %, wR = 8.18 %
R Indices (all data)	R = 6.57 %, wR = 8.40 %
Goodness-of -Fit	1.14

Table 4.3. Selected Bond Distances and Angles for **18.**

		Distances, Å	
Re-C(1)	2.117(24)	Re-C(3)	2.193(12)
Re-C(4)	2.213(16)	Re-C(5)	2.262(11)
Re-C(6)	2.253(17)	Re-C(7)	2.212(19)
Si-C(3)	1.880(13)	Si-C(2)	1.841(13)
C(3)-C(4)	1.473(18)	C(4)-C(5)	1.373(22)
C(5)-C(6)	1.427(20)	C(6)-C(7)	1.457(22)
C(3)-C(7)	1.439(20)		
		Angles, deg	
C(3)-Si-C(3a)	92.9(8)	C(2)-Si-C(2a)	112.2(9)
C(3)-C(7)-C(6)	107.2(12)	C(3)-C(4)-C(5)	107.9(13)
C(5)-C(6)-C(7)	107.0(14)	C(4)-C(3)-C(7)	107.1(11)
C(4)-C(5)-C(6)	110.7(13)		

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]

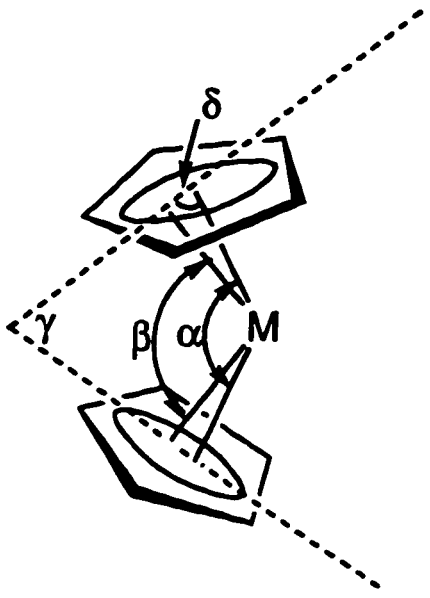


Figure 4.2. Pictorial representation of bending angles for metallocene complexes. Adapted from reference 1.

The bending angle of the cyclopentadienyl rings is a crucial structural factor and can be defined in two ways. The α angle is between the vectors to ring centroids from the metal while the β 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 metallocene complex. This distortion will also be evident by the M–C distances of the Cp ligand which will vary if the α and β angles differ. The deviation from the centroid of the Cp ring and the normal to the ring can be also measured by δ which will be 90° if α and β are equal. The angle between the cyclopentadienyl planes (γ) is supplementary to β. Table 4.4 lists several relevant angles and distances for complex **2**. Although the structure of the parent complex, Cp_2ReCH_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 α and β 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.

Cp(cent)–M–Cp(cent) (α)	145.2°
Cp (normal)–M–Cp(normal) (β)	140.0°
angle between Cp planes (γ)	40.0°
angle between Cp plane and vector to centroid (δ)	87.4°
M–Cp(cent)	1.869 Å
M–C (Cp) (range)	2.262–2.193 Å
Δ M-C (Cp)	0.17 Å or 7.5%

Relevant angles and distances for several crystallographically characterized derivatives of rhenocene are listed in Table 4.5.[34-41] 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(sp^3) distances for the Alcock and Caulton structures are quite similar at 2.24 and 2.27 Å respectively.[34,40] This distance decreases by 0.10 Å for the Re-C(sp^2) structures reported by Herberich.[41] The Re–CH_3 bond length for complex **18** (2.12 Å) is short by comparison, but is not unusual for a Re-C(sp^3) bond distance.

Table 4.5. Selected Bond Distances and Angles for Rhenocene Complexes.

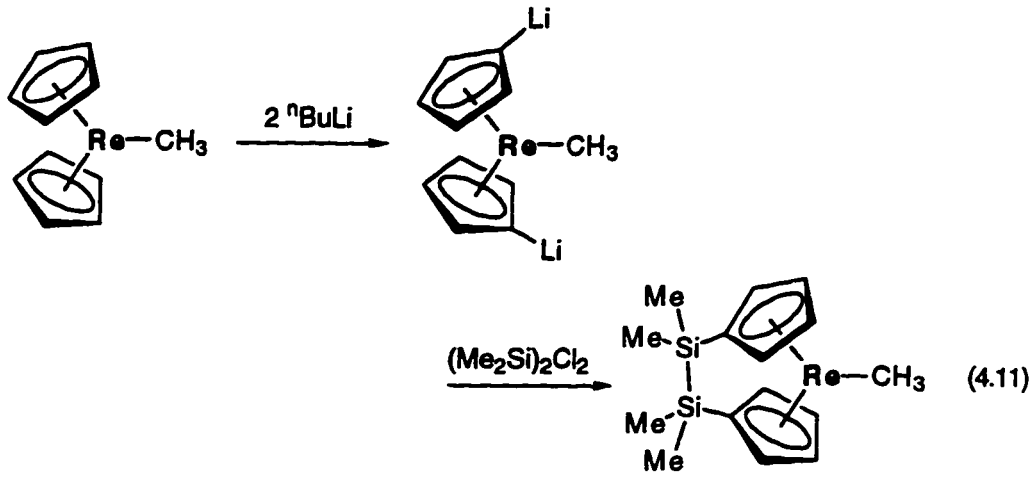
Compound	Cp-Re-Cp, deg	Re-C(Cp) av., Å	Re-Cp(cent), Å	Re-C, Å	ref.
$(C_5H_5)(C_5H_5Me)Re(Me)_2$		2.24		2.24	34
$[Cp_2ReH_2]BF_4$	145.7[a]	2.01	1.88		35
$[Cp_2ReBr_2]BF_4$	139.5[a]	2.26			36
Cp_2ReCl	147.6[b]	2.24	1.87		37
$[Cp_2Re]CuCl_2$	147.5[a], 150.1[b]	2.28	1.90		38
$[Cp_2ReHCuI]_2$	158.0[b]	2.24			39
$Cp_2Re(CHMe)OZrMeCp_2$	150.5[b]	2.25	1.90	2.27	40
$Cp_2Re(alkenyl)$[c]	146.2[a]	2.23		2.15	41
$Cp_2Re(alkenyl)$[d]	146.8[a]	2.24		2.15	41

[a] Cp(normal)–M–Cp(normal) (α). [b] Cp(cent)–M–Cp(cent) (β). [c] $Cp_2Re[\eta^1$-(*E*)-$C(CO_2Me)=CH(CO_2Me)]$
[d] $Cp_2Re[\eta^1$-(Z)-$C(CO_2Me)=CH(CO_2Me)]$

Green and coworkers have compared the structures of *ansa*-bridged complexes of molybdenum with the parent complexes.[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 metallocene to the *ansa*-bridged complexes. The significant structural changes observed for the Green complexes is attributed to the use of carbon bridges; $-C(Me)_2$ and $-C(CH_2)_4$. The carbon bridge should affect a larger difference than a silicon bridge upon the metallocene 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_2C-$(\eta^5$-$C_5H_4)_2WH_2$ is 1.529Å.[24]

Corey and coworkers have recently reported a comparison of several metallocene complexes with silicon and carbon bridges.[42] They have synthesized and reported the crystal structures for $Me_2C(C_5H_4)_2MCl_2$ (M = Ti, Zr, Hf) and compared them to the known parent structures as well as the analogous -$SiMe_2$ 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 $[((CH_3)_2Si)_2$-η^5-$C_5H_4]_2ReCH_3$ (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 $(Me_2Si)_2Cl_2$ was added to a THF solution of $(\eta^5$-$C_5H_4Li)_2ReCH_3$ 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.

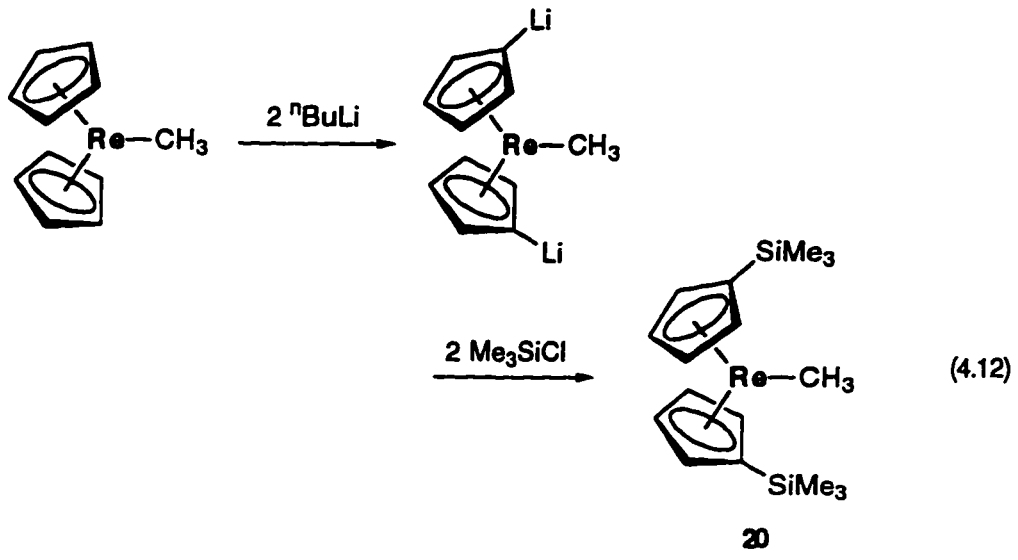


(4.11)

19

The ^{1}H and ^{13}C NMR spectra were similar to that observed for compound **18**. Two pseudotriplet resonances (δ 4.42 and 4.37) were observed in the ^{1}H NMR spectrum for the cyclopentadienyl protons. The methyl protons were observed at δ 0.36 (3 H) and δ 0.25 (12 H) in the ^{1}H NMR spectrum indicating the methyl groups of the *ansa*-bridge are equivalent.

Synthesis and Characterization of $((CH_3)_3Si\text{-}\eta^5\text{-}C_5H_4)_2ReCH_3$ (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_3SiCl is vacuum transferred to a THF solution of $(\eta^5\text{-}C_5H_4Li)_2ReCH_3$ at 0 °C. The solvent was removed *in vacuo* and compound **20** was isolated in 87% yield as an orange solid by vacuum sublimation.



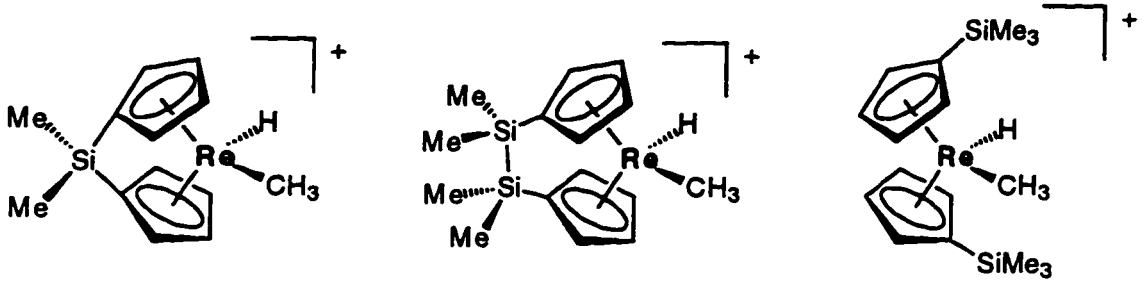
(4.12)

20

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 (δ 4.52 and 3.52) were observed in the ^{1}H NMR spectrum for the cyclopentadienyl protons. The methyl protons were observed at δ 0.19 (18 H) and δ 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 $[H(Et_2O)_2]B(Ar')_4$ 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_2Cl_2 and CD_3CN. 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 $SiMe_3$ protons is not observed for complex **24** since the cyclopentadienyl ligands are able to freely rotate.



22 **23** **24**

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 ^1H NMR spectra. The products of methane elimination often gave complicated ^1H NMR spectra. The decomposition of complex **23** in CD_3CN gave a simple ^1H NMR spectrum consistent with a single product, $[((CH_3)_2Si)_2(\eta^5\text{-}C_5H_4)_2Re(NCCD_3)]B(Ar')_4$ (**25**).

Methane Elimination from Complexes 21-24. The methane elimination from complexes **22-24** and $[Cp_2Re(CH_3)H]B(Ar')_4$ (**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 $Cp_2W(CH_3)H$ and *ansa*-$Cp_2W(CH_3)H$. 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 "Cp_2W" intermediate to attain a parallel structure following reductive elimination of methane and the inability of "*ansa*Cp_2W" to attain a parallel structure.

Perutz and coworkers have obtained evidence that complexes such as Cp_2W and Cp_2Mo 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 Cp_2WH_2 and Cp_2MoH_2 led to the reductive elimination of H_2 and formation of Cp_2W and Cp_2Mo 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 Cp_2Fe. Similar results have been observed for the photolysis of Cp_2ReH which emits a hydrogen atom to form the neutral radical, Cp_2Re.[44] The decamethyl analog, Cp_2^*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.[2b]

The products of methane elimination from the *ansa*-bridged metallocenes, *ansa*-Cp_2M (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, Cp_2Ti.[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 $[Cp_2Re(CH_3)H]^+$ (**21**) and $[Me_2SiCp_2Re(CH_3)H]^+$ (**22**) is depicted in Figure 4.3.

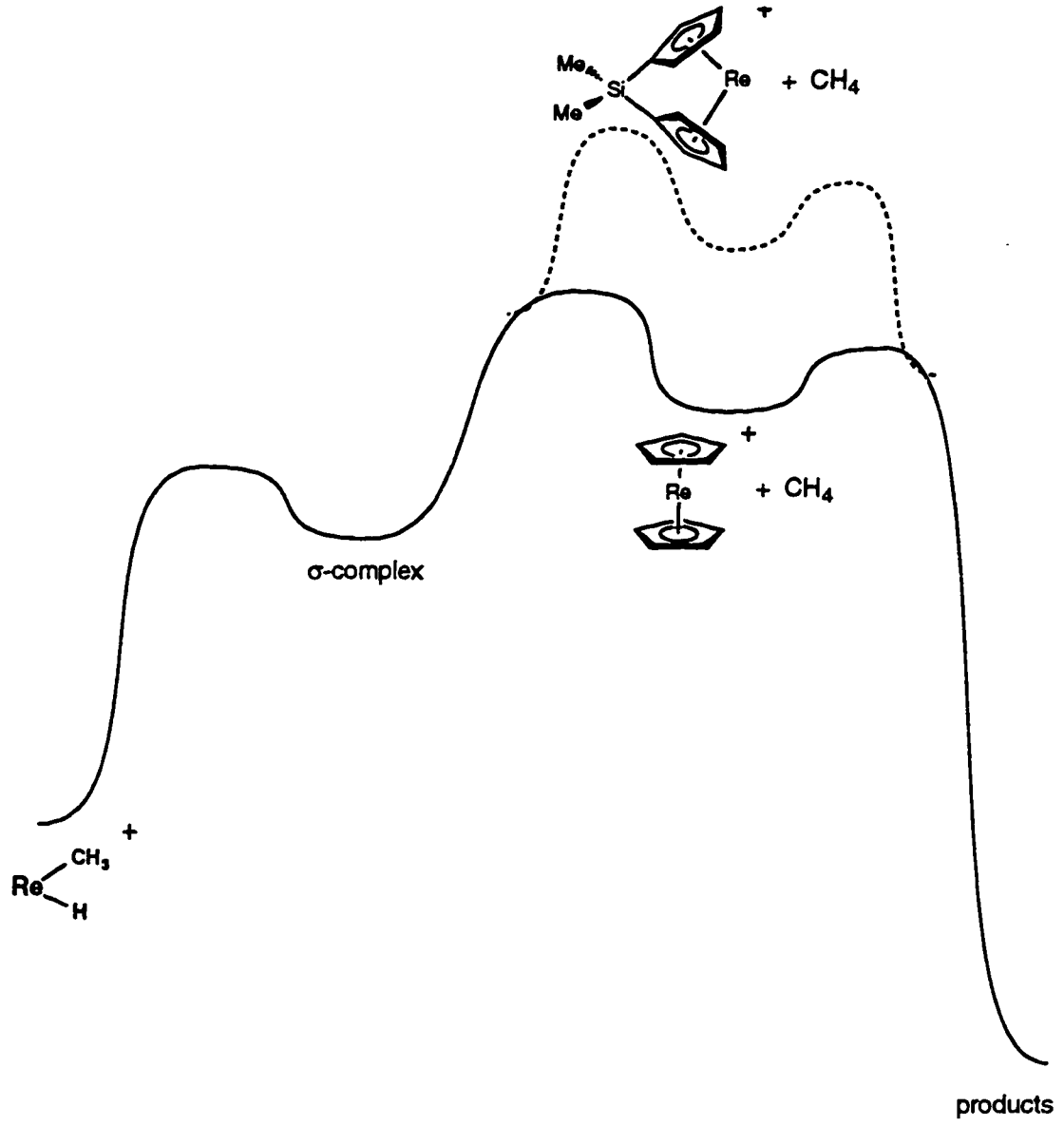
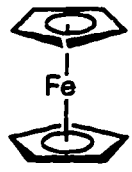
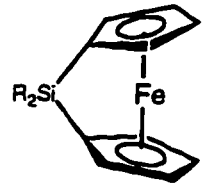


Figure 4.3. Proposed reaction coordinate depicting methane elimination from non*ansa* and ansa-bridged rhenocene methyl hydride complexes (**21** and **22**). Adapted from references 9 and 24b.

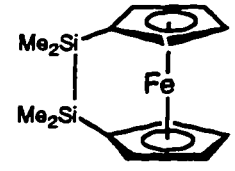
As discussed previously, a single carbon bridge has been observed to have a greater effect upon the bending angle as compared to a single silicon bridge for several coordinatively saturated Cp_2ML_n (n = 1 or 2) type complexes. Unfortunately, a direct comparison of the silicon versus carbon bridged complexes has yet to be made for metallocene complexes without ancillary ligands, Cp_2ML_n (n = 0). The transition state of the bent *ansa*Cp_2Re^+ 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*-Cp_2W and [*ansa*-Cp_2Re]$^+$. The bending angles of Cp_2M (M = Fe, Ru) with various silicon and carbon bridges are shown in Scheme 4.5.[46-51]



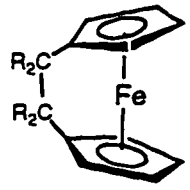
$\gamma = 0°$



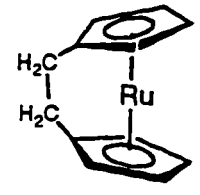
R = Me; $\gamma = 20.8°$
R = Ph; $\gamma = 19.2°$



$\gamma = 4.19°$



R = H; $\gamma = 21.6°$
R = Me; $\gamma = 23°$



$\gamma = 29.6°$

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 then 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*-Cp_2Re^+ or *ansa*-Cp_2W 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 -$SiMe_2$ bridge does have a certain degree of flexibility and can allow the Cp rings to move.[52] 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_2SiCl_2 or $(Me_2Si)_2Cl_2$ to a THF solution of $(\eta^5\text{-}C_5H_4Li)_2ReCH_3$ gives *ansa*-bridged complexes with a single or double silicon linker. A X-ray diffraction study was undertaken to confirm the structure of $(\eta^5\text{-}C_5H_4\text{-}SiMe_2\text{-}\eta^5\text{-}C_5H_4)ReCH_3$. Substituted derivatives of Cp_2ReX (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 $[(\eta^5\text{-}C_5H_4\text{-}SiMe_2\text{-}\eta^5\text{-}C_5H_4)Re(CH_3)H]B(Ar')_4$ 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_2ReCH_3,[7a] and $[H(Et_2O)_2]B(Ar')_4$[54] were prepared by reported procedures. $(Me_2Si)_2Cl_2$ was purchased from Gelest and all other reagents were purchased from Aldrich. The ^1H 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.

$(CH_3\text{-}\eta^5\text{-}C_5H_4)_2ReH$ (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 $ReCl_4(THF)_2$ (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 $LiBH_4$ (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 Cp'_2ReH is 33 % yield (606 mg). ^1H NMR (C_7D_8): 4.21 ("t", 4 H, J_{HH} = 1.7 Hz, η^5-C_5H_4); 4.09 ("t", 4 H, J_{HH} = 2.4 Hz, η^5-C_5H_4); 2.05 (s, 6 H, CH_3-η^5-C_5H_4); -12.64 (s, 1 H, Re-H). ^{13}C NMR (C_7D_8): 84.0 (s, CH_3-η^5-C_5H_4 ipso); 67.1 (d of m, $^1J_{CH}$ = 180 Hz, η^5-C_5H_4); 64.9 (d of quart, $^1J_{CH}$ = 179 Hz, J_{CH} = 6.5 Hz, η^5-C_5H_4); 16.0 (q, J_{CH} = 127 Hz, CH_3-η^5-C_5H_4). Anal. Calcd for $C_{12}H_{15}Re$: C, 41.72; H, 4.38. Found: C, 41.29; H, 4.34.

$(\eta^5\text{-}C_5H_4\text{-}Si(CH_3)_2\text{-}\eta^5\text{-}C_5H_4)ReCH_3$ (18). A small glass vessel with an 8 mm Kontes valve was charged with Cp_2ReCH_3 (274mg, 0.83mmol). THF (20 mL) was vacuum transferred to the vessel and warmed to 0°C. Under an agron flow, 2 equivalents of nBuLi (1.03mL, 1.6M, 1.65mmol) was added via a gas tight syringe. The solution was stirred at 0°C for 45 minutes. Under an argon flow, $(CH_3)_2SiCl_2$ (101μL, 0.83mmol) 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 (CD_2Cl_2): 4.82 (d of d, 4H, J_{HH} = 1.59 Hz, J_{HH} = 1.96 Hz,

η^5-C_5H_4), 4.21 (d of d, 4H, J_{HH} = 1.62 Hz, J_{HH} = 1.94 Hz, η^5-C_5H_4), 0.28 (s, 3H, ReC*H*$_3$), 0.18 (s, 6H, Si(C*H*$_3$)$_2$); ^{1}H NMR (CD_3CN): 4.86 ("t", 4H, J_{HH} = 1.8 Hz, η^5-C_5H_4), 4.12 ("t", 4H, J_{HH} = 1.4 Hz, η^5-C_5H_4), 0.22 (s, 3H, ReC*H*$_3$), 0.15 (s, 6H, Si(C*H*$_3$)$_2$); ^{13}C NMR (CD_2Cl_2): 83.7 (d of quart, J_{CH} = 180 Hz, J_{CH} = 6.6 Hz, η^5-C_5H_4), 75.0 (d of quart, J_{CH} = 183 Hz, J_{CH} = 7.3 Hz, η^5-C_5H_4), 28 (s, η^5-C_5H_4), -5.2 (quart, J_{CH} = 121 Hz, Si(*C*H$_3$)$_2$), -34.0 (quart, J_{CH} = 127 Hz, Re*C*H$_3$). Anal. Calcd for $C_{13}H_{17}ReSi$: C, 40.29; H, 4.42. Found: C, 40.31; H, 4.61.

(η^5-C_5H_4-(Si(CH$_3$)$_2$)$_2$-η^5-C_5H_4)ReCH$_3$ (19). A small glass vessel with an 8 mm Kontes valve was charged with Cp_2ReCH_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, ((CH$_3$)$_2$Si)$_2$Cl$_2$ (27 μL, 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}H NMR (CD_2Cl_2): 4.42 ("t", 4 H, J_{HH} = 1.7 Hz, η^5-C_5H_4), 4.37 ("t", 4 H, J_{HH} = 1.7 Hz, η^5-C_5H_4), 0.36 (s, 3 H, ReC*H*$_3$), 0.25 (s, 12 H, Si(C*H*$_3$)$_2$); ^{13}C NMR (CD_2Cl_2): 83.91 (d of quart, J_{CH} = 181 Hz, J_{CH} = 6.5 Hz, η^5-C_5H_4), 71.24 (d of quart, J_{CH} = 180 Hz, J_{CH} = 7.3 Hz, η^5-C_5H_4), 75.01 (s, η^5-C_5H_4), -1.4 (quart, J_{CH} = 121 Hz, (Si(*C*H$_3$)$_2$)$_2$), -36.77 (quart, J_{CH} = 129 Hz, Re*C*H$_3$). Anal. Calcd for $C_{15}H_{23}ReSi_2$: C, 40.42; H, 5.20. Found: C, 40.41; H, 5.15.

((CH$_3$)$_3$Si-η^5-C_5H_4)$_2$ReCH$_3$ (20). A small glass vessel with an 8 mm Kontes valve was charged with Cp_2ReCH_3 (120mg, 0.362mmol). THF (20 mL) was vacuum transferred to the vessel and warmed to 0°C. Under an argon flow, 2 equivalents of nBuLi (0.45mL, 1.6M, 0.724mmol) 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%). ^{1}H NMR (CD_2Cl_2): 4.52 ("t", 4H, J_{HH} = 1.91 Hz, η^5-C_5H_4), 3.52 ("t", 4H, J_{HH} = 1.93 Hz, η^5-C_5H_4), 0.19 (s, 18H, Si(CH_3)$_3$), 0.18 (s, 3H, ReCH_3); ^{13}C NMR (CD_2Cl_2): 83.9 (d of quart, J_{CH} = 175.9 Hz, J_{CH} = 7.7 Hz, η^5-C_5H_4), 68.7 (d of quart, J_{CH} = 180.3 Hz, J_{CH} = 6.5 Hz, η^5-C_5H_4), 0.58 (quart, J_{CH} = 118.9 Hz, Si(CH_3)$_3$), -36.3 (quart, J_{CH} = 128.2 Hz, ReCH_3). Anal. Calcd for $C_{17}H_{29}ReSi_2$: C, 42.92; H, 6.14. Found: C, 42.04; H, 6.05.

[(η^5-C_5H_5)$_2$Re(CH_3)H]B(Ar')$_4$ (21). A sealable NMR tube was charged with (η^5-C_5H_5)$_2$ReCH_3 (6 mg, 0.018 mmol) and [H(Et_2O)$_2$]B(Ar')$_4$ (18.3 mg, 0.018 mmol). Methylene chloride-d_2 (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. ^{1}H NMR (CD_2Cl_2, 250 K): 5.30 (s, 10 H, η^5-C_5H_5); 0.53 (s, 3 H, Re-CH_3); -11.88 (s, 1 H, Re-H). ^{13}C{^{1}H} (CD_2Cl_2): 84.0 (η^5-C_5H_5); -40.1 (Re-CH_3).

[(η^5-C_5H_4-Si(CH_3)$_2$-η^5-C_5H_4)Re(CH_3)H]B(Ar')$_4$ (22). A sealable NMR tube was charged with ((CH_3)$_2$SiCp_2ReCH_3 (2) (8 mg, 0.021 mmol) and [H(Et_2O)$_2$]B(Ar')$_4$ (21 mg, 0.021 mmol). CD_2Cl_2 was vacuum transferred to the tube and sealed. The tube was kept at -78 °C until it was placed in the NMR probe. ^{1}H NMR (CD_2Cl_2, 250 K): 5.81 (s, 2 H, η^5-C_5H_4); 5.72 (s, 2 H, η^5-C_5H_4); 5.32 (s, 2 H, η^5-C_5H_4); 4.92 (s, 2 H, η^5-C_5H_4); 0.53 (s, 3 H, Re-CH_3); 0.35 (s, 3 H, Si-CH_3); 0.30 (s, 3 H, Si-CH_3); -10.47 (s, 1 H, Re-*H*); ^{1}H NMR (CD_3CN): 7.68 (br, B(Ar')$_4$); 5.99 (s, 2 H, η^5-C_5H_4); 5.89 (s, 2 H, η^5-C_5H_4); 5.48 (s, 2 H, η^5-C_5H_4); 5.13 (s, 2 H, η^5-

C_5H_4); 0.53 (s, 3 H, Re-C*H*$_3$); 0.33 (s, 3 H, Si-C*H*$_3$); 0.30 (s, 3 H, Si-C*H*$_3$); -10.96 (s, 1 H, Re-*H*); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 250 K): 114.7 (η^5-C_5H_4); 89.5 (η^5-C_5H_4); 84.4 (η^5-C_5H_4); 73.5 (η^5-C_5H_4); 49.5 (ipso η^5-C_5H_5); -6.3 (Si-*C*H$_3$); -6.4 (Si-*C*H$_3$); -41.0 (Re-*C*H$_3$).

[(η^5-C_5H_4-(Si(CH$_3$)$_2$)$_2$-η^5-C_5H_4)Re(CH$_3$)H]B(Ar')$_4$ (23). A sealable NMR tube was charged with ((CH$_3$)$_2$Si)$_2$Cp$_2$ReCH$_3$ (**3**) (3 mg, 6.7 x 10^{-3} mmol) and [H(Et$_2$O)$_2$]B(Ar')$_4$ (6.8 mg, 6.7 x 10^{-3} mmol). CD_2Cl_2 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 (CD_2Cl_2, 250 K): 5.44 (s, 2H, η^5-C_5H_4); 5.38 (s, 2H, η^5-C_5H_4); 5.32 (s, 2H, η^5-C_5H_4); 4.31 (s, 2H, η^5-C_5H_4); 0.63 (s, 3H, Re-C*H*$_3$); 0.42 (s, 6H, Si-C*H*$_3$); 0.40 (s, 6H, Si-C*H*$_3$); -12.00 (s, 1 H, Re-*H*); ^1H NMR (CD_3CN, 250 K): 7.68 (br, B(Ar')$_4$); 5.66 (s, 2H, η^5-C_5H_4); 5.54 (s, 2H, η^5-C_5H_4); 5.44 (s, 2H, η^5-C_5H_4); 5.38 (s, 2H, η^5-C_5H_4); 0.57 (s, 3H, Re-C*H*$_3$); 0.39 (s, 6H, Si-C*H*$_3$); 0.34 (s, 6H, Si-C*H*$_3$); -12.24 (s, 1H, Re-*H*).

[((CH$_3$)$_3$Si-η^5-C_5H_4)$_2$Re(CH$_3$)H]B(Ar')$_4$ (24). A sealable NMR tube was charged with ((CH$_3$)$_3$Si)$_2$Cp$_2$ReCH$_3$ (**4**) (12 mg, 0.025 mmol) and [H(Et$_2$O)$_2$]B(Ar')$_4$ (26 mg, 0.025 mmol). CD_2Cl_2 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 (CD_2Cl_2, 250 K): 5.58 (br, 2 H, η^5-C_5H_4), 5.41 (br, 2 H, η^5-C_5H_4), 4.79 (m, 4 H, η^5-C_5H_4), 0.40 (s, 3 H, ReC*H*$_3$), 0.25 (s, 18 H, Si(C*H*$_3$)$_3$), -12.10 (s, 1 H, Re-*H*); ^1H NMR (CD_3CN, 250 K): 7.68 (br, B(Ar')$_4$); 5.78 ("quart", 2H, η^5-C_5H_4); 5.48 ("quart", 2H, η^5-C_5H_4); 4.98 (m, 4H, η^5-C_5H_4); 0.36 (s, 3H, Re-C*H*$_3$); 0.24 (s, 18H, Si-C*H*$_3$); -12.35 (s, 1H, Re-*H*).

[(η^5-C_5H_4-($Si(CH_3)_2$)$_2$-η^5-C_5H_4)Re(CD_3CN)]B(Ar')$_4$ (25). Upon methane elimination from complex **7** at room temperature in CD_3CN a new complex was formed which is assigned as the acetonitrile adduct. ^1H NMR (CD_3CN, 298 K): 7.68 (br, B(Ar')$_4$); 5.12 ("t", 4H, η^5-C_5H_5); 4.57 ("t", 4H, η^5-C_5H_5); 0.32 (s, 12H, Si-CH_3).

X-ray Structure Determination of (η^5-C_5H_4-$Si(CH_3)_2$-η^5-C_5H_4)$ReCH_3$ (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 Theta-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 mosacitiy 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 $[(\eta^5\text{-}C_5H_4\text{-}Si(CH_3)_2\text{-}\eta^5\text{-}C_5H_4)ReCH_3$

Table 1. Atomic coordinates ($x10^5$) and equivalent isotropic displacement coefficients ($Å^2 x10^4$)

	x	y	z	U(eq)
Re	50000	71446(4)	25000	208(3)
Si	50000	92781(40)	25000	254(15)
C(1)	50000	56453(168)	25000	642(111)
C(2)	64257(109)	100051(109)	32986(159)	379(46)
C(3)	51403(102)	83609(78)	8438(168)	194(37)
C(4)	40654(154)	77743(95)	-1521(232)	311(51)
C(5)	45190(130)	69134(108)	-4771(146)	299(40)
C(6)	58465(146)	68730(129)	3049(176)	375(47)
C(7)	62466(150)	77900(85)	11361(246)	287(52)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 2. Bond lengths (Å)

Re-Si	3.012 (6)	Re-C(1)	2.117 (24)
Re-C(3)	2.193 (12)	Re-C(4)	2.213 (16)
Re-C(5)	2.262 (11)	Re-C(6)	2.253 (17)
Re-C(7)	2.212 (19)	Re-C(3A)	2.193 (12)
Re-C(4A)	2.213 (16)	Re-C(5A)	2.262 (11)
Re-C(6A)	2.253 (17)	Re-C(7A)	2.212 (19)
Si-C(2)	1.841 (13)	Si-C(3)	1.880 (13)
Si-C(2A)	1.841 (13)	Si-C(3A)	1.880 (13)
C(3)-C(4)	1.473 (18)	C(3)-C(7)	1.439 (19)
C(4)-C(5)	1.373 (22)	C(5)-C(6)	1.427 (20)
C(6)-C(7)	1.457 (22)		

Table 3. Bond angles (°)

Si-Re-C(1)	180.0(1)	Si-Re-C(3)	38.4(3)
C(1)-Re-C(3)	141.6(3)	Si-Re-C(4)	66.3(4)
C(1)-Re-C(4)	113.7(4)	C(3)-Re-C(4)	39.1(5)
Si-Re-C(5)	98.3(4)	C(1)-Re-C(5)	81.7(4)
C(3)-Re-C(5)	62.2(5)	C(4)-Re-C(5)	35.7(6)
Si-Re-C(6)	99.8(5)	C(1)-Re-C(6)	80.2(5)
C(3)-Re-C(6)	63.2(6)	C(4)-Re-C(6)	62.1(6)
C(5)-Re-C(6)	36.8(5)	Si-Re-C(7)	65.7(4)
C(1)-Re-C(7)	114.3(4)	C(3)-Re-C(7)	38.1(5)
C(4)-Re-C(7)	64.0(6)	C(5)-Re-C(7)	62.4(6)
C(6)-Re-C(7)	38.1(6)	Si-Re-C(3A)	38.4(3)
C(1)-Re-C(3A)	141.6(3)	C(3)-Re-C(3A)	76.9(7)
C(4)-Re-C(3A)	98.5(5)	C(5)-Re-C(3A)	133.8(5)
C(6)-Re-C(3A)	135.8(6)	C(7)-Re-C(3A)	98.1(5)
Si-Re-C(4A)	66.3(4)	C(1)-Re-C(4A)	113.7(4)
C(3)-Re-C(4A)	98.5(5)	C(4)-Re-C(4A)	132.6(7)
C(5)-Re-C(4A)	158.1(6)	C(6)-Re-C(4A)	127.2(6)
C(7)-Re-C(4A)	96.2(6)	C(3A)-Re-C(4A)	39.1(5)
Si-Re-C(5A)	98.3(4)	C(1)-Re-C(5A)	81.7(4)
C(3)-Re-C(5A)	133.8(5)	C(4)-Re-C(5A)	158.1(6)
C(5)-Re-C(5A)	163.4(8)	C(6)-Re-C(5A)	138.7(5)
C(7)-Re-C(5A)	125.6(5)	C(3A)-Re-C(5A)	62.2(5)
C(4A)-Re-C(5A)	35.7(6)	Si-Re-C(6A)	99.8(5)
C(1)-Re-C(6A)	80.2(5)	C(3)-Re-C(6A)	135.8(6)
C(4)-Re-C(6A)	127.2(6)	C(5)-Re-C(6A)	138.7(5)
C(6)-Re-C(6A)	160.4(9)	C(7)-Re-C(6A)	158.0(6)
C(3A)-Re-C(6A)	63.2(6)	C(4A)-Re-C(6A)	62.1(6)
C(5A)-Re-C(6A)	36.8(5)	Si-Re-C(7A)	65.7(4)
C(1)-Re-C(7A)	114.3(4)	C(3)-Re-C(7A)	98.1(5)
C(4)-Re-C(7A)	96.2(6)	C(5)-Re-C(7A)	125.6(5)
C(6)-Re-C(7A)	158.0(6)	C(7)-Re-C(7A)	131.3(7)
C(3A)-Re-C(7A)	38.1(5)	C(4A)-Re-C(7A)	64.0(6)
C(5A)-Re-C(7A)	62.4(6)	C(6A)-Re-C(7A)	38.1(6)
Re-Si-C(2)	123.9(5)	Re-Si-C(3)	46.5(4)
C(2)-Si-C(3)	111.6(6)	Re-Si-C(2A)	123.9(5)
C(2)-Si-C(2A)	112.2(9)	C(3)-Si-C(2A)	113.5(5)
Re-Si-C(3A)	46.5(4)	C(2)-Si-C(3A)	113.5(5)
C(3)-Si-C(3A)	92.9(8)	C(2A)-Si-C(3A)	111.6(6)
Re-C(3)-Si	95.1(6)	Re-C(3)-C(4)	71.2(8)
Si-C(3)-C(4)	121.6(11)	Re-C(3)-C(7)	71.7(8)
Si-C(3)-C(7)	122.0(9)	C(4)-C(3)-C(7)	107.1(11)
Re-C(4)-C(3)	69.7(8)	Re-C(4)-C(5)	74.1(8)
C(3)-C(4)-C(5)	107.9(13)	Re-C(5)-C(4)	70.2(9)
Re-C(5)-C(6)	71.2(7)	C(4)-C(5)-C(6)	110.7(13)
Re-C(6)-C(5)	71.9(9)	Re-C(6)-C(7)	69.4(10)
C(5)-C(6)-C(7)	107.0(14)	Re-C(7)-C(3)	70.2(9)
Re-C(7)-C(6)	72.5(10)	C(3)-C(7)-C(6)	107.2(12)

Table 4. Anisotropic displacement coefficients ($Å^2 x 10^4$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	199(5)	287(6)	154(5)	0	78(3)	0
Si	304(22)	278(25)	214(21)	0	130(18)	0
C(1)	1324(231	433(136	415(117	0	630(143	0
C(2)	402(68)	471(83)	327(62)	-87(62)	207(53)	-50(67)
C(3)	127(46)	253(66)	252(59)	21(38)	132(44)	33(46)
C(4)	251(75)	392(77)	279(82)	-48(50)	68(65)	100(53)
C(5)	519(77)	310(59)	55(48)	-36(64)	69(47)	-54(53)
C(6)	538(81)	435(74)	227(60)	58(74)	230(59)	24(66)
C(7)	253(74)	268(69)	401(95)	-17(43)	190(69)	-4(50)

The anisotropic displacement exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Table 5. H-Atom coordinates ($x10^4$) and isotropic displacement coefficients ($Å^2 x10^3$)

	x	y	z	U
H(1B)	4303	5440	2866	50
H(1C)	5746	5440	3403	50
H(1A)	4957	5308	1399	50
H(1AA)	5043	5308	3601	50
H(1BA)	5697	5440	2134	50
H(1CA)	4254	5440	1597	50
H(2A)	6219	10667	3185	50
H(2B)	6849	9858	4528	50
H(2C)	6962	9858	2596	50
H(4A)	3209	7979	-580	50
H(5A)	4004	6407	-1124	50
H(6A)	6383	6357	225	50
H(7A)	7093	7993	1699	50

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