Inorg. Chem. **2006**, *45*, 4712–4720

Inorganic Chemistry

Article

Synthesis and Structure of CpMo(CO)(dppe)H and Its Oxidation by Ph_3C^+

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Received January 19, 2006

The reaction of CpMo(CO)(dppe)Cl (dppe $= Ph_2PCH_2CH_2PPh_2$) with $Na^+[AlH_2(OCH_2CH_2OCH_3)_2]^-$ gives the molybdenum hydride complex CpMo(CO)(dppe)H, the structure of which was determined by X-ray crystallography. Electrochemical oxidation of CpMo(CO)(dppe)H in CH_3CN is quasi-reversible, with the peak potential at –0.15 V (vs Fc/Fc^+). The reaction of CpMo(CO)(dppe)H with 1 equiv of $Ph_3C^+BF_4^-$ in CD_3CN gives $[CpMo(CO)(dppe)(NCCD_3)]^+$ as the organometallic product, along with dihydrogen and Gomberg's dimer (which is formed by dimerization of $Ph_3C^\bullet$). The proposed mechanism involves one-electron oxidation of CpMo(CO)(dppe)H by Ph_3C^+ to give the radical-cation complex $[CpMo(CO)(dppe)H]^{\bullet+}$. Proton transfer from $[CpMo(CO)(dppe)H]^{\bullet+}$ to CpMo(CO)(dppe)H, loss of dihydrogen from $[CpMo(CO)(dppe)(H)_2]^+$, and oxidation of $Cp(CO)(dppe)Mo^\bullet$ by Ph_3C^+ lead to the observed products. In the presence of an amine base, the stoichiometry changes, with 2 equiv of Ph_3C^+ being required for each 1 equiv of CpMo(CO)(dppe)H because of deprotonation of $[CpMo(CO)(dppe)H]^{\bullet+}$ by the amine. Protonation of CpMo(CO)(dppe)H by HOTf provides the dihydride complex $[CpMo(CO)(dppe)(H)_2]^+OTf^-$, which loses dihydrogen to generate CpMo(CO)(dppe)(OTf).

Introduction

Transition-metal hydrides are involved in numerous homogeneously catalyzed reactions, performing the critical role of delivering hydrogen to organic substrates from a metal complex. Metal hydrides exhibit versatile reactivity patterns, undergoing cleavage of the M−H bond in the form of a proton (H^+),[1] a hydrogen atom ($H^\bullet$),[2,3] or a hydride (H^-).[4] Hydride transfers from metal hydrides to cationic organic compounds constitute a key step in stoichiometric ionic hydrogenations[5] of alkenes,[6] alkynes,[7] ketones,[8] acetals,[9] and acyl chlorides,[10] as well as the analogous steps in the catalytic ionic hydrogenation of ketones.[11] Knowledge of the factors that influence the hydride transfer ability of metal hydrides is useful in the design of such reactions in stoichiometric or catalytic cycles. DuBois and co-workers have reported extensive studies on the thermodynamics of hydride transfer from a series of metal hydrides.[12] We studied the kinetics of hydride transfer for a series of metal carbonyl hydrides in their reaction with $Ph_3C^+BF_4^-$ (eq 1).[13,14]

$$\mathrm{M{-}H} + \mathrm{Ph_3C^+BF_4^-} \xrightarrow{k_{\mathrm{H}^-}} \mathrm{M{-}F{-}BF_3} + \mathrm{Ph_3C{-}H} \qquad (1)$$

The rate constants for kinetic hydricity in CH_2Cl_2 at 25 °C

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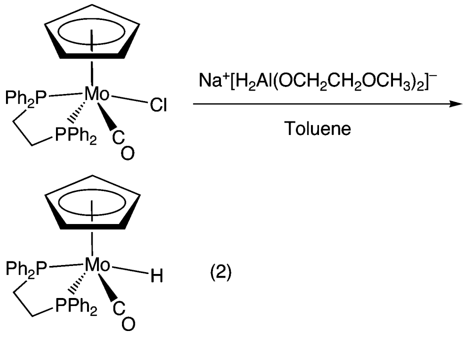
10.1021/ic060111k CCC: $33.50

spanned a range of over 10^6. Replacement of one CO with a phosphine results in a substantially increased kinetic hydricity because of the strong electronic effect of the phosphine. The rate constant k_{H^-} for hydride transfer from $Cp(CO)_3MoH$ was $k_{H^-} = 3.8 \times 10^2$ M^{-1} s^{-1}, while the rate constant for hydride transfer from *trans*-$Cp(CO)_2(PPh_3)MoH$ was about 1000 times higher, $k_{H^-} = 5.7 \times 10^5$ M^{-1} s^{-1}. These phosphine-substituted hydrides $Cp(CO)_2(PR_3)MoH$ exist as interconverting mixtures of cis/trans isomers, and the trans isomers were much more reactive than the cis isomers, which have the hydride cis to the phosphine. The rate constant for hydride transfer from *trans*-$Cp(CO)_2(PCy_3)MoH$ is about 3 orders of magnitude higher than that of *cis*-$Cp(CO)_2(PCy_3)MoH$. This indicates that a phosphine cis to a hydride exerts a substantial steric effect that decreases the rate of hydride transfer, compared to the electronic effect of phosphines, which greatly enhances the rate of hydride transfer. Evaluation of our data suggests[13] that hydride transfer from metal hydrides to $Ph_3C^+BF_4^-$ proceeds by a single-step hydride transfer rather than an initial electron transfer followed by hydrogen-atom transfer. Smith et al. also found single-step hydride transfer from $Cp(CO)_2(PPh_3)MoH$ to protonated acetone.[15]

These studies have shown that a phosphine can have a dramatic effect on the reactivity of metal hydrides and that both steric and electronic factors influence the reactivity. In this paper, we report the synthesis and structure of CpMo(CO)(dppe)H (dppe = $Ph_2PCH_2CH_2PPh_2$), its electrochemical oxidation, its reaction with Ph_3C^+, and its protonation by acid to give a dihydride complex. The chelating diphosphine in this complex places the hydride cis to one phosphine and trans to the other. We report evidence that the reaction of this metal hydride complex with $Ph_3C^+BF_4^-$ proceeds by an initial electron-transfer reaction rather than single-step hydride transfer.

Results and Discussion

Synthesis and Characterization of CpMo(CO)(dppe)H. The reaction of CpMo(CO)(dppe)Cl[16] with $Na^+[AlH_2(OCH_2CH_2OCH_3)_2]^-$ led to replacement of the chloride with hydride (eq 2), and CpMo(CO)(dppe)H was isolated in 64% yield. Other potential routes to CpMo(CO)(dppe)H that were tried proved less satisfactory. Substitution of one CO of $CpMo(CO)_3H$ by PR_3 has long been known to provide a good synthetic route to $Cp(CO)_2(PR_3)MoH$ for PPh_3,[17] PMe_3,[18] and PCy_3.[13] These ligand substitution reactions were shown by Brown and co-workers to proceed by radical chain mechanisms.[19] Our attempts to use this type of reaction to synthesize CpMo(CO)(dppe)H were unsuccessful. The predominant product appears to be $CpMo(CO)_2(\eta^1\text{-dppe})H$ in which only one "arm" of the diphosphine is coordinated, but other products were also observed, and it became clear that this route was not attractive for the synthesis of CpMo(CO)(dppe)H. CpMo(CO)(dppe)Cl did not appear to react at all with $LiBH_4$ (60 °C, 1 h). The stronger hydride donor $LiBHEt_3$ did convert CpMo(CO)(dppe)Cl to CpMo(CO)(dppe)H, but other products were formed, including free dppe. Reduction of CpMo(CO)(dppe)Cl with NaK in THF gave evidence for the molybdenum anion $K^+[CpMo(CO)(dppe)]^-$ [ν(CO) 1793 (s) cm^{-1}] and protonation with EtOH generated CpMo(CO)(dppe)H, but neither the yield nor the purity was as high as that obtained using $Na^+[AlH_2(OCH_2CH_2OCH_3)_2]^-$.



(2)

Although there is evidence for protonation of the anion $[CpMo(CO)(dppe)]^-$ to give the metal hydride, we have not attempted to determine the pK_a of CpMo(CO)(dppe)H. This hydride would likely have a very low acidity, considering the presence of a diphosphine ligand as an electron donor that would lower the stability of the metal anion. A rough estimate of the acidity of CpMo(CO)(dppe)H is p$K_a > 25$ in CH_3CN, based on the pK_a of $CpMo(CO)_3H$ (13.9 in CH_3CN)[1,20] and the substantially lower acidity of $Cp(CO)_2(PMe_3)WH$ (pK_a = 26.6 in CH_3CN) compared to that of $CpW(CO)_3H$ (pK_a = 16.1 in CH_3CN).[20]

The $^{31}P\{^1H\}$ NMR spectrum of CpMo(CO)(dppe)H at −87 °C appears as a quartet due to the two phosphorus atoms being nonequivalent. This pattern, which was verified by computer simulation, indicates that the two phosphorus atoms of the diphosphine are at slightly different chemical shifts (δ 95.0 and 95.6) with $^2J_{PP} = 38$ Hz. The hydride resonance

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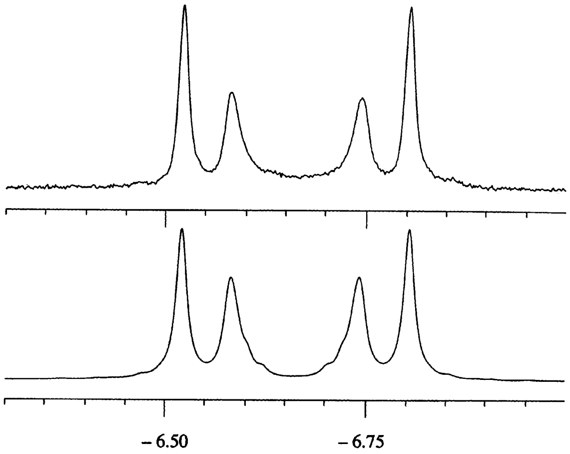

Figure 1. ^1H NMR spectrum of the Mo−H resonance of CpMo(CO)(dppe)H at −87 °C. The upper spectrum is the experimental spectrum, and the lower trace is the simulated spectrum.

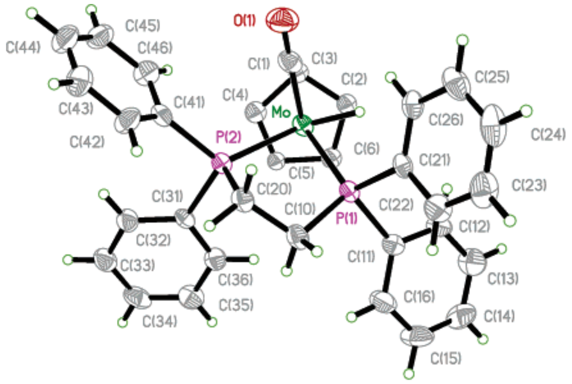

Figure 2. Molecular structure of CpMo(CO)(dppe)H showing 30% probability ellipsoids.

in the ^1H NMR spectrum at −87 °C exhibits the pattern shown in the upper part of Figure 1. This spectrum was also simulated (lower part of Figure 1), providing values of $^2J_{PH}$ = 16 Hz for the coupling of the hydride to the trans phosphine and $^2J_{PH}$ = 69 Hz for the coupling of the hydride to the cis phosphine. The magnitude of these coupling constants is comparable to those directly observed in interconverting cis/trans isomer mixtures of related phosphine hydride complexes $CpMo(CO)_2(PPh_3)H$ ($^2J_{PH}$ = 21 Hz for trans; $^2J_{PH}$ = 64 Hz for cis)[21] and $CpMo(CO)_2(PCy_3)H$ ($^2J_{PH}$ = 20 Hz for trans; $^2J_{PH}$ = 60 Hz for cis).[13]

The IR spectrum of CpMo(CO)(dppe)H exhibits one ν(CO) band. The location of ν(CO) often varies somewhat with different solvents, but we found an unusually large solvent dependence on the energy of the ν(CO) band of CpMo(CO)(dppe)H, ranging from 1859 cm^{-1} in hexane, to 1840 cm^{-1} in toluene, to 1821 cm^{-1} in CH_2Cl_2. We were unable to find a band that could be confidently assigned to the ν(M−H) stretching vibration, even in concentrated solutions.

Structural Determination of CpMo(CO)(dppe)H. The structure of CpMo(CO)(dppe)H was determined by single-crystal X-ray diffraction. An ORTEP diagram is shown in Figure 2, and Table 1 gives details of the data collection and refinement. The crystal has one molecule of toluene (not shown in Figure 2). Selected bond distances and angles are provided in Table 2.

Table 1. Crystallographic Data and Refinement Information

formula	$C_{39}H_{38}MoOP_2$
fw	680.57
temp (K)	293(2)
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	10.830(3)
b (Å)	11.307(3)
c (Å)	14.309(4)
α (deg)	96.65(2)
β (deg)	105.50(2)
γ (deg)	96.43(2)
V (Å^3)	1658.3(8)
Z	2
m (mm^{-1})	0.522
λ (Å)	0.710 73
ρ_{calc} (g cm^{-3})	1.363
total no. of reflns	7590
no. of param	397
final R indices [$I > 2\sigma(I)$]^a	R1 = 0.0579, wR2 = 0.1196
R indices (all data)^a	R1 = 0.2393, wR2 = 0.1578

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(|F_o^2| - |F_c^2|)^2]/\Sigma[w|F_o^2|^2]\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for CpMo(CO)(dppe)H

Mo−C(1)	1.916(8)	P(1)−Mo−P(2)	78.4(1)
Mo−P(1)	2.3923(18)	P(2)−Mo−C(1)	81.3(2)
Mo−P(2)	2.4161(17)	P(1)−Mo−C(1)	100.23(19)

The P(1)−Mo−P(2) angle of 78.4(1)° in CpMo(CO)(dppe)H is slightly larger than the P−Mo−P angle of 75.3(1)° found in the chloride complex CpMo(CO)(dppe)Cl.[22] Poli and co-workers found[23] a larger P−Mo−P angle of 80.60(3)° in $Cp^*Mo(dppe)Cl_2$, a 17-electron Mo complex that has an unusual trans geometry of the two phosphine ligands. The molybdenum trihydride complex $Cp^*Mo(dppe)H_3$ was found[24] to have a P−Mo−P angle of 81.21(4)°.

Electrochemical Oxidation of CpMo(CO)(dppe)H. Electrochemical oxidation of CpMo(CO)(dppe)H was studied by cyclic voltammetry in CH_3CN with a 0.1 M $Bu_4N^+PF_6^-$ electrolyte. The peak potential for the oxidation wave was found at −0.15 V (vs the Fc/Fc^+ couple); the cyclic voltammetry trace is shown in the Supporting Information. The oxidation is only quasi-reversible and does not provide a reliable value for $E_{1/2}$. For comparison, Tilset and co-workers reported that the peak potential for oxidation of $CpMo(CO)_3H$ was found at E_{ox} = +0.800 V (vs Fc/Fc^+).[25] As expected, substitution of one CO by a phosphine makes the metal hydride much more readily oxidized; electrochemical oxidation of $CpMo(CO)_2(PPh_3)H$ was reported at +0.26 V (vs Fc/Fc^+) by Smith and Tilset.[26] Poli and co-workers reported[27] +0.23 V (vs Fc/Fc^+) for the anodic peak potential of $CpMo(CO)_2(PPh_3)H$, in good agreement with Tilset's

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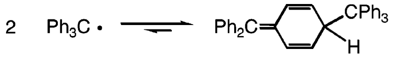
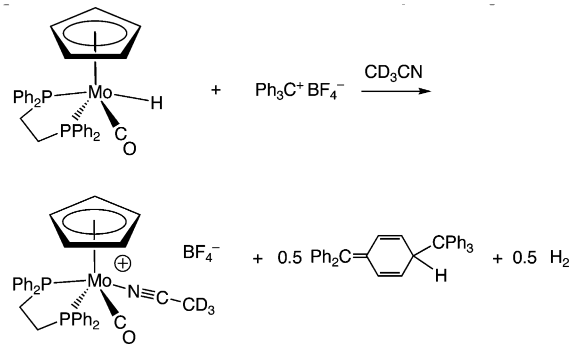
value. Substitution of another CO by a phosphine also has a large effect: our value for the oxidation potential of CpMo(CO)(dppe)H shows that it is easier to oxidize (by roughly 0.4 V) than CpMo$(CO)_2(PPh_3)$H. As expected, substitution of the last CO for a phosphine produces a metal hydride that is very readily oxidized: Poli and co-workers found that electrochemical oxidation of CpMo$(PMe_3)_3$H was reversible, with $E_{1/2} = -1.46$ V (vs Fc/Fc$^+$).[28]

Reaction of CpMo(CO)(dppe)H with Ph_3C^+. We previously found that a variety of metal carbonyl hydrides cleanly transfer hydride to $Ph_3C^+BF_4^-$ in CH_2Cl_2, producing Ph_3CH and metal complexes with weakly bound FBF_3^- ligands (eq 1).[13,14] Reaction of CpMo(CO)(dppe)H with $Ph_3C^+BF_4^-$ in CD_2Cl_2 gave several organometallic products, as indicated by ^{1}H and ^{31}P NMR. The organic products of this reaction were Ph_3CH (49%, based on NMR integration versus an internal standard) and Gomberg's dimer (0.20 equiv; 40% yield of $Ph_3C^•$). The formation of Ph_3CH indicates that hydride is transferred from the metal to Ph_3C^+, and this product was expected because many metal hydrides react cleanly according to eq 1. Gomberg's dimer,[29] shown in eq 3, is formed through dimerization of two $Ph_3C^•$ radicals. Formation of Gomberg's dimer implies that $Ph_3C^•$ was formed by one-electron oxidation of CpMo(CO)(dppe)H by Ph_3C^+.



(3)

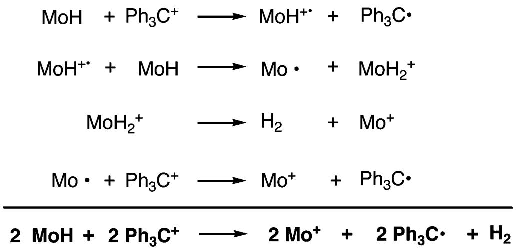
Because a mixture of products were formed from reactions of CpMo(CO)(dppe)H with $Ph_3C^+BF_4^-$ in CD_2Cl_2, experiments were conducted in CD_3CN because in that case the solvent could bind to unsaturated molybdenum intermediates. The reaction of CpMo(CO)(dppe)H with $Ph_3C^+BF_4^-$ in CD_3CN (eq 4) led to the formation of [CpMo(CO)(dppe)$(NCCD_3)]^+[BF_4]^-$ (88%) along with dihydrogen. Gomberg's dimer was formed in 86% yield [calculated with the stoichiometry shown in eq 4; i.e., 0.86 equiv of "$Ph_3C^•$" produced for each 1 equiv of CpMo(CO)(dppe)H], with a smaller amount (13%) of Ph_3CH being detected.



(4)

The reaction was also carried out in CD_2Cl_2 solvent with ~6 equiv of CH_3CN present. Using those conditions, $[CpMo(CO)(dppe)(NCCH_3)]^+[BF_4]^-$ (79%) was formed, along with Gomberg's dimer (66%), Ph_3CH (34%), and dihydrogen.

Scheme 1



We propose the mechanism shown in Scheme 1, which begins with oxidation of CpMo(CO)(dppe)H by $Ph_3C^+BF_4^-$. Although $Cp(CO)_2(PPh_3)$MoH and other metal hydrides have been shown[13] to transfer hydride to Ph_3C^+ or to protonated acetone[15] in a single step, the second phosphine ligand in dppe makes CpMo(CO)(dppe)H much easier to oxidize, so one-electron oxidation of the metal hydride by Ph_3C^+ occurs rather than direct hydride transfer. The electrochemical reduction of $Ph_3C^+PF_6^-$ by cyclic voltammetry in CH_3CN studied was reported to be partially reversible with $E_{1/2} \approx +0.26$ V (vs SCE),[30] in agreement with an earlier report of $E_{1/2} = +0.27$ V (vs SCE) determined by polarography.[31] Conversion to a Fc/Fc$^+$ reference (by subtraction of 380 mV)[32] gives an estimate of $E_{1/2} \approx -0.12$ V (vs Fc/Fc$^+$) for the reduction potential of Ph_3C^+. A comparison of this value to the electrochemical oxidation potentials for molybdenum hydrides discussed above reveals that while oxidation of Cp$(CO)_2(PPh_3)$MoH by Ph_3C^+ is thermodynamically unfavorable by about 0.37 V, one-electron transfer to Ph_3C^+ from CpMo(CO)(dppe)H is roughly thermoneutral.

Oxidation of metal hydrides is well-known to produce transient radical cations ($MH^{•+}$),[25,26,33−37] which are generally very reactive. Studies by Tilset and co-workers have shown that $MH^{•+}$ complexes are about 19−22 pK_a units more acidic than the corresponding MH.[25,34,35] We suggest that the second step of the mechanism (Scheme 1) is proton transfer from

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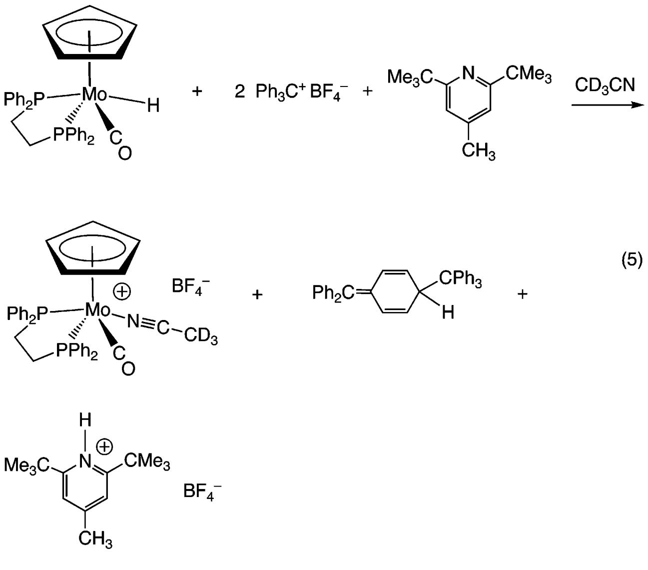
the radical cation $[\mathrm{CpMo(CO)(dppe)H}]^{\bullet+}$ to the neutral hydride CpMo(CO)(dppe)H, producing the 17-electron molybdenum radical $\mathrm{Cp(CO)(dppe)Mo^{\bullet}}$ and the cationic dihydride $[\mathrm{CpMo(CO)(dppe)(H)_2}]^+$ (vide infra). Dihydrogen is observed as a product of decomposition of the dihydride complex. Oxidation of molybdenum radical $\mathrm{Cp(CO)(dppe)Mo^{\bullet}}$ by $\mathrm{Ph_3C^+}$ produces the metal cation, which is trapped by MeCN to give the observed product, $[\mathrm{CpMo(CO)(dppe)(NCCH_3)}]^+$. Proton transfer from $[\mathrm{CpMo(CO)(dppe)H}]^{\bullet+}$ to CpMo(CO)(dppe)H may occur by direct metal-to-metal proton transfer, but it is possible that this reaction could occur by a more complicated pathway. Tilset and co-workers carried out detailed electrochemical studies of $\mathrm{Cp(PPh_3)_2RuH}$[36] and found that its radical cation $[\mathrm{MH}]^{\bullet+}$ disproportionates to give the dicationic hydride $[\mathrm{MH}]^{2+}$ and the neutral hydride MH, with subsequent proton transfer from the highly acidic $[\mathrm{MH}]^{2+}$ to MH leading to $[\mathrm{M}]^+$ and the dihydride $[\mathrm{MH_2}]^+$. Further experiments would be required to determine whether a complex mechanism of this type could be operative in our Mo example studied here.

In contrast to the high reactivity of radical cations formed through one-electron oxidation of metal carbonyl hydrides, Poli and co-workers have found that some 17-electron molybdenum(III) complexes of metal halides are sufficiently stable for isolation and complete characterization.[38] For example, CpMo(CO)(dppe)Cl and Cp*Mo(CO)(dppe)Cl are reversibly oxidized in electrochemical experiments, and a crystal structure was reported for $[\mathrm{Cp^*Mo(CO)(dppe)Cl}]^{\bullet+}$.

Reaction of CpMo(CO)(dppe)H with $\mathrm{Ph_3C^+}$ with a Base Present. When the oxidation of CpMo(CO)(dppe)H by $\mathrm{Ph_3C^+}$ is carried out in the presence of an amine base, 2 equiv of $\mathrm{Ph_3C^+}$ are consumed for each 1 equiv of metal hydride (eq 5). The proposed mechanism is shown in Scheme 2. In contrast to Scheme 1, where intermolecular proton transfer from the radical cation $[\mathrm{CpMo(CO)(dppe)H}]^{\bullet+}$ occurs to the metal hydride as a base, the proton transfer in Scheme 2 occurs to the nitrogen of the amine base, producing a metal radical $\mathrm{Cp(CO)(dppe)Mo^{\bullet}}$ that is subsequently oxidized by $\mathrm{Ph_3C^+}$ to give the metal cation.



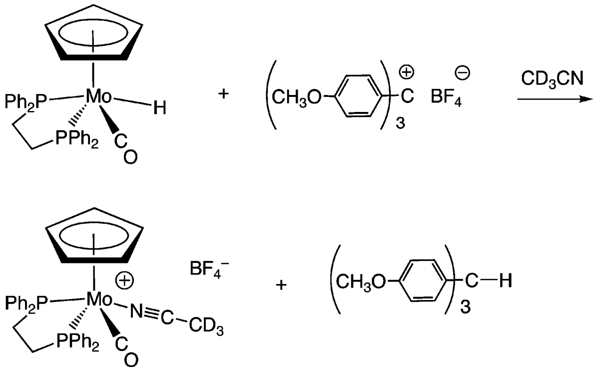
(5)

Scheme 2

$$\begin{array}{lllll}
\mathrm{MoH} + \mathrm{Ph_3C^+} & \longrightarrow & \mathrm{MoH^{+\bullet}} & + & \mathrm{Ph_3C\bullet} \\
\mathrm{MoH^{+\bullet}} + \mathrm{B} & \longrightarrow & \mathrm{Mo\bullet} & + & \mathrm{BH^+} \\
\mathrm{Mo\bullet} + \mathrm{Ph_3C^+} & \longrightarrow & \mathrm{Mo^+} & + & \mathrm{Ph_3C\bullet} \\
\hline
\mathbf{MoH + 2\,Ph_3C^+} & \longrightarrow & \mathbf{Mo^+} & + & \mathbf{2\,Ph_3C\bullet + BH^+}
\end{array}$$

Tilset and co-workers reported several examples in which oxidation of metal hydrides in the presence of an amine base required 2 equiv of the oxidizing agent.[25,26,34,37] One complex exhibiting this behavior is the molybdenum complex $\mathrm{Cp(CO)_2(PPh_3)MoH}$, which was shown[26] to react with $(p\text{-}\mathrm{MeOC_6H_4})\mathrm{Ph_2C^+}$ in $\mathrm{CH_3CN}$ to give $[trans\text{-}\mathrm{Cp(CO)_2(PPh_3)Mo(NCCH_3)}]^+$ by a single-step hydride transfer. In contrast, oxidation of $\mathrm{Cp(CO)_2(PPh_3)MoH}$ by $\mathrm{Cp_2Fe^+}$ in $\mathrm{CH_3CN}$ in the presence of an amine base required 2 equiv of $\mathrm{Cp_2Fe^+}$ and produced $[cis\text{-}\mathrm{Cp(CO)_2(PPh_3)Mo(NCCH_3)}]^+$. Poli and co-workers reported similar observations when $\mathrm{Cp(CO)_2(PPh_3)MoH}$ was oxidized in the presence of water as a base.[27]

Reaction of CpMo(CO)(dppe)H with $(p\text{-}\mathrm{MeOC_6H_4})_3\mathrm{C^+}$. Substitution of one or more Ph groups on $\mathrm{Ph_3C^+}$ with an electron-donating MeO group provides substituted trityl cations that are far less reactive.[39] The rate constant for hydride transfer (eq 1) from $\mathrm{Cp^*Mo(CO)_3H}$ to $\mathrm{Ph_3C^+}$ is $k = 6.5 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$ ($\mathrm{CH_2Cl_2}$ solvent at 25 °C), while the hydride transfer of the same hydride to $(p\text{-}\mathrm{MeOC_6H_4})_3\mathrm{C^+}$ is 3 orders of magnitude lower ($k = 1.4\ \mathrm{M^{-1}\ s^{-1}}$).[13] The reaction of CpMo(CO)(dppe)H with $\mathrm{Ph_3C^+BF_4^-}$ in $\mathrm{CH_3CN}$ discussed above is complete within minutes, but the reaction of $(p\text{-}\mathrm{MeOC_6H_4})_3\mathrm{C^+}$ with CpMo(CO)(dppe)H (eq 6) occurs much more slowly. The reaction was about 74% complete after 4 h and over 90% complete after 24 h. In contrast to the reaction with $\mathrm{Ph_3C^+}$, which gives Gomberg's dimer, the reaction with $(p\text{-}\mathrm{MeOC_6H_4})_3\mathrm{C^+}$ leads to C−H bond formation, giving $(p\text{-}\mathrm{MeOC_6H_4})_3\mathrm{CH}$. This reaction proceeds by hydride transfer, as found for other hydrides (eq 1). Electrochemical studies[31,40] show that $\mathrm{Ph_3C^+}$ is easier to reduce than $(p\text{-}\mathrm{MeOC_6H_4})_3\mathrm{C^+}$, by about 0.5 V. We interpret these results to indicate that the increased barrier for one-



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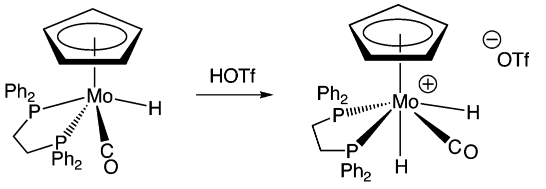
electron oxidation of CpMo(CO)(dppe)H by (p-$MeOC_6H_4)_3C^+$ (compared to oxidation by Ph_3C^+) changes the mechanism to hydride transfer. This hydride transfer could occur in a single step or by oxidation of the metal hydride to give $[CpMo(CO)(dppe)H]^{\bullet +}$, which then transfers a hydrogen atom to (p-$MeOC_6H_4)_3C^{\bullet}$. Because the para position of (p-$MeOC_6H_4)_3C^+$ is substituted by a MeO group, it would not be possible to form an analogue of Gomberg's dimer in this reaction.

Attempted Hydrogen-Atom Abstraction from CpMo(CO)(dppe)H. Hydrogen-atom transfers from metal hydrides to organic substrates are involved in certain types of hydrogenations,[41] hydroformylations,[42] and polymerizations.[43] The kinetics of hydrogen-atom transfer from a series of metal hydrides to a substituted trityl radical were reported by Norton and co-workers.[3] A metal−metal-bonded complex forms through dimerization of the metal radical that results from hydrogen-atom transfer from the metal hydride. Reaction of the molybdenum hydride $Cp(CO)_2(PPh_3)MoH$ with Gomberg's dimer was reported to be complete within 5 min, providing the Mo−Mo-bonded dimer $[Cp(CO)_2(PPh_3)Mo]_2$.[44] We repeated this reaction and found it to proceed as reported. In contrast, attempted reaction of Gomberg's dimer with CpMo(CO)(dppe)H in CD_2Cl_2 for 7 days at room temperature gave no evidence for hydrogen-atom transfer; a small amount of free dppe was observed as a decomposition product. Similar observations were made when a solution of CpMo(CO)(dppe)H and Gomberg's dimer were heated in C_6D_6 for 7 days at 80 °C. Thus, we find no evidence for hydrogen-atom transfer from CpMo(CO)(dppe)H to trityl radical, even with prolonged heating.

Protonation of CpMo(CO)(dppe)H. No reaction was observed by NMR upon the addition of HOAc to CpMo(CO)(dppe)H. Addition of the stronger acid HOTf (OTf = OSO_2CF_3) to a CD_2Cl_2 solution of CpMo(CO)(dppe)H at −87 °C leads to protonation of the metal hydride complex to give a cationic dihydride complex, $[CpMo(CO)(dppe)(H)_2]^+[OTf]^-$, which is formed in 99% yield (eq 7). It is possible that the initial site of protonation is at the metal hydride bond, initially producing a cationic dihydrogen complex,[45] $[CpMo(CO)(dppe)(\eta^2\text{-}H_2)]^+$, though no evidence for a dihydrogen complex was obtained. A doublet of doublets at δ −4.26 (J_{PH} = 43.0 Hz; $J_{P'H}$ = 23.0 Hz) is observed for the dihydride hydrogens at −87 °C. The T_1 for the dihydride resonance at −87 °C was 244 ms, indicating a dihydride rather than a dihydrogen complex. The dihydride resonance becomes a triplet (J_{PH} = 32.7 Hz) at −58 °C. In the $^{31}P\{^1H\}$ NMR at −87 °C, two resonances are observed at δ 69.6 and 68.2 (J_{PP} = 10.7 Hz) for the inequivalent phosphines. These resonances broaden with the loss of observable coupling at −58 °C, and a $^{31}P\{^1H\}$ NMR spectrum at −35 °C showed coalescence to a broad singlet. These data do not definitively indicate the geometry of $[CpMo(CO)(dppe)(H)_2]^+[OTf]^-$; the geometry shown in eq 7 is based on the crystal structure of the related dihydride complex $[CpW(CO)_2(PMe_3)(H)_2]^+[OTf]^-$, which has one of the hydrides trans to the Cp ligand.[46] The NMR data indicate that a fluxional process makes the two phosphorus atoms equivalent; at all temperatures studied, the two hydrides remained equivalent.



(7)

Protonation of CpMo(CO)(dppe)H with DOTf gives a doublet of doublets (J_{PH} = 43.0 Hz; $J_{P'H}$ = 23.0 Hz) for $[CpMo(CO)(dppe)(H)(D)]^+[OTf]^-$ at δ −4.285 at −87 °C, which differs by −0.030 ppm from the resonance for $[CpMo(CO)(dppe)(H)_2]^+[OTf]^-$ at δ −4.255. Precedent for an upfield ^1H NMR chemical shift upon partial deuteration of a dihydride or polyhydride complex comes from several studies. Crabtree and co-workers found upfield chemical shifts upon successive replacement of hydrogen by deuterium in polyhydride complexes.[47] For example, ^1H NMR spectra of a series of rhenium heptahydride complexes ReH_7L_2 (L_2 = bidentate phosphine) were compared with those of the partially labeled complexes $ReH_{7-x}D_xL_2$ (x = 0−6), and they found that replacing hydrogen by deuterium led to an upfield shift of −0.002 to −0.009 ppm for each deuterium substituted. Heinekey and co-workers found larger upfield isotope effects on chemical shifts (up to −0.075 ppm) when one hydrogen in the trihydride complex $[Cp(PPh_3)Ir(H)_3]^+$ was substituted by deuterium.[48] The change in chemical shift upon deuteration that we observed for $[CpMo(CO)(dppe)(H)(D)]^+[OTf]^-$ is further evidence that the protonated complex is a dihydride rather than a dihydrogen complex because $M(\eta^2\text{-}HD)$ complexes exhibit a 1:1:1 triplet, which is often used in the characterization of dihydrogen com-

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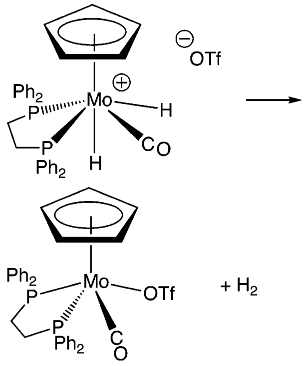
plexes.[45] No J_{HD} was detected in our experiments on $[CpMo(CO)(dppe)(H)(D)]^+[OTf]^-$. In cases where they can be measured,[49] J_{HH} values are small, usually 5 Hz or less, so the corresponding J_{HD} might not be easily observed.

While the dihydride can be observed at low temperatures by NMR, at higher temperatures it decomposes, releasing dihydrogen and forming the metal triflate complex CpMo(CO)(dppe)(OTf) (eq 8). This triflate complex was isolated as a red solid in 80% yield.



(8)

Conclusions

Oxidation of CpMo(CO)(dppe)H by 1 equiv of $Ph_3C^+BF_4^-$ in CD_3CN gives $[CpMo(CO)(dppe)(NCCD_3)]^+$, along with dihydrogen and Gomberg's dimer. The proposed mechanism involves an initial one-electron oxidation of CpMo(CO)(dppe)H by Ph_3C^+. This initial step of electron transfer from CpMo(CO)(dppe)H contrasts with the reactivity of related complexes such as $Cp(CO)_2(PPh_3)MoH$, which were previously shown to react with Ph_3C^+ by single-step hydride transfer, forming Ph_3CH. When the oxidation of CpMo(CO)(dppe)H by Ph_3C^+ is carried out in the presence of an amine base, 2 equiv of Ph_3C^+ are consumed for each metal hydride. The proposed mechanism for this reaction involves proton transfer from the initially generated radical cation $[CpMo(CO)(dppe)H]^{\bullet+}$ to the amine base. Protonation of CpMo(CO)(dppe)H by HOTf produces the dihydride complex $[CpMo(CO)(dppe)(H)_2]^+OTf^-$, which is characterized in solution but decomposes to release dihydrogen and form the triflate complex CpMo(CO)(dppe)(OTf).

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of argon using Schlenk or vacuum-line techniques or in a Vacuum Atmospheres drybox. ^1H NMR chemical shifts were referenced to the residual proton peak of CD_2Cl_2 at δ 5.32. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory (Woodside, NY). NMR spectra were recorded on a Bruker AM-300 spectrometer (300 MHz for ^1H NMR). $Ph_3C^+BF_4^-$ was purchased from Aldrich and purified by recrystallization from CH_2Cl_2/Et_2O. $(p\text{-}MeOC_6H_4)_3C^+BF_4^-$ was prepared as previously reported.[50] Et_2O and hexane were distilled from sodium benzophenone, and CH_2Cl_2 was distilled from P_2O_5. CpMo(CO)(dppe)Cl[16] was synthesized by a previously reported route. HOTf was purified by distillation. Other reagents were obtained from Aldrich and used without further purification.

Preparation of CpMo(CO)(dppe)H. A 50-mL Schlenk flask was charged with CpMo(CO)(dppe)Cl (500 mg, 0.803 mmol), and THF (20 mL) was added. To this red solution was added $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ ("Red-Al" obtained from Aldrich; 1.00 mmol, 0.3 mL, of a 65% solution in toluene, diluted to ~8 mL with toluene). The reaction mixture was stirred at ambient temperature and gradually turned dark red. An IR spectrum showed that the reaction was complete after 2.5 h. Ethanol (0.5 mL) was added with vigorous stirring, and dihydrogen evolution was observed. The solvent was removed under vacuum from the yellowish-brown solution, and the residue was extracted with benzene (15 mL) and filtered through an alumina column (2.5 × 4 cm). The yellow filtrate was concentrated to 5 mL, and hexane (15 mL) was added. The solution mixture was concentrated and triturated to give a yellow solid. The product was isolated by filtration and washed with hexane (300 mg, 64% yield). The product can be recrystallized by slow evaporation from toluene. ^1H NMR (CD_2Cl_2, 25 °C): δ 7.75−7.22 (br m, 20 H, *Ph*), 4.45 (s, 5 H, *Cp*), 2.74−1.81 (br m, 4 H, CH_2), −6.44 (1 H, Mo*H*; see text and Figure 1 for more details; simulations were computed using gNMR). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −87 °C): δ 95.3 (apparent quartet, analyzed and simulated with nonequivalent chemical shifts of δ 95.0 and 95.6; $^2J_{PP} = 38$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −35 °C): δ 243.6 (dd, *C*O, $J_{CP} = 18.1$ Hz, $J_{CP'} = 4.8$ Hz), 132.6 (dd, $J = 10.2$ and 9.6 Hz, *Ph*), 130.8 (d, $J = 9.7$ Hz, *Ph*), 130.2 (d, $J = 9.1$ Hz, *Ph*), 129.4−127.5 (multiple resonances, *Ph*), 86.1 (s, C_5H_5), 30.5 (dd, CH_2, $J_{CP} = 28.1$ Hz, $J_{CP'} = 24.6$ Hz), 28.7 (t, CH_2, $J_{CP} = J_{CP'} = 19.0$ Hz). IR (hexane): ν(CO) 1859 (s) cm^{-1}. IR (toluene): ν(CO) 1841 (s) cm^{-1}. IR (THF): ν(CO) 1840 (s) cm^{-1}. IR (CH_2Cl_2): ν(CO) 1821 (s) cm^{-1}. Anal. Calcd for $C_{32}H_{30}OP_2Mo$: C, 65.31; H, 5.14. Found: C, 65.34; H, 5.49.

Electrochemical Experiments. Cyclic voltammetry was carried out using a BAS 100B electrochemical analyzer using glassy carbon as the working electrode, Pt wire as the counter electrode, and Ag/Ag^+ (0.1 M $AgNO_3$) as the reference electrode in a CH_3CN solution containing 0.1 M $Bu_4N^+PF_6^-$. The concentration of the Mo complex was 0.01 M CpMo(CO)(dppe)H, and sweep rates up to 2 V s^{-1} were used. The peak potential for the quasi-reversible oxidation was found at −0.15 V (vs the Fc/Fc^+ couple). The potential was calibrated using the Cp_2Fe/Cp_2Fe^+ (Fc/Fc^+) couple. A trace from the cyclic voltammetry experiment is shown in the Supporting Information.

Reactions of CpMo(CO)(dppe)H with $Ph_3C^+BF_4^-$. (a) In CD_2Cl_2. A 5-mm NMR tube was loaded with CpMo(CO)(dppe)H (7.4 mg, 0.013 mmol, 1 equiv), CD_2Cl_2 (~0.4 mL), and 1,2-dichloroethane (1.5 μL, internal integration standard). After the initial spectrum was recorded, this solution was added to a solution of $Ph_3C^+BF_4^-$ (4.2 mg, 0.013 mmol, 1 equiv) in CD_2Cl_2 (~0.1 mL), and the reaction mixture turned from yellow to orange. The ^1H NMR spectrum of the resulting solution showed the formation of Gomberg's dimer (40% yield; i.e., 0.40 equiv of "$Ph_3C^\bullet$" based on HMo), Ph_3CH (49%), and several organometallic products (including ~8% $[CpMo(CO)(dppe)(H)_2]^+[BF_4]^-$).

(b) In CD_3CN. The analogous procedure described above was used except CD_3CN was the solvent. The ^1H NMR spectrum of the resulting solution showed the formation of $[CpMo(CO)(dppe)(NCCD_3)]^+[BF_4]^-$ (88%), Gomberg's dimer (0.86 equiv of "$Ph_3C^\bullet$"

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formed per HMo), and Ph_3CH (δ 5.59 for CH resonance, 13%). A resonance for dihydrogen at δ 4.56 was also observed. IR (CD_3CN) for $[CpMo(CO)(dppe)(CD_3CN)]^+[BF_4]^-$: ν(CO) 1871 (s) cm^{-1}.

(c) In CD_2Cl_2 with CH_3CN Added. CpMo(CO)(dppe)H (6.1 mg, 0.010 mmol) was dissolved in CD_2Cl_2 (∼0.4 mL) containing 1,2-dichloroethane (0.5 μL, internal integration standard) and CH_3CN (3 μL, 0.0574 mmol). After measurement of the initial spectrum, this solution was added to a solution of $Ph_3C^+BF_4^-$ (3.5 mg, 0.010 mmol) in CD_2Cl_2 (∼0.2 mL). The ^1H NMR spectrum of the resulting solution showed the formation of Gomberg's dimer (0.66 equiv of "$Ph_3C^\bullet$" formed per HMo), Ph_3CH (34%), and $[CpMo(CO)(dppe)(NCCH_3)]^+[BF_4]^-$ (86%); a signal for dihydrogen was observed at δ 4.62. ^1H NMR (CD_2Cl_2, 25 °C) of $[CpMo(CO)(dppe)(NCCH_3)]^+[BF_4]^-$: δ 4.98 (d, 5 H, *Cp*, $J_{PH} = 2.0$ Hz), 3.01−2.18 (br m, 4 H, CH_2), 1.79 (d, 3 H, CH_3, $J_{PH} = 2.4$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) of $[CpMo(CO)(dppe)(NCCH_3)]^+[BF_4]^-$: δ 85.8 (d, $J_{PP} = 37.7$ Hz), 74.9 (d, $J_{PP} = 37.7$ Hz).

Reaction of CpMo(CO)(dppe)H with 2 equiv of $Ph_3C^+BF_4^-$ in the Presence of 2,6-Di-*tert*-butyl-4-methylpyridine. CpMo(CO)(dppe)H (5.0 mg, 0.0085 mmol, 1 equiv) and 2,6-di-*tert*-butyl-4-methylpyridine (2.0 mg, 0.010 mmol, 1.2 equiv) were placed in an NMR tube, along with CD_3CN (0.4 mL) and 1,2-dichloroethane (1 μL, internal integration standard). The initial ^1H NMR spectrum was recorded. ^1H NMR (CD_3CN, 25 °C) of 2,6-di-*tert*-butyl-4-methylpyridine: δ 7.01 (s, 2 H, C*H*), 2.28 (s, 3 H, CH_3), 1.30 (s, 18 H, CCH_3). This solution was mixed with a solution of $Ph_3C^+BF_4^-$ (5.6 mg, 0.017 mmol, 2 equiv) in CD_3CN (∼0.3 mL). The reaction was complete in less than 10 min. The ^1H NMR spectrum showed the formation of $[CpMo(CO)(dppe)(NCCD_3)]^+[BF_4]^-$ (89%), Gomberg's dimer (1.82 equiv of "$Ph_3C^\bullet$" formed per HMo), Ph_3CH (10%), and protonated 2,6-di-*tert*-butyl-4-methylpyridine (89%). ^1H NMR (CD_3CN, 25 °C) of protonated 2,6-di-*tert*-butyl-4-methylpyridine: 2.59 (s, 3 H, CH_3), 1.49 (s, 18 H, CCH_3), signals for C*H* obscured by the phenyl region.

Reaction of CpMo(CO)(dppe)H with $(p\text{-}MeOC_6H_4)_3C^+BF_4^-$. CpMo(CO)(dppe)H (5.9 mg, 0.010 mmol, 1 equiv) and hexamethylbenzene (0.5 mg, internal integration standard) were weighed in an NMR tube along with CD_3CN (∼0.4 mL). After the initial spectrum was taken, this solution was added to an orange-red solution of $(p\text{-}MeOC_6H_4)_3C^+BF_4^-$ (4.2 mg, 0.010 mmol, 1 equiv) in CD_3CN (∼0.3 mL); the solution turned lighter orange. The reaction was monitored by NMR spectroscopy and showed $[CpMo(CO)(dppe)(CD_3CN)]^+$ (23% after 15 min; 74% after 4 h). After 24 h, a 95% yield of $[CpMo(CO)(dppe)(CD_3CN)]^+$ was observed, with 5% CpMo(CO)(dppe)H remaining. The yield of $(p\text{-}MeOC_6H_4)_3CH$ after 24 h was 85%.

NMR Tube Reaction of CpMo(CO)(dppe)H with HOTf. CpMo(CO)(dppe)H (9.5 mg, 0.016 mmol, 1 equiv) was weighed in an NMR tube along with CD_2Cl_2 (∼0.4 mL) and 1,2-dichloroethane (1 μL, internal integration standard). After the initial spectrum was recorded, HOTf (1.5 μL, 0.017 mmol, 1.1 equiv) was added, and the tube was shaken. The color of the solution turned from yellow to orange, and gas (dihydrogen) bubbling was observed. The NMR spectrum of the resulting solution showed CpMo(CO)(dppe)(OTf) (73%) and $[CpMo(CO)(dppe)(H)_2]^+[OTf]^-$ (27%) as the products. ^1H NMR (CD_2Cl_2, 25 °C) of CpMo(CO)(dppe)(OTf): δ 4.65 (d, 5 H, *Cp*, $J_{PH} = 2.5$ Hz). ^1H NMR (CD_2Cl_2, 25 °C) of $[CpMo(CO)(dppe)(H)_2]^+[OTf]^-$: δ 4.64 (s, 5 H, *Cp*), −4.07 (t, 2 H, Mo*H*, $J_{PH} = 32.8$ Hz) (signal for dihydrogen at δ 4.60 was observed). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) of CpMo(CO)(dppe)(OTf): δ 90.7 (d, $J_{PP} = 37.1$ Hz), 68.3 (d, $J_{PP} = 37.1$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) of $[CpMo(CO)(dppe)(H)_2]^+[OTf]^-$: δ 70.0 (s). An NMR spectrum recorded after the tube had been kept at room temperature for 6 h showed that the dihydride complex, $[CpMo(CO)(dppe)(H)_2]^+[OTf]^-$, had completely converted to CpMo(CO)(dppe)(OTf).

Preparation of CpMo(CO)(dppe)OTf. A two-neck, 25-mL round-bottomed flask attached to a frit assembly was charged with CpMo(CO)(dppe)H (100 mg, 0.17 mmol), and CH_2Cl_2 (10 mL) was vacuum transferred into this flask. HOTf (14 μL, 0.16 mmol) was added at room temperature through a syringe (this reaction is carried out with a slight molar deficiency of HOTf because excess HOTf causes a further reaction that is being investigated). The reaction mixture gradually turned from yellow to red. After 30 min, the solvent was reduced to 2 mL and Et_2O (∼3 mL) was added, followed by hexane (10 mL), to give a red precipitate. The product was collected by filtration and dried under vacuum (yield 93 mg, 0.13 mmol, 80% based on HOTf). ^1H NMR (CD_2Cl_2, 25 °C): δ 7.69−7.26 (m, 20 H, *Ph*), 4.66 (d, 5 H, *Cp*, $J_{PH} = 2.5$ Hz), 3.20−2.78 (m, 2 H, CH_2), 2.41−2.20 (m, 1 H, CH_2), 1.80−1.58 (m, 1 H, CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 90.7 (d, $J_{PP} = 37.0$ Hz), 68.3 (d, $J_{PP} = 37.0$ Hz). IR (CH_2Cl_2): ν(CO) 1858 cm^{-1}. Anal. Calcd for $C_{33}H_{29}F_3O_4P_2SMo$: C, 53.81; H, 3.97. Found: C, 53.83; H, 4.20.

Protonation of CpMo(CO)(dppe)H To Give $[CpMo(CO)(dppe)(H)_2]^+[OTf^-]$ at Low Temperature. HMo(CO)(dppe)Cp (16.0 mg, 0.027 mmol, 1 equiv) was weighed in a screw-capped NMR tube along with CD_2Cl_2 (∼0.6 mL) and 1,2-dichloroethane (3 μL, internal integration standard). The initial spectrum was recorded at −87 °C. The solution was cooled to −78 °C, and HOTf (4 μL, 0.045 mmol, 1.7 equiv) was added. The tube was shaken and then quickly inserted into a precooled NMR probe (−87 °C). The NMR spectrum of the resulting solution showed the formation of $[CpMo(CO)(dppe)(H)_2]^+[OTf]^-$ (99% yield). ^1H NMR (CD_2Cl_2, −87 °C): δ 8.0−7.4 (m, 20 H, Ph), 4.51 (s, 5 H, *Cp*), 3.0−1.9 (m, 4H, CH_2), −4.26 (dd, 2 H, Mo*H*, $J_{PH} = 43.0$ Hz, $J_{P'H} = 23.0$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 186 K): δ 69.6 (d, $J_{PP} = 10.7$ Hz), 68.2 (d, $J_{PP} = 10.7$ Hz). The temperature was increased to −58 °C, and the two hydride resonances became a triplet. ^1H NMR (CD_2Cl_2, −58 °C): δ 4.55 (s, 5 H, *Cp*), −4.19 (t, 2 H, Mo*H*, $J_{PH} = 32.7$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −58 °C): δ 69.9 (br s), 68.3 (br s). When the temperature was increased to −35 °C, the two phosphorus resonances of dppe coalesced to one broad singlet at δ 69.7 in the $^{31}P\{^1H\}$ spectrum. This dihydride complex was stable at −12 °C for about 30 min without noticeable decomposition.

Attempted Reaction of CpMo(CO)(dppe)H with Gomberg's Dimer. CpMo(CO)(dppe)H (5.9 mg, 0.010 mmol) was weighed in an NMR tube along with CD_2Cl_2 (∼0.4 mL) and 1,2-dichloroethane (0.5 μL, internal integration standard). After the initial spectrum was taken, this NMR solution was added to a solution of Gomberg's dimer (2.4 mg, 0.010 mmol calculated as $Ph_3C^\bullet$) in CD_2Cl_2 (∼0.2 mL); the color of the mixture remained yellow. After 10 min, the NMR spectrum showed no reaction. After 7 days, only a small amount of decomposition (free dppe) was observed in the NMR spectrum. A similar experiment in C_6D_6 was heated for 4 days at 80 °C and also showed a small amount of decomposition, giving free dppe.

Collection and Reduction of X-ray Data. Crystals of CpMo(CO)(dppe)H were yellow prisms. A crystal was mounted on a glass fiber and used for data collection. Some crystals appeared to be twinned, and others seemed to quickly lose solvent molecules and turn white and powdery, while others, like the crystal used for data collection, retained their yellow color. Diffraction data obtained using an Enraf Nonius CAD-4 diffractometer with molybdenum radiation and a graphite monochromator indicated triclinic symmetry consistent with the space groups $P1$ and $P\bar{1}$. Crystal data and information about the data collection and refinement are provided in Table 1.

Determination and Refinement of the Structure. The structure was solved by standard heavy-atom Patterson methods. Space group $P\bar{1}$ was used for the solution and refinement of the structure. In the least-squares refinement, anisotropic temperature parameters were used for all of the non-hydrogen atoms. The hydrogen atoms were placed at calculated positions and allowed to "ride" on the atom to which they were attached, except for the hydrogen atoms on the cylcopentadiene ligand and the toluene of solvation. Both of these were disordered so the hydrogen atoms on these groups were not included in the refinement. The hydride atom was located on a difference Fourier map and included in the final cycles of refinement and its coordinates and isotropic thermal parameter were refined. A common isotropic thermal parameter was refined for the other hydrogen atoms. A Gaussian absorption correction was applied.

Acknowledgment. Research at Brookhaven National Laboratory (BNL) was carried out under Contract DE-AC02-98CH10886 with the U.S. Department of Energy and was supported by its Division of Chemical Sciences, Office of Basic Energy Sciences, and by BNL LDRD funding. We thank Dr. Etsuko Fujita and Dr. Carol Creutz for helpful discussions.

Supporting Information Available: Plot of the cyclic voltammetry experiment, crystal data and structural refinement, and other X-ray crystallographic data (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

IC060111K