Synthesis and Reactivity of the Cationic Methylene Complex $[Cp_2Re{=}CH_2]^+$

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Received August 11, 1997[⊗]

Reaction of Cp_2ReCH_2R (R = H, CH_3) (Cp = η^5-C_5H_5) with $[Ph_3C]B(Ar')_4$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$) generates carbene complexes $[Cp_2Re{=}CH_2]B(Ar')_4$ (**1**) and $[Cp_2Re{=}CH(CH_3)]B(Ar')_4$ (**3**). Complex **1** is thermally robust and is only observed to decompose to $[Cp_2Re(C_2H_4)]^+$ and $[Cp_2Re(NCCD_3)]^+$ upon prolonged thermolysis in acetonitrile-d_3 or upon addition of BF_4^- or PF_6^- salts. The formation of **1** is also observed upon reaction of $[Cp_2Re(CH_3)H]B(Ar')_4$ with CH_2Cl_2 at 0 °C to give $[Cp_2Re(CH_2Cl)Cl]B(Ar')_4$ (**2**) followed by treatment with Mg. The electrophilic nature of **1** is confirmed by adduct formation with PPh_3, pyridine, and CN^tBu. Complex **1** reacts with halogens by 1,2-addition across the Re−C double bond to form halomethyl halide complexes $[Cp_2Re(CH_2X)X]B(Ar')_4$ (X = Cl, Br, I). Reaction of **1** with pyridine *N*-oxide gives the formaldehyde complex $[Cp_2Re(\eta^2\text{-}H_2C{=}O)]B(Ar')_4$. The formaldehyde ligand can be displaced in solution by reaction with PPh_3, acetonitrile, or methylene chloride. Complex **1** reacts with sulfur-atom donor reagents to give the thioformaldehyde complex $[Cp_2Re(\eta^2\text{-}H_2C{=}S)]B(Ar')_4$. Reaction of **1** with $N_2CHSiMe_3$ generates the olefin complex $[Cp_2Re(\eta^2\text{-}H_2C{=}CHSiMe_3)]B(Ar')_4$.

Introduction

Despite the extensive development of the chemistry of metal carbene complexes, few examples of bound methylene, the simplest type of carbene complex, have been completely characterized. The first methylene complex was synthesized by Schrock in 1975 *via* deprotonation of $[Cp_2TaMe_2]^+$ to give $Cp_2TaCH_3(=CH_2)$.[1] The number of *isolable* methylene complexes has grown slowly since this time.[2] Several synthetic 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 $[Ph_3C]^+$.

A very important example of a methylene complex which is not isolable is provided by Cp_2TiCH_2. This titanium methylene complex is very reactive,[3] and has only been characterized by indirect methods, including formation of a phosphine adduct.[4] Related methylene complexes of group VI metallocenes are not known, but $Cp_2W{=}CHPh$ has been isolated and structurally characterized.[5]

Stucky and co-workers have reported that the reaction of $[Ph_3C]BF_4$ with Cp_2ReCH_3 led to an unstable methylene complex by abstraction of an α hydride.[6] The ^1H NMR resonances for $[Cp_2ReCH_2]BF_4$ were quickly replaced by signals assigned to the ethylene complex, $[Cp_2Re(C_2H_4)]BF_4$. Reaction of $Cp_2ReCH_2CH_3$ with $[Ph_3C]BF_4$ also affords $[Cp_2Re(C_2H_4)]BF_4$, proposed to result from β-hydride abstraction from the ethyl group, although labeling studies were not performed to confirm the site of hydride abstraction.

We have found that reaction of $[Ph_3C]B(Ar')_4$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$)[7] with Cp_2ReCH_3 leads to a stable, cationic methylene complex $[Cp_2ReCH_2]B(Ar')_4$. Addition of $[Ph_3C]B(Ar')_4$ to $Cp_2ReCH_2CH_3$ leads to hydride abstraction from the α carbon to generate an ethylidene complex $[Cp_2ReCH(CH_3)]B(Ar')_4$. The thermal stability of these complexes is greatly increased with use of the non-nucleophilic and noncoordinating anion $B(Ar')_4$.[7−11]

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1997.

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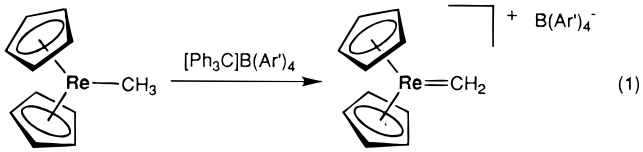
S0276-7333(97)00706-1 CCC: $15.00
Publication on Web 01/05/1998

The electrophilic nature of the methylene complex is confirmed by reactions with various nucleophiles, leading to several new complexes of rhenocene.

Results

Preparation and Characterization of $[Cp_2Re{=}CH_2]^+$ (1). 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 1). Complex **1** is



(1)

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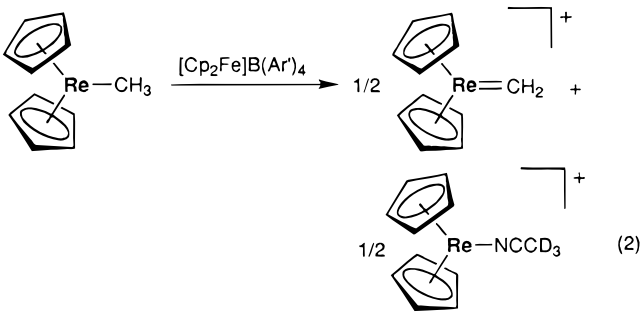
precipitated from solution by addition of pentane and isolated by filtration (97% yield). Complex **1** has been characterized by ^1H and ^{13}C NMR spectroscopy as well as by elemental analysis. The downfield resonances observed in the ^1H and ^{13}C NMR spectra are particularly indicative of the formation of a transition-metal carbene complex. The ^1H NMR spectrum of **1** in CD_2Cl_2 shows two resonances for the cation; a singlet for the 10 equivalent cyclopentadienyl protons at 5.60 ppm and a singlet for the two protons of the carbene ligand at 13.19 ppm. The carbon resonance of the carbene ligand appears at 247.7 ppm as a triplet due to coupling of the two equivalent protons with $^1J_{CH} = 152$ Hz.

Contrary to the extreme air sensitivity of the alkyl complexes of rhenocene, **1** is air stable in the solid state and in solution, showing little decoloration over several days. Complex **1** was formed as a tetraphenylborate salt upon reaction of Cp_2ReCH_3 with $[Ph_3C]BPh_4$ in CH_2Cl_2 and isolated as a pink solid. Complex **1-BPh$_4$** is thermally stable, but its low solubility in CH_2Cl_2 makes it inconvenient for the synthesis of further derivatives.

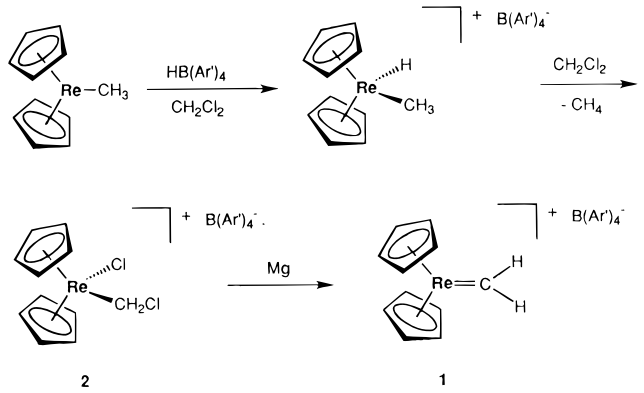
Reaction of Cp_2ReCH_3 with $[Cp_2Fe]B(Ar')_4$ at room temperature in acetonitrile-d_3 affords a 50/50 mixture of the methylene complex **1** and $[Cp_2Re(NCCH_3)]B(Ar')_4$ (eq 2). Monitoring the reaction at low temperature by



(2)

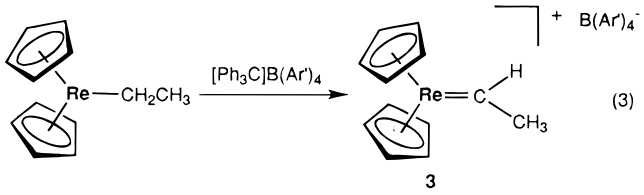
^1H NMR spectroscopy indicates the formation of $[Cp_2Re(CH_3)H]B(Ar')_4$, which then proceeds to generate $[Cp_2Re(NCCH_3)]B(Ar')_4$ at room temperature by loss of methane.[12]

Scheme 1



Generation of Complex 1 from Methylene Chloride. Consistent with previous reports,[12,13] the protonation of Cp_2ReCH_3 with $[H(Et_2O)_2]B(Ar')_4$ results in the formation of $[Cp_2Re(CH_3)H]B(Ar')_4$, which has been characterized by ^1H and ^{13}C NMR spectroscopy at 250 K (Scheme 1). Warming a solution of the methyl hydride complex to room temperature in methylene chloride results in methane elimination and the formation of $[Cp_2Re(CH_2Cl)Cl]B(Ar')_4$ (**2**). Confirmation of the structure of **2** was obtained by ^1H and ^{13}C NMR spectroscopy as well as by generating the compound by another route (*vide infra*). The ^1H NMR spectrum of **2** shows a single Cp resonance at 6.02 ppm and a resonance at 4.40 ppm which integrates for two protons. The ^{13}C NMR resonance for $Re{-}CH_2Cl$ appears as a triplet at δ 11.5 ($J_{CH} = 163$ Hz). Complex **2** reacts with Mg turnings to generate **1**.

Preparation and Characterization of $[Cp_2ReCH(CH_3)]B(Ar')_4$ (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 3). Complex **3** is



(3)

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isolated by precipitation with pentane followed by filtration to give a pale orange solid in 94% yield. The ^1H and ^{13}C NMR spectra indicate the formation of an ethylidene complex and a small amount (<5%) of the previously reported ethylene complex.[6] The ^1H NMR spectrum of **3** in CD_2Cl_2 reveals a doublet at 1.53 ppm for the methyl group of the ethylidene ligand and a quartet at 13.82 ppm for the carbene proton ($^3J_{HH} = 8$ Hz). The cyclopentadienyl resonances are observed as two singlets at 5.56 and 5.51 ppm. The ^{13}C NMR spectrum of **3** exhibits a doublet at 266.0 ppm for the carbene carbon with a one-bond CH coupling constant of 143 Hz. A quartet is observed for the methyl carbon

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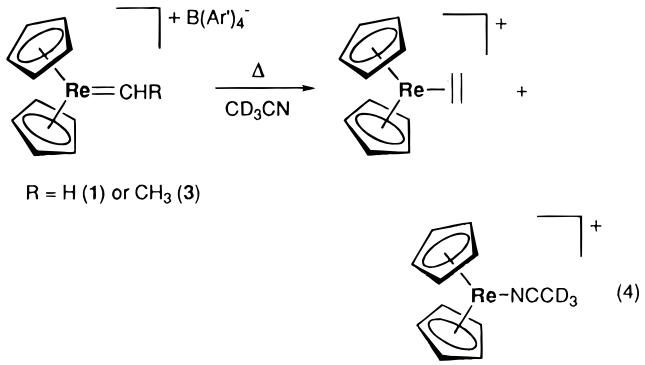
of the ethylidene ligand at 45.0 ppm with a one-bond CH coupling constant of 128 Hz.

Stability of Carbene Complexes 1 and 3. Complex **1**-$B(Ar')_4$ has been found to be indefinitely stable as a solid, and no decomposition has been observed in CD_2Cl_2 at room temperature. Complexes **1** and **3** were heated in CD_2Cl_2 at 40 °C and monitored periodically by ^1H NMR spectroscopy. Gradual formation of complex product mixtures was observed over 2 weeks. The thermolysis of **1** and **3** in CD_3CN led to cleaner reactions. Complete disappearance of starting material was observed after 2 weeks at 55 °C. The two main products identified by their ^1H NMR spectra are $[Cp_2Re(C_2H_4)]B(Ar')_4$[6] and $[Cp_2Re(NCCD_3)]B(Ar')_4$[12] (eq 4).



(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 $[Cp_2ReCH_2]BF_4$ as well as a small amount of $[Cp_2Re(NCCD_3)]BF_4$. The carbene complex undergoes complete conversion to $[Cp_2Re(C_2H_4)]BF_4$ and $[Cp_2Re(NCCD_3)]BF_4$ after 24 h at room temperature.

In either CD_2Cl_2 or CD_3CN, the reaction of $Cp_2ReCH_2CH_3$ with $[Ph_3C]BF_4$ gives $[Cp_2Re(C_2H_4)]^+$ immediately. Minor amounts of the carbene complex (**3**) are 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. $[Cp_2ReCH(CH_3)]BF_4$ is cleanly generated when the reaction is monitored at low temperature, but the complex isomerizes to the ethylene complex at room temperature. Addition of 1,8-bis(dimethylamino)naphthalene to solutions of $[Cp_2ReCH(CH_3)]B(Ar')_4$ does not inhibit isomerization to the ethylene complex.

Addition of BF_4^- or PF_6^- salts to CD_3CN solutions of **1**-$B(Ar')_4$ induces decomposition, which is similar to the outcome of 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 rapid, presumably due to greater solubility in CD_3CN. Clean formation of $[Cp_2Re(C_2H_4)]BF_4$, $[Cp_2Re(NCCD_3)]BF_4$, and a small amount of free ethylene (δ 5.4) was observed. The reaction with NH_4BF_4 affords the ethylene and acetonitrile products in a 50/50 ratio while the $NaBF_4$ reaction gave 33/66, respectively.

Reactivity of $[Cp_2ReCH_2]B(Ar')_4$ (1). Addition of 1 equiv of PPh_3 to a solution of **1** in methylene chloride results in an immediate color change from pink to pale orange (Scheme 2). A crystalline solid is precipitated in 90% yield by addition of pentane. The ^1H, ^{31}P, and ^{13}C NMR data are consistent with the formation of the phosphine−ylide complex $[Cp_2Re(CH_2PPh_3)]B(Ar')_4$ (**4**). The ^1H and ^{13}C resonances of the methylene ligand have shifted considerably to higher field at 2.58 and −32.7 ppm, respectively. The methylene resonance in the ^1H NMR appears as a doublet due to a ^{31}P coupling of 10.8 Hz. 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} = 126.2 Hz).

Addition of 3 equiv of pyridine to **1** in CD_2Cl_2 resulted in the formation of a pyridine−ylide complex $[Cp_2Re(CH_2NC_5H_5)]B(Ar')_4$ (**5**). 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 those due to **5** and $[Cp_2ReCH_2]^+$ (**1**). Addition of excess pyridine to the solution resulted in conversion back to the sharp ^1H NMR resonances of **5** as noted above.

Addition of ^{t}BuNC to a CH_2Cl_2 solution of **1** gives a pale orange solution from which $[Cp_2ReCH_2CN^tBu]B(Ar')_4$ (**6**) is isolated in 86% yield. 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.

We find that complex **1** does not react with CO, CH_3CN, PhNCO, CO_2, or CS_2. Complex **1** also fails to undergo any reaction with olefins such as ethylene or styrene to generate cyclopropanes.

Complex **2** can also be formed by the reaction of $[Cp_2ReCH_2]B(Ar')_4$ (**1**) with Cl_2 in CH_2Cl_2. $[Cp_2Re(CH_2X)X]B(Ar')_4$ (X = Br (**7**) I (**8**)) are formed upon addition of Br_2 or I_2 to a CH_2Cl_2 solution of **1**. Complexes **2**, **7**, and **8** 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, consistent with prior reports.[14]

$[Cp_2ReCH_2]B(Ar')_4$ (**1**) reacts cleanly with pyridine *N*-oxide (pyO) to form $[Cp_2Re(\eta^2\text{-}CH_2O)]B(Ar')_4$ (**9**) in CH_2Cl_2. Complex **9** was isolated as a pale orange solid in 93% yield by crystallization from CH_2Cl_2/pentane followed by filtration. 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 ^{13}C NMR resonance of the formaldehyde ligand was located at 46.2 ppm.

The formaldehyde ligand can be displaced by reaction with solvent or nucleophiles. Heating a solution of **9** in CD_3CN at 55 °C for several days eventually led to the formation of $[Cp_2ReNCCD_3]^+$. Complex **9** reacts similarly with CD_2Cl_2 to form $[Cp_2Re(CD_2Cl)Cl]^+$ (**2**)

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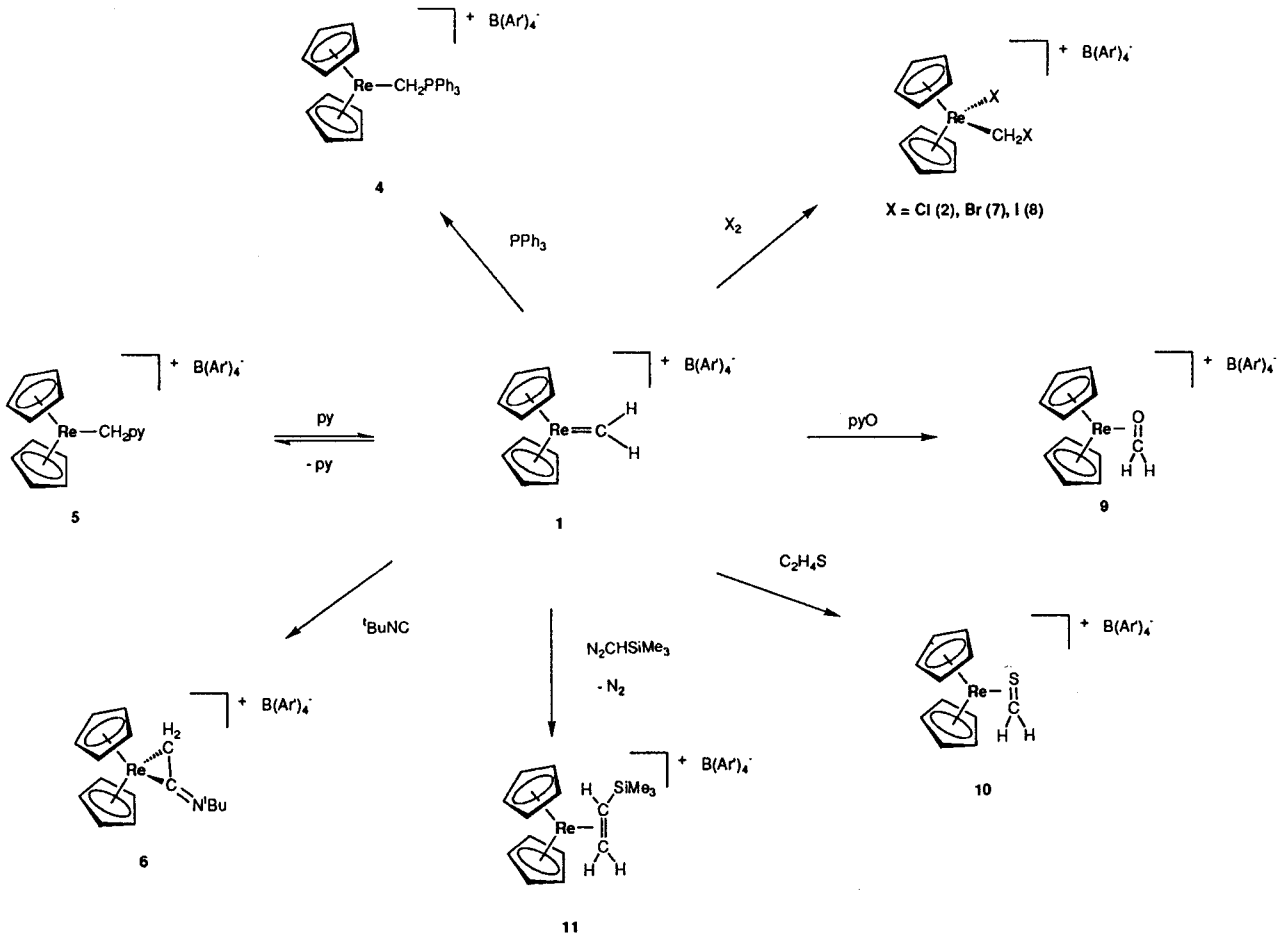
Scheme 2



after several days at 55 °C. A solution of **9** and PPh_3 in CD_2Cl_2 slowly forms $[Cp_2RePPh_3]^+$ [15] after 1 week at room temperature.

Heating complex **1** with excess sulfur in CD_2Cl_2 for 3 h at 50 °C leads to the clean formation of a thioformaldehyde complex. $[Cp_2Re(\eta^2\text{-}CH_2S)]B(Ar')_4$ (**10**) can be more conveniently formed by reaction of **1** with excess ethylene sulfide at room temperature. A bright orange/yellow solid is isolated in 89% yield by crystallization from CH_2Cl_2/pentane. 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 exhibits a triplet at 13.7 ppm for CH_2S with $^1J_{CH} = 168$ Hz.

The phosphonium-ylide complex $[Cp_2ReCH_2PPh_3]^+$ (**4**) reacts rapidly with excess ethylene sulfide to form complex **10** and $SPPh_3$. Addition of $SPPh_3$ to complex **1** produces equal amounts of complexes **4** and **10**. The thioformaldehyde ligand of **10** is not displaced by PPh_3 but reacts rapidly to form $[Cp_2ReCH_2PPh_3]^+$ and $S{=}PPh_3$.

Addition of $N_2CHSiMe_3$ (2 M in hexanes) to a methylene chloride solution of complex **1** results in a color change from pink to light tan, accompanied by rapid evolution of N_2. The olefin complex $[Cp_2Re(CH_2{=}CHSiMe_3)]B(Ar')_4$ (**11**) is isolated in 69% yield by crystallization from a concentrated CH_2Cl_2 solution layered with pentane. The ^1H NMR spectrum exhibits two cyclopentadienyl resonances at 5.13 and 5.10 ppm, indicating hindered rotation of the olefin ligand.

Discussion

Synthesis and Characterization of Complexes 1 and 3. Reaction of Cp_2ReCH_3 with $[Ph_3C]B(Ar')_4$ generates the stable methylene complex in nearly quantitative yield. The abstraction of an α hydride from a neutral metal alkyl with trityl cation is well-known, with several examples reported by Gladysz and coworkers in the preparation of cationic rhenium carbene complexes of the general formula $[CpRe(NO)(PPh_3)(=CHR)]^+$.[16]

Hydride abstraction by trityl cation has been proposed to proceed by an initial electron transfer from the metal alkyl complex followed by a hydrogen-atom transfer for complexes which are electron rich and easily oxidized.[17,18] Cooper has provided clear evidence for this mechanism by the isolation and characterization of stable radical cations, $[Cp_2W(CH_3)(C_2H_5)]^{\bullet+}$, which react

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further with $Ph_3C^\bullet$ by hydrogen-atom abstraction to generate a carbene complex.[17]

In order to investigate the possibility of an initial electron transfer in the formation of complex **1**, we investigated the reactivity of Cp_2ReCH_3 with $[Cp_2Fe]^+$.[19] The reaction of $[Cp_2Fe]B(Ar')_4$ with Cp_2ReCH_3 at low temperature in acetonitrile-d_3 generates complex **1**, $[Cp_2Re(CH_3)H]^+$, and Cp_2Fe. We propose that initial electron transfer affords the 17-electron radical cation $[Cp_2ReCH_3]^{\bullet+}$. Rapid proton transfer to Cp_2ReCH_3 leads to $[Cp_2Re(CH_3)H]^+$ and Cp_2ReCH_2, which is rapidly oxidized to afford complex **1**. This result demonstrates the utility of a chemical oxidant to generate carbene complexes (in a 50% yield) when reacted with electron-rich metal alkyl complexes.

An independent preparation of complex **1** is provided by dehalogenation of the chloromethyl chloride complex **2**. Complex **2** is generated by the oxidative addition of CH_2Cl_2 upon loss of methane from the thermally unstable $[Cp_2Re(CH_3)H]^+$. Complex **2** can only be isolated using the $B(Ar')_4$ anion. The synthesis of chloromethyl chloride complexes have been reported by several groups. Typically, these complexes are formed *via* oxidative addition of CH_2Cl_2 to a coordinatively unsaturated metal complex.[20−24] A different approach has been taken by Hubbard and co-workers, who have reported the stepwise addition of diazomethane to $Cp^*Ru(NO)Cl_2$ to generate the chloromethyl chloride complex and the bis(chloromethyl) complex.[25]

$Cp^*Ru(NO)(CH_2Cl)Cl$ has been shown to form polymethylene upon thermolysis or photolysis, and $Cp^*Ru(NO)(CH_2Cl)(CH_2Cl)$ extrudes ethylene with the dichloride $Cp^*Ru(NO)Cl_2$ formed as the final product. In contrast, complex **2** is thermally robust. Thermolysis of complex **2** did not result in any conversion to the known[26] $[Cp_2ReCl_2]^+$.

The displacement of the halide from halomethyl ligands is a common synthetic technique to generate such complexes as cationic ylides by reaction with a phosphine or to generate hydroxymethyl and alkoxymethyl complexes by reaction with water or alcohols.[14,27] Hubbard has reported the dehalogenation of $CpCr(NO)_2CH_2Cl$ with Ag^+ to generate a very reactive methylene complex which then rapidly inserts into a C−H bond of the Cp ligand to generate $[(\eta^5\text{-}C_5H_4Me)Cr(NO)_2]^+$.[28] Caulton has recently reported the formation of a known methlylene compound $Ru{=}CH_2(PCy_3)_2Cl_2$[2g] by reaction of $Ru(H_2)_2H_2(PCy_3)_2$ with CH_2Cl_2 (with loss of 3 equiv of dihydrogen).[29] We find that reaction of complex **2** with Mg turnings affords the methylene complex **1** quantitatively by ^1H NMR. While this preparation is less convenient than the trityl abstraction procedure, it serves to verify the formulation of complex **2** as a chloromethyl chloride. Additional confirmation is provided by the reaction of complex **1** with elemental chlorine, which leads to clean formation of the chloromethyl chloride complex **2**.

The reaction of $Cp_2ReCH_2CH_3$ with $[Ph_3C]B(Ar')_4$ results almost exclusively in abstraction of an α hydride. A small amount (<5%) of the $[Cp_2Re(\eta^2\text{-}C_2H_4)]B(Ar')_4$ complex is formed as a result of β-hydride abstraction. The ratio between the ethylidene and the ethylene complexes does not change upon standing at room temperature for 1 week. Gladysz and co-workers observed a similar ratio of α vs β-hydride abstraction for $CpRe(NO)(PPh_3)_2(CH_2CH_3)$ with a greater percentage of β hydride abstraction occurring for higher alkyls.[30]

Stability of the Carbene Complexes: Anion Effects. Stucky and co-workers have previously described the reactivity of Cp_2ReCH_3 and $Cp_2ReCH_2CH_3$ with $[Ph_3C]BF_4$.[6] In both cases, the main product was identified as $[Cp_2Re(C_2H_4)]BF_4$. Formation of a thermally unstable methylene complex by α-hydride abstraction from Cp_2ReCH_3 was suggested, while a stable ethylene complex was thought to be formed by β-hydride abstraction from $Cp_2ReCH_2CH_3$. In contrast to these results, we find that $[Cp_2ReCH_2]^+$ (**1**) and $[Cp_2ReCH(CH_3)]^+$ (**3**) are readily isolable and thermally robust when the counterion employed is $B(Ar')_4$. Acetonitrile solutions of complex **1** react with added BF_4^- and PF_6^- salts while undergoing relatively clean conversion to the corresponding ethylene complex $[Cp_2ReC_2H_4]^+$ and $[Cp_2Re(CH_3CN)]^+$. These results are consistent with the operation of a bimolecular coupling mechanism. In several previous reports, complexes of the type $L_nM{=}CH_2$ have 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. The mechanism of this reaction has been studied by Gladysz and co-workers for $[CpRe(NO)(PPh_3)(CH_2)]BF_4$ and was shown to proceed through a bimolecular coupling.[31] Consistent with this, the bulkier complex, $[Cp^*Re(NO)(PPh_3)(CH_2)]BF_4$, is considerably more stable than the Cp complex.[16e] Direct evidence for the bimolecular decomposition pathway is provided in one case by the isolation of a 1,3-dimetallacyclobutane complex from a reaction thought to produce "$Cp_2Ti{=}CH_2$".[32]

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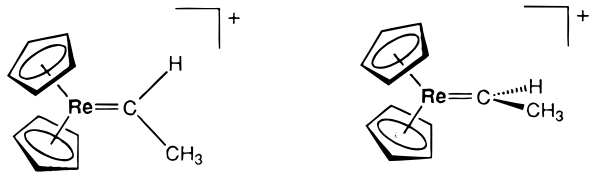
Scheme 3



A B

Several complexes of the form $LnMCH(CH_3)$ have also been observed to form the 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. In our case, we find that complex **3** in acetonitrile isomerizes to the ethylene complex in the presence of added BF_4^- and PF_6^- salts. Gladysz and co-workers have explored the conversion of $[CpRe(NO)(PPh_3)(CHR)]BF_4$ complexes to the corresponding olefin complexes.[30] In this case, a solvent-coordinated species would not be expected to form.

We propose that the larger anions such as $B(Ar')_4$ and BPh_4 hinder the bimolecular coupling reaction of complex **1**. This interpretation is speculative, since we have not observed any ^1H or ^{13}C NMR evidence which suggests any interaction between the anions and the methylene complex. Presumably, complexes such as **1** form tight ion pairs with anions such as $B(Ar')_4$, which would not be effectively separated by solvent. Caulton and co-workers have recently reported the structure of an η^2-CH_2Cl_2 adduct of $[RuH(CO)(P^tBu_2Me)_2]B(Ar')_4$ in which the hydrogens of the dichloromethane ligand are observed to have a hydrogen-bond interaction with the phenyl rings of the anion, forming an overall ion pair.[33] On the basis of the observation that complex **3** is also stabilized with the $B(Ar')_4$ anion, we consider it possible that the 1,2-hydrogen shift to afford the olefin complex could be assisted by a bimolecular reaction.

Structure of the Carbene Complexes. The equivalent protons of the methylene ligand in complex **1** do not give an indication of the alignment of the methylene ligand nor the barrier to rotation. Additional information about the structure of the carbene complex can be gained from an unsymmetrical carbene ligand. The observation of two inequivalent Cp resonances in the ^1H and ^{13}C NMR spectra of $[Cp_2ReCH(CH_3)]B(Ar')_4$ (**3**) indicates that the methyl group is aligned with one Cp while the hydrogen of the carbene ligand is aligned with the other Cp (structure A; Scheme 3).

The rotation of the carbene ligand must be slow on the NMR time scale 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 $\Delta G^{\ddagger} \geq 17.7$ kcal/mol. This large barrier to rotation is formally a reflection of the difference in energy between conformers A and B, and although the barrier is not directly related to the strength of the π bond, the π contribution from structure B is likely negligible.[34] Caulton and co-workers have synthesized $Cp_2W{=}CH(CH_3)$, which also shows inequivalent cyclopentadienyl rings by ^1H NMR spectroscopy and have confirmed this arrangement with a crystal structure of $Cp_2W{=}CH(Ph)$.[5]

Reactivity of Complex 1. Complex **1** displays electrophilic reactivity, as expected for a cationic methylene complex. The addition of PPh_3 to **1** forms a stable ylide complex, while pyridine forms a less stable ylide complex that reversibly dissociates pyridine in solution. Complex **1** shows no reaction in the presence of a large excess of dimethyl sulfide. In a similar system, Gladysz and co-workers have found that isolable ylide complexes can be generated by reaction of $[CpRe(NO)(PPh_3)CH_2]^+$ with PPh_3, NC_5H_5, and SMe_2.[16b,35] With ^{t}Bu isonitrile, we find that complex **1** forms an adduct which we formulate as the ketenimine complex **6** based primarily on the IR spectrum, which is consistent with a significant decrease in the CN bond order.

Complex **1** reacts with elemental chlorine to give the chloromethyl chloride complex **2**. This novel reaction has precedent in the work of Roper and co-workers who report that $Os(=CH_2)(PPh_3)_2(NO)(Cl)$ reacts with chlorine to form a chloromethyl chloride complex, $Os(CH_2Cl)(PPh_3)_2(NO)Cl_2$.[2f]

Our preparation of a bound formaldehyde ligand is similar to that reported by Gladysz and co-workers using reaction of a nucleophilic oxygen-atom donor with an electrophilic methylene complex.[36] Oxygen-atom donors react with complex **1** to give the formaldehyde complex **9**, which is characterized as an η^2-CH_2O structure based on the high-field ^{13}C NMR resonance of the formaldehyde ligand at 46.2 ppm. 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 ν_{CO} could not be located in the expected region between 1300−1000 cm^{-1}, which was obscured by bands from the anion. In closely related complexes, an intense ν_{CO} band 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}.[37] The lack of a CO stretch in the IR spectrum between 1400 and 1600 cm^{-1} rules out an end-bound formaldehyde ligand.

Reports from the groups of Gladysz and Grubbs note 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.[38,39] Consistent with this, we find that methylene complex **1** reacts with various sulfur-

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atom sources to afford the thioformaldehyde complex $[Cp_2Re(\eta^2\text{-}H_2C{=}S)]B(Ar')_4$ (**10**). Reactivity studies of complexes **9** and **10** with nucleophiles are in agreement with the observations of Gladysz and co-workers that the thioformaldehyde ligand is less labile than the formaldehyde ligand.

Conclusion

A convenient preparation of cationic rhenocene carbene complexes using hydride abstraction from the neutral alkyls has been demonstrated. The stability of the carbene complexes is dramatically increased by the use of unreactive tetraphenylborate counteranions. The carbene ligand has a high barrier to rotation and exhibits reactivity consistent with electrophilic character of the carbene carbon.

Experimental Section

General Procedures. 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 high-vacuum or Schlenk techniques. Chlorinated solvents were distilled from CaH_2. Hydrocarbon solvents were distilled from Na/K benzophenone ketyl. Deuterated solvents (Cambridge Isotope Labs) were dried and stored in the same manner as their protio analogs. All solvents were vacuum-transferred immediately prior to use. Reagent grade chemicals were used as received unless stated otherwise. Cp_2ReCH_3,[13] $Cp_2ReCH_2CH_3$,[13] $[Ph_3C]B(Ar')_4$,[7] $[Ph_3C]BPh_4$,[40] $[H(Et_2O)_2]B(Ar')_4$,[9] and $SPPh_3$[41] were prepared using literature methods. ^{t}BuNC (Strem) was degassed and stored under argon. Pyridine *N*-oxide (pyO) (Aldrich) was sublimed prior to use and stored under argon. Ethylene sulfide was degassed and stored under vacuum in a vessel equipped with a Teflon needle valve.

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AC-200 (200.133 MHz ^{1}H, 81.015 MHz ^{31}P), AF-300 (300.117 MHz ^{1}H, 75.465 MHz ^{13}C), and WM-500 (500.136 MHz ^{1}H) spectrometers. ^{1}H 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 NMR chemical shifts (δ) are reported in parts per million relative to 85% H_3PO_4 (external standard). The cyclopentadienyl protons of rhenocene complexes have been observed to relax slowly, and a relaxation delay of 120 s is required to observe appropriate integrals. All NMR-tube reactions were conducted in flame sealed tubes or J. Young screw-cap tubes. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, B.C.

$[Cp_2ReCH_2]B(Ar')_4$ (1). A 20 mL round-bottom flask was charged with Cp_2ReCH_3 (250 mg, 0.754 mmol) and $[Ph_3C]B(Ar')_4$ (835 mg, 0.754 mmol) and attached to a swivel -frit apparatus. The swivel frit was attached to a vacuum line, and 10 mL of CH_2Cl_2 was vacuum transferred at −78 °C. The red solution was warmed to room temperature and stirred for a few minutes. The solvent volume was reduced under vacuum 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, Cp). ^{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, $^2J_{CH}$ = 7 Hz, Cp). Anal. Calcd for $C_{43}H_{24}BF_{24}Re$: C, 43.27; H, 2.03. Found: C, 43.19; H, 2.06. The ^{1}H and ^{13}C NMR resonances for $B(Ar')_4^-$ are identical with those reported for complex **1** and have been omitted from the spectral characterization of subsequent complexes.

$[Cp_2ReCH_2]BPh_4$ (1-BPh$_4$). The preparation of **1-BPh$_4$** is similar to that for **1-B(Ar′)$_4$**. Cp_2ReCH_3 (76.5 mg, 0.231 mmol) is reacted with $[Ph_3C]BPh_4$ (130 mg, 0.231 mmol) in CH_2Cl_2 followed by precipitation with pentane. The pink solid was collected in 80% yield (120 mg). ^{1}H NMR (CD_2Cl_2): 12.95 (s, 2H, Re−CH_2), 7.4−6.8 (m, BPh_4), 5.29 (s, 10H, Cp).

$[Cp_2Re(CH_3)H]B(Ar')_4$. A sealable NMR tube was charged with Cp_2ReCH_3 (6 mg, 0.018 mmol) and $[H(Et_2O)_2]B(Ar')_4$ (18.3 mg, 0.018 mmol). CD_2Cl_2 (0.5 mL) was vacuum transferred to the tube. The tube was sealed and 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, Cp), 0.53 (s, 3 H, Re−CH_3), −11.88 (s, 1 H, Re−H). ^{13}C{^{1}H} NMR (CD_2Cl_2): 84.0 (Cp), −40.1 (Re−CH_3).

$[Cp_2Re(CH_2Cl)Cl]B(Ar')_4$ (2). Method A. A small glass vessel with an 8 mm Kontes valve was charged with Cp_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 min. 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 min at 0 °C, a precipitate forms. The peach-colored solid is dried under dynamic vacuum. Yield: 180 mg (94%). ^{1}H 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, Cp), 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.

Method B. A sealable NMR tube was charged with complex **1** (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. After 3 freeze−pump−thaw cycles, the tube was sealed. ^{1}H NMR (CD_2Cl_2): 6.02 (s, 10 H, Cp); 4.40 (s, 2 H, Re−CH_2Cl).

$[Cp_2ReCH(CH_3)]B(Ar')_4$ (3). The preparation of compound **3** is similar to that for **1-B(Ar′)$_4$**. $Cp_2ReCH_2CH_3$ (50 mg, 0.145 mmol) is reacted with $[Ph_3C]B(Ar')_4$ (160 mg, 0.145 mmol) in CH_2Cl_2 followed by precipitation with pentane. 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, Cp), 5.51 (s, 5 H, Cp), 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=CH(CH_3)), 86.0 (d of quint, J_{CH} = 187 Hz, J_{CH} = 6 Hz, Cp), 85.6 (d of quint, J_{CH} = 187 Hz, J_{CH} = 6 Hz, Cp), 45.0 (quart, J_{CH} = 128 Hz, Re=CH(*C*H$_3$)).

$[Cp_2Fe]B(Ar')_4$. Ferrocene (0.625 g, 3.36 mmol) was dissolved in 12.5 mL of H_2SO_4. The dark blue solution was stirred for 2 h then added to 185 mL of H_2O and filtered. The solution was sparged with Ar in a Schlenk flask, and $NaB(Ar')_4$ (1 g, 1.13 mmol) was added. After 24 h of stirring, a light blue precipitate was collected by filtration, rinsed with H_2O, and dried under dynamic vacuum. Yield: 0.892 g (76%). ^{1}H NMR (acetone-d_6): 28 (s, 10 H, Cp_2Fe^+), 7.8 (s, 4 H, *p*-$B(Ar')_4$), 7.7 (s, 8 H, *o*-$B(Ar')_4$).

$[Cp_2ReCH_2PPh_3]B(Ar')_4$ (4). A small glass vessel with an 8 mm Kontes valve was charged with **1** (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 min. The solvent volume 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

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by cannula, and the solid was dried under dynamic vacuum. The pale orange solid was collected in 90% yield (55 mg). ^{1}H NMR (CD_2Cl_2): 7.4−7.9 (m, 15 H, PPh_3), 4.16 (s, 10 H,Cp), 2.58 (d, 2 H, J_{PH} = 10.8 Hz, Re−CH_2). ^{31}P{sel ^{1}H} 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, Cp), −32.7 (d of t, J_{CP} = 25.6 Hz, J_{CH} = 126.2 Hz, Re−*C*H_2). Anal. Calcd for $C_{61}H_{39}BF_{24}PRe$: C, 50.32; H, 2.70. Found: C, 49.48; H, 2.68.

Reaction of [Cp$_2$ReCH$_2$)]B(Ar′)$_4$ with Pyridine. A sealable NMR tube was charged with compound **1** (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 3 freeze−pump−thaw cycles, and the tube was sealed. ^{1}H 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, Cp).

[Cp$_2$ReCH$_2$CN^{t}Bu]B(Ar′)$_4$ (6). A small glass vessel with an 8 mm Kontes valve was charged with **1** (60 mg, 0.0503 mmol). Dichloromethane (15 mL) was vacuum transferred to the vessel. Under an argon flow, CN^{t}Bu (6 μL, 0.0503 mmol) was added via a gas-tight syringe. The solution was stirred for 10 min, and the solvent volume 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 pale orange solid was dried under vacuum. Yield: 55 mg, 86%. ^{1}H NMR (CD_2Cl_2): 5.15 (s, 10 H,Cp), 1.64 (s, 2 H, Re−CH_2), 1.26 (s, 9 H, CN^t*Bu*). ^{13}C NMR (CD_2Cl_2): 158.5 (s, *C*N^{t}Bu), 84.0 (d of quint, $^1J_{CH}$ = 188 Hz, J_{CH} = 6.4 Hz, Cp), 28.8 (quart, J_{CH} = 125.9 Hz, CN^t*Bu*), −31.8 (t, J_{CH} = 163.8, Re−*C*H_2). IR (cm^{-1}, Nujol, ν_{CN}): 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.

[Cp$_2$Re(CH$_2$Br)Br]B(Ar′)$_4$ (7). A small glass vessel with an 8 mm Kontes valve was charged with **1** (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 discharged. The solution was stirred for 10 min and the volatiles were removed under vacuum. 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, Cp), 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, Cp), −5.58 (t, J_{CH} = 162.4 Hz, Re−*C*H_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.

[Cp$_2$Re(CH$_2$I)I]B(Ar′)$_4$ (8). A small glass vessel with an 8 mm Kontes valve was charged with **1** (60 mg, 0.0503 mmol). CH_2Cl_2 (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 under vacuum, and the solid was recrystallized from CH_2Cl_2/pentane. The product was isolated as a light green solid (63 mg, 86%). ^{1}H NMR (CD_2Cl_2): 6.06 (s, 10 H, Cp), 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, Cp), −44.0 (t, J_{CH} = 158.8 Hz, Re−*C*H_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.

[Cp$_2$Re(H$_2$C=O)]B(Ar′)$_4$ (9). A 20 mL round-bottom flask was charged with **1** (105 mg, 0.088 mmol) and 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 under vacuum 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 rinsed 5 times by condensation of the filtrate solvent. The pale orange solid was collected in 93% yield (99 mg). ^{1}H NMR (CD_2Cl_2): 5.49 (s, 10 H, Cp), 3.69 (s, 2 H, Re-(*H*$_2$C=O)). ^{13}C NMR (CD_2Cl_2): 88.4 (d of quint, $^1J_{CH}$ = 189 Hz, J_{CH} = 6.7 Hz, Cp), 46.2 (t, J_{CH} = 178.7 Hz, H_2*C*O). 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 [Cp$_2$Re(H$_2$C=O)]B(Ar′)$_4$ with PPh$_3$. A sealable NMR tube was charged with $[Cp_2Re(H_2C{=}O)]B(Ar')_4$ (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 1 week at room temperature, the starting material had been completely consumed. ^{1}H NMR (CD_2Cl_2): 9.65 (s, free CH_2O), 7.7−7.3 (m, Re−PPh_3), 4.53 (d, J_{HP} = 3.83 Hz, Cp). ^{31}P{^{1}H} NMR (CD_2Cl_2): 23.1 (s, Re−PPh_3).

[Cp$_2$Re(H$_2$C=S)]B(Ar′)$_4$ (10). A 20 mL round-bottom flask was charged with **1** (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 again exposed to ethylene sulfide. Pentane (10 mL) was vacuum transferred to the solution to give a bright yellow/orange precipitate. The solid was collected on the frit and rinsed by condensation of the filtrate solvent which was repeated 5 times. The solid was collected in 89% yield (82 mg). ^{1}H NMR (CD_2Cl_2): 5.47 (s, 10 H, Cp), 3.41 (s, 2 H, Re(*H*$_2$C=S)). ^{13}C NMR (CD_2Cl_2): 88.2 (d of quint, $^1J_{CH}$ = 189 Hz, J_{CH} = 6.4 Hz, Cp), 13.7 (t, J_{CH} = 168.4 Hz, H_2*C*S). Anal. Calcd for $C_{43}H_{24}BF_{24}ReS$: C, 42.14; H, 1.97. Found: C, 42.19; H, 1.97.

Reaction of [Cp$_2$Re(CH$_2$)]B(Ar′)$_4$ with Sulfur. A sealable NMR tube was charged with $[Cp_2ReCH_2]B(Ar')_4$ (5 mg, 0.004 mmol) and excess sulfur. Methylene chloride-d_2 (0.5 mL) was vacuum transferred to the tube, which was sealed. An initial ^{1}H NMR spectrum showed no reaction. After the mixture was heated at 50 °C for 3 h, the color changed from pink to orange. ^{1}H NMR (CD_2Cl_2): 5.47 (s, 10 H, Cp), 3.41 (s, 2 H, (*H*$_2$C=S)).

[Cp$_2$Re(CH$_2$CH(SiMe$_3$))]B(Ar′)$_4$. A small glass vessel with an 8 mm Kontes valve was charged with **1** (100 mg, 0.0838 mmol). CH_2Cl_2(10 mL) was vacuum transferred to the vessel. Under an argon flow, $N_2CHSiMe_3$ (45 μL, 2 M, 0.0838 mmol) was added via a gas-tight syringe. The solution was stirred for 10 min, and the solvent volume 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. Yield: 74 mg, 69%. ^{1}H NMR (CD_2Cl_2): 5.13 (s, Cp), 5.10 (s, Cp), 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$_Z$*H*$_E$), 1.73 (d of d, J_{HH} = 15.1, 12.1 Hz, C*H*SiMe$_3$), 0.18 (s, $SiMe_3$).

Acknowledgment. This research was supported by the Department of Energy, Office of Basic Energy Science. C.E.R. is grateful to the University of Washington for a Ritter Fellowship. We thank Professor George L. Gould for helpful discussions.

OM970706A