Stable Mononuclear, 17-Electron Molybdenum(III) Carbonyl Complexes. Synthesis, Structure, Thermal Decomposition, and Cl^- Addition Reactions

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Abstract: The first examples of stable, mononuclear 17-electron carbonyl complexes of Mo(III) have been synthesized, isolated, and characterized by IR and EPR spectroscopy. Oxidation of $Cp^*MoCl(CO)(PMe_3)_2$ (**1**; $E_{1/2} = -0.48$ V vs Fc/Fc^+), Cp*MoCl(CO)(dppe) (**2**; $E_{1/2} = -0.44$ V), and CpMoCl(CO)(dppe) (**3**; $E_{1/2} = -0.25$ V) with $Fc^+PF_6^-$ yields [**1**]PF_6, [**2**]PF_6, and [**3**]PF_6, respectively. The IR stretching vibration of the 17-electron oxidation products are 136−153 cm^{-1} blue-shifted with respect to the corresponding stretching vibrations of the parent Mo(II) compounds. The room temperature EPR spectra show observable coupling to the Mo and P nuclei and indicate a *trans* geometry for $\mathbf{1}^+$ and a *cis* geometry for $\mathbf{2}^+$ and $\mathbf{3}^+$. The four-legged piano stool geometry of $\mathbf{2}^+$ with the phosphines atoms in relative *cis* positions has been confirmed by a single-crystal X-ray analysis. The X-ray data for [**2**]PF_6·THF are the following: monoclinic, $P2_1/n$, $a = 13.7394(14)$ Å, $b = 20.421(2)$ Å, $c = 14.857(2)$ Å, $\beta = 99.119(8)°$, $V = 4115.8(8)$ Å^3, $Z = 4$, $D_x = 1.469$ g·cm^{-3}, λ(Mo Kα) = 0.71073 Å, μ (Mo Kα) = 0.562 mm^{-1}, $R(F) = 4.59\%$, $R(wF^2) = 10.77\%$ for 4299 data with $F_o > 4\sigma(F_o)$. The thermal stability of the cations decreases with increasing carbonyl stretching frequencies in the order $\mathbf{1}^+ > \mathbf{2}^+ \gg \mathbf{3}^+$. The decarbonylated product of thermolysis of $\mathbf{3}^+$, $[CpMoClF(dppe)(MeCN)]^+PF_6^-$, [**4**]$PF_6$, which is believed to arise via a 15-electron $[CpMoCl(dppe)]^+$ intermediate, has been isolated and characterized by ^1H, ^{31}P, and ^{19}F NMR spectroscopies as well as a single-crystal X-ray analysis. The structure of $\mathbf{4}^+$ shows a distorted pseudooctahedral geometry with the Cp ring and the F atom occupying the two axial coordination sites and the two phosphine atoms of the dppe occupying two *cis* equatorial sites. The data for [**4**]PF_6·MeCN are as follows: monoclinic, $P2_1/n$, $a = 13.160(2)$ Å, $b = 10.942(2)$ Å, $c = 25.010(3)$ Å, $\beta = 95.225(10)°$, $V = 3586.4(9)$ Å^3, $Z = 4$, $D_x = 1.557$ g·cm^{-3}, μ(Mo Kα) = 0.71073 Å, $R(F) = 4.11\%$, $R(wF^2) = 11.81\%$ for 5964 data with $F_o > 4\sigma(F_o)$. The nucleophilic addition of Cl^- to $\mathbf{1}^+$, $\mathbf{2}^+$, or $\mathbf{3}^+$ is followed by redox processes to afford mixtures of the parent Mo(II) carbonyl complexes **1**−**3** and Mo(IV) or Mo(V) products, depending on the nature of the ligands. The mechanism of these reactions has been elucidated through parallel chemical and electrochemical studies.

Introduction

Organometallic radicals, especially those characterized by a 17-electron configuration, are receiving a great deal of attention in view of their involvement as intermediates in a variety of fundamental processes.[1,2] Stable 17-electron compounds containing carbon monoxide as a ligand are generally confined to the low oxidation states. For complexes of molybdenum, very few such species have been isolated to date and these all contain the metal in the oxidation state +1, e.g. $[Mo(CO)_2(L{-}L)_2]^+$ (L−L = dmpe, dppe),[3,4] $[Mo(CO)_2(CNxylyl)_2(PEt_2Ph)_2]^+$,[5] $[Mo(CO)_2L_2(t\text{-Bu-DAB})]^+$ (L = MeCN, MeNC, *t*-BuNC; DAB = 1,4-diaza-1,3-butadiene),[6] $Tp^*Mo(CO)_3$ [Tp* = hydridotris(3,5-dimethylpyrazolyl)borate].[7] Upon increasing the oxidation state, it is expected that the metal−CO bond weakens. For instance, although the $CpMoX(CO)_3$ (X = halogen) complexes are thermally stable toward CO loss, the corresponding $CpMoX_3(CO)_2$ complexes[8,9] fully decarbonylate at the mild CH_2Cl_2 reflux.[10] In addition, a greater kinetic lability is expected for the metal−CO bond in odd-electron systems.[1,2] We report here the synthesis, isolation, and characterization of the first examples of *stable* mononuclear, 17-electron Mo(III) carbonyl derivatives. Stable CO derivatives of Mo(III) were previously limited to dinuclear, metal−metal bonded, diamagnetic compounds, e.g. $[Cp_2Mo_2(\mu\text{-SR})_2(CO)_3L]^{2+}$ (R = Me, Ph; L = CO, MeCN, *t*-BuCN),[11−13] $[Cp_2Mo_2(\mu\text{-SMe})_3(CO)_2]^+$,[14] and $[Cp_2Mo_2(\mu\text{-SMe})(\mu\text{-S}_2CH_2)(CO)_2]^+$.[15]

Experimental Section

General Data. All operations were carried out under an atmosphere of argon with standard Schlenk-line techniques. Solvents were purified by conventional methods and distilled under argon prior to use. FT-

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IR spectra were recorded on a Perkin-Elmer 1800 spectrophotometer with a liquid IR cell equipped with KBr plates. NMR spectra were recorded on Bruker WP200, AF200, and AM400 spectrometers; the peak positions are reported with positive shifts downfield of TMS as calculated from the residual solvent peaks (^{1}H), downfield of external 85% H_3PO_4 (^{31}P), or downfield of external TFA (^{19}F). For each ^{31}P and ^{19}F-NMR spectrum a sealed capillary containing H_3PO_4 or TFA was immersed in the same NMR solvent used for the measurement and this was used as the reference. Samples for EPR spectra were placed in 3-mm glass tubes and were recorded on a Bruker ER200 spectrometer upgraded to ESP 300 equipped with an X-band microwave generator, using DPPH ($g = 2.004$) as an external calibrant. Cyclic voltammograms were recorded with an EG&G 362 potentiostat connected to a Macintosh computer through MacLab hardware/software. The electrochemical cell used consisted of a modified Schlenk tube with a Pt counter electrode sealed through uranium glass/Pyrex glass seals. The cell was fitted with a Ag/AgCl reference electrode and a Pt disk working electrode. All half-wave potentials were measured and are reported with respect to the ferrocene/ferricenium couple. The ferrocene was added to the solution at the end of each measurement as an internal standard. No IR correction was applied during the measurements. The elemental analyses were carried out by M-H-W Laboratories, Phoenix, AZ, Galbraith Laboratories Inc., Knoxville, TN, and Desert Analytics Laboratory, Tucson, AZ. Cp*$MoCl_4$[16,17] and $\{CpMoCl_2\}_n$[18] were prepared as previously described. PMe_3 (Aldrich), dppe (Strem), and CO (Air Products) were used without any further purification.

Synthesis of Cp*MoCl(PMe_3)$_2$(CO) (1). Cp*$MoCl_4$ (0.460 g, 1.23 mmol) was added to a THF solution (20 mL) of PMe_3 (0.255 mL, 2.46 mmol) containing Na/Hg (0.090 g, 3.91 mmol in 10 g of Hg) giving a purple colored solution, which was stirred at room temperature. Over a period of 12 h the color changed from purple to red-brown to yellow-brown. An aliquot was taken for an NMR in C_6D_6 to confirm the identity of Cp*MoCl(PMe_3)$_2$[19] and to verify the complete consumption of the intermediate Cp*$MoCl_2$(PMe_3)$_2$ (see Results). The THF solution was filtered through Celite and then evaporated to dryness under reduced pressure. The residue was dissolved in heptane (10 mL) and the argon atmosphere was then replaced with CO, resulting in an immediate color change to red-orange. The heptane solution was concentrated to ca. $^1/_2$ of the original volume and then placed at −80 °C overnight. Orange crystals were isolated and dried under vacuum. Yield: 0.160 g, 29%. MS (CI, negative ions): 448 ($[M]^-$, 100%), 372 ($[M]^- - PMe_3$, 93%). IR (THF): 1782 cm^{-1}. ^{1}H-NMR (C_6D_6): δ 1.66 (s, 15 H, C_5Me_5), 1.30 (vt, $J_{PH} = 4$ Hz, 18 H, PMe_3). ^{31}P{^{1}H}-NMR (C_6D_6): δ 18.5.

Synthesis of [Cp*MoCl(PMe_3)$_2$(CO)]PF_6 ([1]PF_6). $Cp_2Fe^+PF_6^-$ (0.179 g, 0.512 mmol) was added to a stirring THF solution (10 mL) of **1** (0.229 g, 0.512 mmol). An immediate reaction occurred quenching the blue color of the Fc^+. The THF was concentrated under reduced pressure to approximately 3 mL and the product $\mathbf{1}^+PF_6^-$ was precipitated with heptane (15 mL), filtered, washed with heptane (3 × 5 mL), and dried under vacuum. Yield: 0.207 g, 68%. *Anal.* Calcd (found) for $C_{17}H_{33}ClF_6MoOP_3$: C, 34.51 (33.27); H, 5.62 (5.68). Low C analyses (erratically in the range of 30.33−33.27% from different commercial laboratories, with differences greater than 0.5% even for duplicate analyses on the same preparation) for this compound have been repeatedly obtained on several different preparations, in spite of the homogeneity of the crystalline samples upon optical inspection and the spectroscopic purity. We tentatively attribute this phenomenon to incomplete combustion during the analytical procedure. No EPR-active impurity is observed in the EPR spectrum (see Results section) and no diamagnetic impurity is observed in the NMR spectrum (in d^8-THF), the latter showing only the solvent resonances. IR (THF): 1920 cm^{-1}. EPR (THF): $g = 2.005$ (t with Mo satellites; $a_P = 23.0$ G; $a_{Mo} = 26.3$ G).

Synthesis of Cp*MoCl(dppe)(CO) (2). Cp*$MoCl_4$ (0.260 g, 0.778 mmol) was added to a THF solution (25 mL) of dppe (0.310, 0.778 mmol), containing Na/Hg (0.060 g, 2.60 mmol in 7 g of Hg). Stirring for approximately 5 min gave a light brown colored solution with a brown precipitate. The argon atmosphere was replaced with CO and the solution was allowed to stir overnight, during which time the solution became clear and dark orange in color. The THF was removed under reduced pressure, the residue was extracted with toluene (10 mL), and the resulting solution was then filtered through Celite. The Celite was rinsed with toluene (2 × 2 mL) and the rinsings added to the original toluene extract. The toluene solution was concentrated to ca. 2 mL and heptane (20 mL) was added, precipitating an orange solid. The mixture was placed at −80 °C for 1 h, after which time the solid was filtered, washed with heptane (2 × 5 mL), and dried under vacuum. Yield: 0.318 g, 60%. *Anal.* Calcd (found) for $C_{37}H_{39}ClMoOP_2$: C, 64.12 (63.91); H, 5.67 (5.59). IR (THF): 1835 cm^{-1}. ^{1}H-NMR (C_6D_6): δ 7.77 (m, 4 H, $\mathit{Ph}_2PCH_2CH_2P\mathit{Ph}_2$), 7.61 (m, 20 H, $\mathit{Ph}_2PCH_2CH_2P\mathit{Ph}_2$), 1.55 (br, 4H, $Ph_2P\mathit{CH_2CH_2}PPh_2$), 1.41 (s, 15H, C_5Me_5). ^{31}P{^{1}H}-NMR (C_6D_6): δ 90.2 (d, $J_{PP} = 38$ Hz, 1 P), 64.5 (d, $J_{PP} = 38$ Hz, 1 P).

Synthesis of [Cp*MoCl(dppe)(CO)]PF_6 ([2]PF_6). By a procedure analogous to that described above for $\mathbf{1}^+$, the interaction of 0.383 g (0.508 mmol) of **2** with 0.180 g (0.515 mmol) of $Fc^+PF_6^-$ yielded 320 g (75% yield) of [**2**]PF_6. *Anal.* Calcd (found) for $C_{37}H_{39}ClF_6MoOP_3$: C, 53.03 (52.6); H, 4.69 (4.90). IR (THF): 1971 cm^{-1}. EPR (THF): $g = 2.003$ (dd with Mo satellites; $a_{P1} = 28.1$ G; $a_{P2} = 17.7$ G; $a_{Mo} = 29.8$ G).

Synthesis of CpMoCl(dppe)(CO) (3). $CpMoCl_2$(dppe) was prepared in situ from $\{CpMoCl_2\}_n$ (0.544 g, 2.34 mmol) and dppe (0.932 g, 2.34 mmol) in CH_2Cl_2 (5 mL) as previously described,[20] and recovered as a solid by reducing the volume to ca. 1 mL and precipitation with heptane (10 mL). The solid was washed with heptane (2 × 5 mL) and then suspended in THF (40 mL). The THF suspension was transferred via cannula onto Na/Hg (0.058 g, 2.52 mmol in 6 g of Hg) and the atmosphere of argon was replaced with CO. After stirring overnight the solution was dark orange in color. The THF solution was concentrated to ca. 10 mL and an orange solid was precipitated by adding heptane (30 mL). The solid was washed with heptane (3 × 5 mL) and dried under vacuum. Yield: 0.867 g, 60%. The spectroscopic properties of this material are identical to those previously reported.[21] IR (THF): 1853 cm^{-1}. ^{1}H-NMR (C_6D_6): δ 7.88 (m, 4 H, $\mathit{Ph}_2PCH_2CH_2P\mathit{Ph}_2$), 7.74 (m, 8H, $\mathit{Ph}_2PCH_2CH_2P\mathit{Ph}_2$), 7.63 (m, 8H, $\mathit{Ph}_2PCH_2CH_2P\mathit{Ph}_2$), 4.50 (s, 5 H, Cp), 2.69 (br, $Ph_2P\mathit{CH_2CH_2}PPh_2$), 1.77 (br, $Ph_2P\mathit{CH_2CH_2}PPh_2$). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 92.9 (d, $J_{PP} = 38$ Hz, 1 P), 68.0 (d, $J_{PP} = 37$ Hz, 1 P).

Synthesis of [CpMoCl(dppe)(CO)]PF_6 ([3]PF_6). By a procedure analogous to that described above for [**1**]PF_6, the interaction of 0.240 g (0.385 mmol) of **3** with 0.143 g (0.409 mmol) of $Fc^+PF_6^-$ yielded 207 g (70% yield) of [**3**]PF_6. *Anal.* Calcd (found) for $C_{31}H_{29}ClF_6MoOP_3{\cdot}(C_7H_{16})_{0.25}$: C, 51.12 (51.21); H, 4.19 (4.26). The presence of heptane was confirmed by ^{1}H-NMR spectroscopy. IR (THF): 2002 cm^{-1}. EPR (THF): $g = 2.002$ (dd with Mo satellites; $a_{P1} = 28.6$ G; $a_{P2} = 16.6$ G; $a_{Mo} = 30.2$ G).

General Procedure For Studying the Thermal Stability of the Carbonyl Cations. Approximately 0.050 g of [**1**]PF_6, [**2**]PF_6, and [**3**]PF_6 was dissolved in THF (5 mL). The solutions were heated in an oil bath thermostated at 55 °C. The concentrations of the carbonyl cations were then analyzed by monitoring the intensity of the ν_{CO} bands in the IR spectra of the solutions.

Synthesis of [CpMoClF(dppe)(MeCN)]PF_6 ([4]PF_6). A THF solution (5 mL) of [**3**]PF_6 (0.164 g, 0.214 mmol) was heated for 1 h at 55 °C. The red precipitate that had formed was filtered off and dried under vacuum. Yield: 0.036 g, 44% based on [CpMoClF(dppe)]PF_6. *Anal.* Calcd (found) for $C_{31}H_{29}ClF_7MoP_3$: C, 49.06 (48.83); H, 3.85 (4.02). The red solid was dissolved in MeCN and crystals of [**4**]PF_6 (0.030 g) were obtained by slow diffusion of a Et_2O layer. ^{1}H-NMR (d^3-MeCN): δ 8.29 (m, 2H, $\mathit{Ph}_2PCH_2CH_2P\mathit{Ph}_2$), 7.78 (m, 4H, $\mathit{Ph}_2PCH_2CH_2P\mathit{Ph}_2$), 7.48 (m, 14H, $\mathit{Ph}_2PCH_2CH_2P\mathit{Ph}_2$), 5.17 (t, 5H, $J_{PH} = 7.2$ Hz, C_5H_5), 3.25 (m, 4H, $Ph_2P\mathit{CH_2CH_2}PPh_2$). ^{31}P{^{1}H}-NMR

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(d^3-MeCN): δ 55.5 (br, d, 1P, $J_{PF} = 73$ Hz), 45.6 (br, d, 1P, $J_{PF} = 53$ Hz). ^{19}F-NMR (d^3-MeCN): δ 13.17 (dd, MoF, $J_{FP1} = 75$ Hz, $J_{FP2} = 61$ Hz), 9.47 (d, PF$_6$, $J_{FP} = 706$ Hz).

Synthesis of Cp*MoCl$_2$(dppe) [6]. Cp*MoCl$_4$ (0.382 g, 1.02 mmol) was added to a THF solution (20 mL) of dppe (0.406 g, 1.02 mmol) containing Na(sand) (0.053 g, 2.31 mmol) and napthalene (0.020 g, 0.16 mmol) giving a brown colored solution, which was stirred at room temperature. Over a period of 12 h the color changed from brown to red-brown. The THF was removed under reduced pressure and the residue extracted into CH_2Cl_2 (15 mL). The CH_2Cl_2 solution was filtered and concentrated to $^1/_3$ of its original volume. A brown solid was precipitated by adding heptane (15 mL). The solid was dried and isolated. Yield: 0.457g, 67%. The compound was recrystallized by layering CH_2Cl_2 solution with heptane. *Anal.* Calcd (found) for $C_{36}H_{39}Cl_2MoP_2$: C, 61.73 (61.69); H, 5.61 (5.55). EPR (THF): $g = 1.987$ (t; $a_{Mo} = 28.9$ G, $a_P = 27.2$ G).

General Procedure for the Reaction of Carbonyl Cations with PPN$^+$Cl$^-$. Approximately 0.040 g of [**1**]PF$_6$, [**2**]PF$_6$, and [**3**]PF$_6$ was dissolved in THF (5 mL). An excess (2 to 3 equiv) of PPN$^+$Cl$^-$ was added to each of the solutions. An immediate color change was observed in all three solutions. The reactions were monitored by IR, EPR, and NMR spectroscopies. For the NMR measurements, an aliquot of the solution was transferred into a separate Schlenk tube and evaporated to dryness, and the residue was redissolved in the suitable deuterated solvent (see Results).

X-ray Crystallography. (a) [2]PF$_6$·THF. A reddish-orange crystal with dimensions 0.58 × 0.38 × 0.05 mm was placed and optically centered on the Enraf-Nonius CAD-4 diffractometer. The crystal cell parameters and orientation matrix were determined from 25 reflections in the range $33.5 < 2\theta < 39.2°$, and confirmed with axial photographs. Three nearly orthogonal standard reflections were monitored at 1-h intervals of X-ray exposure and showed insignificant variation in intensity. Seven ψ-scan reflections were collected over the range $7.1 < \theta < 13.1°$; the absorption correction was applied with transmission factors ranging from 0.2938 to 0.5577.[22] The data were corrected for Lorentz and polarization factors. The space group was uniquely determined by systematic absences from the data. Direct methods allowed the location of the heavy atoms, i.e., the Mo, Cl, P, and F atoms, and fragments of the phenyl rings and carbonyl ligand. The remaining non-hydrogen atoms were found from two subsequent difference-Fourier maps. Although the molecule of interest and the counterion (PF$_6$) were located and refined relatively well, the area of the unit cell involving the THF molecule was found to be a highly randomized "ball" of electron density. Many difference maps and trial orientations were tested and optimized with the final result consisting in three different orientations, the sum of the occupancies being 1. Hydrogen atoms attached to carbon atoms were placed in calculated positions. All of the non-hydrogen atoms were refined anisotropically, except for the disordered THF molecule. The selected crystal data are reported in Table 1 and selected bond distances and angles are collected in Table 2.

(b) [4]PF$_6$·MeCN. A reddish-orange crystal with dimensions 0.50 × 0.50 × 0.45 mm was placed and optically centered on the Enraf-Nonius CAD-4 diffractometer. The crystal cell parameters and orientation matrix were determined from 25 reflections in the range $23.8 < 2\theta < 36.0°$ and confirmed with axial photographs. Six standard reflections were monitored at 1-h intervals of X-ray exposure and showed an insignificant variation of intensity. Four ψ-scan reflections were collected over the range $7.8 < \theta < 10.1°$; the absorption correction was not applied as the various reflections were not internally or comparably consistent. The data were corrected for Lorentz and polarization factors. The space group was uniquely determined by systematic absences from the data. Direct methods allowed the location of the Mo, Cl, P, and F atoms, and fragments of the phenyl rings. The remaining non-hydrogen atoms were found from three subsequent difference-Fourier maps. A molecule of solvation, MeCN, was also found in the asymmetric unit and refined well. Hydrogen atoms attached to carbon atoms were placed in calculated positions. All of the non-hydrogen atoms were refined anisotropically. The selected crystal data are reported in Table 1 and selected bond distances and angles are collected in Table 3.

Table 1. Crystal Data for [**2**]PF$_6$·THF and [**4**]PF$_6$·MeCN

	[**2**]PF$_6$·THF	[**4**]PF$_6$·MeCN
empirical formula	$C_{41}H_{47}ClF_6MoO_2P_3$	$C_{35}H_{35}ClF_7MoN_2P_3$
formula wt	910.09	840.95
temp, K	153(2)	153(2)
wavelength, Å	0.71073	0.71073
crystal system	monoclinic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)/*n*
unit cell dimensions		
a, Å	13.7394(14)	13.160(2)
b, Å	20.421(2)	10.942(2)
c, Å	14.857(2)	25.010(3)
B, deg	99.119(8)	95.225(10)
vol, Å^3	4115.8(8)	3586.4(9)
Z	4	4
density (calcd), mg/m^3	1.469	1.557
absn coeff, mm^{-1}	0.562	none
F(000)	1868	1704
independent reflcns	5367 [$R_{int} = 0.0572$]	6310 [$R_{int} = 0.0368$]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/ parameters	5366/0/495	6310/0/445
goodness-of-fit on F^2	1.057	1.098
final *R* indices [$I > 2\sigma(I)$]		
R	0.0459	0.0411
R_w	0.1077 [4299 data]	0.1181 [5964 data]
largest diff peak and hole, e·A^{-3}	1.114 and −1.112	0.872 and −0.911

Table 2. Selected Bond Distances (Å) and Angles (deg) for [**2**]PF$_6$·THF

Mo(1)−C(1)	2.053(6)	Mo(1)−P(2)	2.4902(13)
Mo(1)−Cl(1)	2.473(2)	Mo(1)−CNT[a]	2.006(5)
Mo(1)−P(1)	2.5555(13)		
C(1)−Mo(1)−Cl(1)	78.89(14)	Cl(1)−Mo(1)−P(2)	127.67(5)
C(1)−Mo(1)−P(1)	133.13(14)	CNT[a]−Mo(1)−C(1)	109.9(2)
C(1)−Mo(1)−P(2)	82.74(14)	CNT[a]−Mo(1)−Cl(1)	113.1(2)
Cl(1)−Mo(1)−P(1)	84.66(5)	CNT[a]−Mo(1)−P(1)	116.9(2)
P(1)−Mo(1)−P(2)	73.38(4)	CNT[a]−Mo(1)−P(2)	119.2(2)

[a] CNT = center of gravity of atoms C(10)−C(14).

Table 3. Selected Bond Distances (Å) and Angles (deg) for [**4**]PF$_6$·MeCN

Mo(1)−F(1)	1.951(2)	Mo(1)−P(1)	2.5313(10)
Mo(1)−N(6)	2.182(3)	Mo(1)−P(2)	2.5479(9)
Mo(1)−Cl(1)	2.4984(10)	Mo(1)−CNT[a]	1.990(4)
F(1)−Mo(1)−N(6)	77.30(10)	Cl(1)−Mo(1)−P(2)	87.51(3)
F(1)−Mo(1)−Cl(1)	80.41(6)	P(1)−Mo(1)−P(2)	81.33(3)
F(1)−Mo(1)−P(1)	68.74(6)	CNT[a]−Mo(1)−F(1)	174.1(1)
F(1)−Mo(1)−P(2)	75.65(6)	CNT[a]−Mo(1)−N(6)	102.3(1)
N(6)−Mo(1)−Cl(1)	82.87(8)	CNT[a]−Mo(1)−Cl(1)	105.4(1)
N(6)−Mo(1)−P(1)	93.77(8)	CNT[a]−Mo(1)−P(1)	105.5(1)
N(6)−Mo(1)−P(2)	152.43(8)	CNT[a]−Mo(1)−P(2)	105.1(1)
Cl(1)−Mo(1)−P(1)	148.90(3)		

[a] CNT = center of gravity of atoms C(1)−C(5).

Results

Synthesis and Cyclic Voltammetric Studies of 1, 2, and 3. Compound **1** has been synthesized by addition of CO to the recently reported stable 16-electron Cp*MoCl(PMe$_3$)$_2$[19] (see eq 1). The formation of **1** is fast and quantitative; work-up of the product must be carried out immediately because if **1** is left under a CO atmosphere, a much slower substitution of one of the PMe$_3$ ligands by CO occurs, as indicated by the growth of

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[22] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 351−359.

CO stretching vibrations in the IR spectrum at 1946 and 1851 cm^{-1}, these being tentatively assigned to compound $Cp^*MoCl(CO)_2(PMe_3)$. Another problem of this synthesis is that the reduction of $Cp^*MoCl_4/2PMe_3$ with Na proceeds through the previously described[23] $Cp^*MoCl_2(PMe_3)_2$ intermediate and the last reduction step from Mo(III) to Mo(II) is rather slow, leaving variable amounts of the less soluble Mo(III) intermediate in the final carbonylated solution, which then co-crystallizes with the desired compound **1**. The amount of Mo(III) impurity can be eliminated by utilizing a slight excess of Na and longer reaction times; this procedure inevitably causes overreduction, lowering the yield and introducing another impurity in the final solution, namely $Cp^*MoH(PMe_3)_3$, but the latter species has a higher solubility and does not hamper the isolation of pure **1**. The reported somewhat low yield of **1** in the Experimental Section (29%) is due to this overreduction procedure and to the subsequent short contact time with CO, required to obtain the ultra-pure material required for the studies presented here. The complex has been isolated also several times in higher yields, i.e. greater than 75%, but a 10−15% impurity of the Mo(III) complex $Cp^*MoCl_2(PMe_3)_2$ is always present in those cases. Compound **2** may also be synthesized by a procedure identical to that described for **1**, proceeding through the CO addition to the 16-electron, Cp*MoCl(dppe), which is synthesized from Cp^*MoCl_4, Na/Hg, and dppe in the appropriate stoichiometric amounts.[24] It was found, however, that the straight reduction from Cp^*MoCl_4 under an atmosphere of CO improved the yield and is a more convienent one-step synthesis (eq 2). Compound **3** has previously been synthesized by interaction of $CpMoCl(CO)_3$ with dppe in refluxing toluene.[21] We report here an alternative preparation of **3** by reduction of $CpMoCl_2(dppe)$, which is quantitatively generated in situ from $\{CpMoCl_2\}_n$ and dppe in CH_2Cl_2,[20] with 1 equiv of Na/Hg under an atmosphere of CO (eq 3). The IR, ^1H, and ^{31}P-NMR spectroscopic properties are fully consistent with 18-electron, diamagnetic, Mo(II) complexes for compounds **1**, **2**, and **3**.

$$Cp^*MoCl(PMe_3)_2 + CO \rightarrow Cp^*MoCl(PMe_3)_2(CO) \quad (1)$$

$$Cp^*MoCl_4 + dppe + 3Na + CO \rightarrow Cp^*MoCl(dppe)(CO) \quad (2)$$

$$CpMoCl_2(dppe) + Na + CO \rightarrow CpMoCl(dppe)(CO) \quad (3)$$

All three compounds **1**, **2**, and **3** exhibit reversible oxidation waves in the cyclic voltammogram at relatively low potentials, $E_{1/2} = -0.48$ V for **1** and −0.44 V for **2** vs the ferrocene standard in THF. The reversible oxidation of **3** in CH_2Cl_2 had already been reported by Gipson *et al.* at $E_{1/2} = -0.25$ V on the same scale.[25,26] While it is clear that the carbonyl cations are stable at least on the CV time scale, the question is whether they are sufficiently stable to be isolated. Lau and Gipson attempted bulk electrolysis of the iodide anologue of **3**, CpMoI(dppe)(CO), in CH_2Cl_2 at low temperatures and generated the corresponding cation, but found a reversion back to the neutral Mo(II) parent complex upon warming the mixture to room temperature. The oxidation of **3** in an IR spectrochemical cell has been reported to give $\mathbf{3}^+$, characterized by a stretching vibration at 2011 cm^{-1}, but bulk electrolysis or chemical oxidation studies on **3** have not been described. It was, however, stated that $\mathbf{3}^+$ is less stable than the iodide analogue.[25]

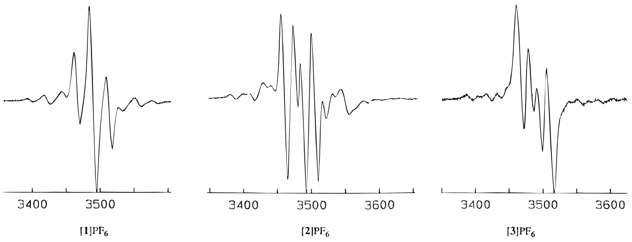

Figure 1. EPR spectra (X band) of $[\mathbf{1}]PF_6$, $[\mathbf{2}]PF_6$, and $[\mathbf{3}]PF_6$ (solvent = THF, room temperature).

Synthesis and Characterization of $\mathbf{1}^+$, $\mathbf{2}^+$, and $\mathbf{3}^+$ by Chemical Oxidation. The interaction of compounds **1**, **2**, and **3** with 1 equiv of $Fc^+PF_6^-$ in THF at room temperature affords stable solutions of the corresponding cations, $\mathbf{1}^+$, $\mathbf{2}^+$, and $\mathbf{3}^+$ (see eq 4). The cations can be isolated as PF_6^- salts without decomposition by precipitation from THF with heptane, and were characterized by chemical analysis and by IR and EPR spectroscopies. The CO ligands offer a convenient marker for the electron density on the metal center. The IR data for both the neutral Mo(II) complexes and the carbonyl cations show standard textbook trends, related to the different donating abilities of PMe_3 versus dppe and Cp* versus Cp. Upon oxidation, blue shifts of 138 (**1**), 136 (**2**), and 150 cm^{-1} (**3**) for ν_{CO} are observed as expected, in agreement with the removal of electron density from the Mo center. The EPR data give useful structural information (Figure 1). Complex $\mathbf{1}^+$ shows a binomial triplet indicating equivalent phosphines, whereas both $\mathbf{2}^+$ and $\mathbf{3}^+$ show a doublet of doublets, indicating the inequivalence of the two phosphorus nuclei. Since all structurally characterized $CpMo^{III}$ complexes with four addtional monodentate donors exhibit the ubiquitous 4-legged piano stool structure,[27] for instance $[(ring)MoCl(PMe_3)_3)]^+$ (ring = Cp, Cp*),[28] it is logical to propose that $\mathbf{1}^+$, $\mathbf{2}^+$, and $\mathbf{3}^+$ also adopt such a geometry. However, the two phosphorus donors are located in relative trans positions in $\mathbf{1}^+$, whereas they are necessarily cis for the two complexes with the chelating dppe ligand. The proposed structure for $\mathbf{2}^+$ has been confirmed by a single-crystal X-ray analysis (vide infra). The EPR parameters for $\mathbf{1}^+$ show a larger P (23.0 G) and a smaller Mo (26.3 G) hyperfine coupling constant with respect to $Cp^*MoCl_2(PMe_3)_2$ ($a_P = 15$ G, $a_{Mo} = 36$ G).[23] Complexes $\mathbf{2}^+$ and $\mathbf{3}^+$ exhibit spectral parameters similar to those of $\mathbf{1}^+$: $a_{Mo} = 29.8$ and 30.2; average $a_P = 22.9$ and 22.6, respectively.

$$(ring)MoClL_2(CO) + Cp_2Fe^+PF_6^- \rightarrow [(ring)MoClL_2(CO)]^+PF_6^- + Cp_2Fe \quad (4)$$

$$(ring = Cp^*,\ L_2 = (PMe_3)_2,\ dppe;\ ring = Cp,\ L_2 = dppe)$$

Thermal Stability of $\mathbf{1}^+$, $\mathbf{2}^+$, and $\mathbf{3}^+$. In order to probe the stability of $\mathbf{1}^+$, $\mathbf{2}^+$, and $\mathbf{3}^+$, thermolysis in THF was performed and monitored by IR spectroscopy. Complex $\mathbf{1}^+$ shows the greatest stability with less than 5% decomposition after 30 min at 55 °C, and complex $\mathbf{2}^+$ is only slightly less stable with less than 10% decomposition after 30 min under the same conditions. The least stable by far was $\mathbf{3}^+$, which showed 75% decomposition within 30 min at 55 °C. The decomposition of $\mathbf{3}^+$ produced the neutral parent molecule, **3**, which accumu-

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[23] Baker, R. T.; Calabrese, J. C.; Harlow, R. L.; Williams, I. D. *Organometallics* **1993**, *12*, 830−841.

[24] Full details of the preparation of this compound, which has also been crystallographically characterized, will be reported in a subsequent contribution.

[25] Lau, Y. Y.; Gipson, S. L. *Inorg. Chim. Acta* **1989**, *157*, 147−149.

[26] Lau, Y. Y.; Huckabee, W. W.; Gipson, S. L. *Inorg. Chim. Acta* **1990**, *172*, 41−44.

[27] Poli, R. *J. Coord. Chem. B* **1993**, *29*, 121−173.

[28] Fettinger, J. C.; Kraatz, H.-B.; Poli, R.; Rheingold, A. L. *Acta Crystallogr., Sect. C* **1995**, *C51*, 364−367.

lated in solution, and a red precipitate, which was isolated, crystalized from a MeCN/Et_2O layering, and identified as $[CpMoClF(dppe)(MeCN)]^+PF_6^-$, [**4**]$PF_6$. The NMR properties of $\mathbf{4}^+$ are fully consistent with an 18-electron Mo(IV) complex. The ^{19}F NMR showed two resonances in a 6:1 ratio, a doublet at 9.47 ppm ($J_{PF} = 706$ Hz) for the PF_6 anion, and a doublet of doublets at 13.17 ppm ($J_{PF} = 75$ Hz, $J_{PF} = 61$ Hz), assigned to the Mo-bound fluoride, split by the two inequivalent phosphorus nuclei. The ^{1}H NMR showed a triplet for the Cp resonance corresponding to coupling to two similar phosphine ligands which, in addition to the ^{19}F data, would seem to indicate that the two phosphorus donors occupy inequivalent equatorial sites while the F occupies the axial site in a pseudo-octahedral structure, the Cp ligand occupying the opposite axial site. This assumption has been confirmed by a single-crystal X-ray analysis (vide infra). In addition to being thermally unstable, compound $\mathbf{3}^+$ is also light sensitive, decomposing to $\mathbf{4}^+$ after an overnight exposure of a THF solution to fluorescent light. Irradiation with a UV lamp caused a faster (<10 min) decomposition to the same red precipitate obtained by the thermal treatment. A possible route to compound [**4**]PF_6 will be proposed in the Discussion section.

Reaction of $\mathbf{1}^+$, $\mathbf{2}^+$, and $\mathbf{3}^+$ with PPN^+Cl^-. One of the predicted characteristics of the 17-electron Mo(III) carbonyl cationic complexes was the reactivity toward nucleophiles. The expected outcome of the reaction with Cl^- was the product of CO substitution, to yield the known class of stable paramagnetic (ring)$MoCl_2L_2$ compounds.[27] These reactions, however, were complicated by electron transfer processes, which have been fully rationalized as shown below with the aid of IR, NMR, and EPR monitoring and the parallel study of related chemical and electrochemical processes.

Treatment of $\mathbf{1}^+$ with excess Cl^- caused an immediate consumption of the molybdenum complex as shown by IR spectroscopy. However, the IR spectrum also showed the growth of an absorption corresponding to the ν_{CO} of the neutral parent Mo(II) material, **1**. ^{1}H-NMR confirmed the identity of **1**, but did not show any other NMR active product. The EPR spectrum of the reaction mixture, however, revealed the formation of a paramagnetic material which exhibits a doublet with Mo satellites ($g = 1.984$, $a_{Mo} = 45$ G, $a_P = 28$ G). This material was shown to be the 17-electron Mo(V) complex, $Cp^*MoCl_4(PMe_3)$ (**5**), by comparison with the EPR spectrum of a genuine sample prepared from Cp^*MoCl_4 and PMe_3, and with the spectrum reported in the literature.[16] The nature of the observed products demands the stoichiometry of eq 5.

$$3[Cp^*MoCl(PMe_3)_2(CO)]^+ + 3\ Cl^- \rightarrow 2Cp^*MoCl(PMe_3)_2(CO) + Cp^*MoCl_4(PMe_3) + CO + PMe_3 \quad (5)$$

The result of this reactivity originally appeared confusing, a Mo(III) complex leading to a Mo(V) and a Mo(II) complex by simply adding Cl^-. In order to elucidate the reaction path, a number of control experiments were carried out. Since the reaction obviously involved electron transfer steps, the electrochemical properties of the possible intermediates was considered, beginning with the expected $Cp^*MoCl_2(PMe_3)_2$ product of CO substitution by Cl^-. It was, as a matter of fact, already known from previous investigations carried out in this laboratory that $Cp^*MoCl_2(PMe_3)_2$ is a fairly good reducing agent ($E_{1/2} = -0.84$ V)[29] and is therefore capable of reducing $\mathbf{1}^+$ to **1** ($E_{1/2} = -0.48$ V). Following the formation of the $[Cp^*MoCl_2(PMe_3)_2]^+$ complex by this electron transfer process, this may reasonably be expected to add Cl^- to afford an 18-electron adduct $Cp^*MoCl_3(PMe_3)_2$, and this product could further eliminate a PMe_3 ligand, generating the previously described[30] neutral Mo(IV) complex, $Cp^*MoCl_3(PMe_3)$. This complex is paramagnetic ($S = 1$) and is characterized by a broad ^{1}H-NMR resonance at δ 2.3 ppm ($w_{1/2}$= 184 Hz). The parallel study of the interaction between $[Cp^*MoCl_2(PMe_3)_2]^+$ and Cl^- *in stoichiometric amounts* indeed produced the expected resonances of free PMe_3 (^{1}H: δ 1.31; ^{31}P: δ -61) for $Cp^*MoCl_3(PMe_3)$.

With the final product being a complex of Mo(V), the electrochemistry of $Cp^*MoCl_3(PMe_3)$ was investigated. This compound shows an irreversible oxidation wave with an anodic peak potential of $E_{pa} = +0.22$ V, i.e., too high to engage in an electron transfer process with $\mathbf{1}^+$. We then considered that the addition of excess Cl^- to afford an 18-electron $[Cp^*MoCl_4(PMe_3)]^-$ species, or an equilibrium with a *small* amount of the bis-PMe_3 adduct, may render the metal more susceptible to oxidation, through the increase of electron density at the metal. However, an equilibrium with a bis-phosphine adduct is discounted because the addition of free PMe_3 to $Cp^*MoCl_3(PMe_3)$ causes no change either to the resonance of the 16-electron Mo(IV) species or to the resonance of free PMe_3, and does not produce new resonances attributable to a new diamagnetic species. The interaction between $Cp^*MoCl_3(PMe_3)$ and excess Cl^- was therefore investigated next. The addition of excess PPN^+Cl^- to the CV cell containing $Cp^*MoCl_3(PMe_3)$ did not change the cyclic voltammogram, except for a slight decrease in the peak height for the oxidation of $Cp^*MoCl_3(PMe_3)$. This experiment indicates that, if an equilibrium with an 18-electron $[Cp^*MoCl_4(PMe_3)]^-$ is involved (eq 6), its position must be shifted toward the left. The existence of such an equilibrium, however, is demonstrated by the NMR and electrochemical experiments descibed below. The interaction between $Cp^*MoCl_3(PMe_3)$ with PPN^+Cl^- showed that the characteristic resonance of the Mo complex slightly shifted to ca. δ 1.9 ($w_{1/2} = 224$ Hz). New diamagnetic resonances were not observable in the ^{1}H- and ^{31}P-NMR spectra. This result suggests that any 18-electron $[Cp^*MoCl_4(PMe_3)]^-$ species must be in rapid exchange with the 16-electron neutral complex on the NMR time scale. The same resonance at δ 1.9 is also obtained from the interaction of the previously described[31] $[Cp^*MoCl_4]^-$ with PMe_3. In this latter experiment, no residual peak due to $[Cp^*MoCl_4]^-$ (reported at -13.3 ppm),[31] is observed. Therefore, of the two available equilibria relating the 18-electron $[Cp^*MoCl_4(PMe_3)]^-$ complex with its possible dissociation products (eqs 6 and 7), the first one allows both

$$Cp^*MoCl_3(PMe_3) + Cl^- \rightleftharpoons [Cp^*MoCl_4(PMe_3)]^- \quad (6)$$

$$[Cp^*MoCl_4]^- + PMe_3 \rightarrow [Cp^*MoCl_4(PMe_3)]^- \quad (7)$$

species to be present at equilibrium, whereas the second one is totally shifted to the right. Finally, an independent cyclic voltammetric study of **5** showed an irreversible reduction with a cathodic peak potential $E_{pc} = -1.0$ V, showing that the primary reduction product, $[Cp^*MoCl_4(PMe_3)]^-$, immediately decomposes. This decomposition leads to the formation of $Cp^*MoCl_3(PMe_3)$ by Cl^- dissociation, as clearly demonstrated by the observation of an irreversible oxidation wave with $E_{pa} = +0.22$ V during the reverse scan, corresponding exactly to the observed irreversible oxidation wave for $Cp^*MoCl_3(PMe_3)$,

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[29] Poli, R.; Owens, B. E.; Linck, R. G. *Inorg. Chem.* **1992**, *31*, 662−667.

[30] Abugideiri, F.; Gordon, J. C.; Poli, R.; Owens-Waltermire, B. E.; Rheingold, A. L. *Organometallics* **1993**, *12*, 1575−1582.

[31] Abugideiri, F.; Brewer, G. A.; Desai, J. U.; Gordon, J. C.; Poli, R. *Inorg. Chem.* **1994**, *33*, 3745−3751.

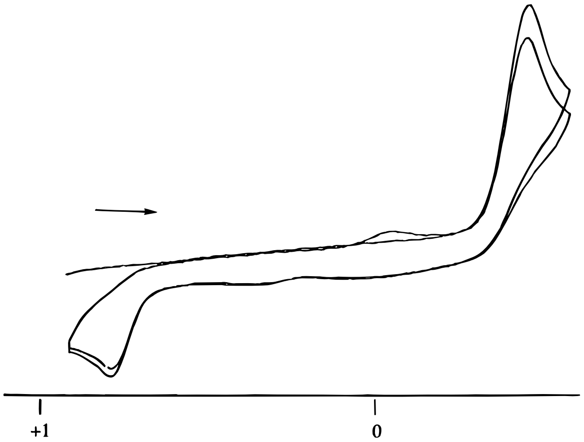


Figure 2. Cyclic voltammogram of Cp*$MoCl_4(PMe_3)$.

see Figure 2. Thus, this cyclic voltammetric experiment confirms that equilibrium 6 must be shifted largely to the left and, in addition, it demonstrates the feasibility of the oxidation of [Cp*$MoCl_4(PMe_3)]^-$ by $\mathbf{1}^+$. In conclusion, electrochemical and NMR studies give consistent results and both point to the oxidation of [Cp*$MoCl_4(PMe_3)]^-$ by $\mathbf{1}^+$ to generate the observed Mo(V) product.

The reaction of $\mathbf{2}^+$ with excess Cl^- also proceeds immediately and quantitatively as shown by IR and EPR spectroscopies. The IR spectrum of the reaction mixture revealed once again the formation of the parent Mo(II) material, **2**, whose identity was also confirmed by ^1H- and ^{31}P-NMR spectroscopies in $CDCl_3$. In contrast to the reaction of $\mathbf{1}^+$ with Cl^- described above, no EPR active material was produced. Instead, a paramagnetically shifted and broadened peak at -8 ppm was observed in the ^1H-NMR spectrum, indicating the formation of another paramagnetic, EPR-inactive material. Proceeding along similar lines of thought as illustrated above for the corresponding reaction of $\mathbf{1}^+$, the electrochemistry of the expected product of CO substitution, e.g. **6**, was investigated, showing that the compound is reversibly oxidized at $E_{1/2} = -0.58$ V. Similar to the Cp*/PMe_3 system, **6** has sufficient reducing power to take the starting material, $\mathbf{2}^+$, to the parent Mo(II) complex, **2**, producing in turn the Mo(IV) complex [Cp*$MoCl_2(dppe)]^+$, $\mathbf{6}^+$. A genuine sample of $\mathbf{6}^+$ was prepared by interacting **6** with 1 equiv of $Fc^+PF_6^-$, which showed a ^1H-NMR spectrum in $CDCl_3$ identical to that of the Cl^- addition reaction product. A ^1H-NMR experiment also showed that $\mathbf{6}^+$ does not interact with Cl^-, explaining the difference in final outcome between this system and the $\mathbf{1}^+/Cl^-$ system. Therefore, the reaction between $\mathbf{2}^+$ and Cl^- is described by eq 8.

$$2[\mathrm{Cp^*MoCl(dppe)(CO)}]^+ + \mathrm{Cl}^- \rightarrow \mathrm{Cp^*MoCl(dppe)(CO)} + [\mathrm{Cp^*MoCl_2(dppe)}]^+ + \mathrm{CO} \quad (8)$$

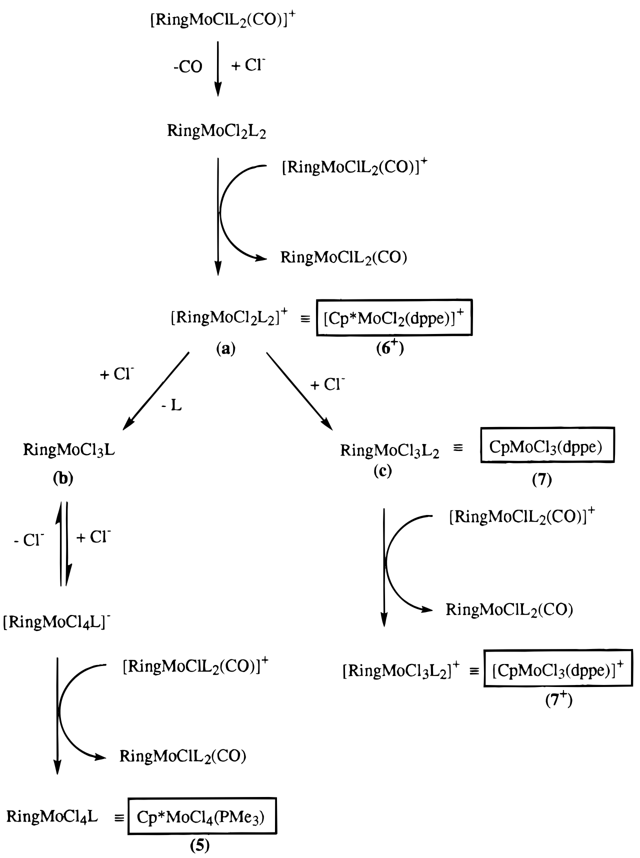
The reaction of $\mathbf{3}^+$ with excess Cl^- proceeds similarly to that of $\mathbf{1}^+$ in that the final products are a Mo(V) and a Mo(II) material. Once again, the reaction with Cl^- consumes all of the $\mathbf{3}^+$ and the IR confirms the production of the neutral parent complex, **3**. The ^1H- and ^{31}P-NMR spectra of the reaction products in $CDCl_3$ indicated two NMR active materials, one being **3** and the other being *eq,eq*-$CpMoCl_3(dppe)$, **7**, by comparison to literature characterization.[21] However, the EPR spectrum of the reaction mixture in THF or CH_2Cl_2 at room temperature shows a strong, slightly broadened singlet with Mo satellites ($g = 1.948$, $a_{Mo} = 52$ G). This spectrum slightly sharpened upon cooling to 213 K but not sufficiently to allow the phosphorus hyperfine splitting to be observed, and then it broadened again upon further cooling to 193 K. Given the result of the Cl^- addition to $\mathbf{1}^+$ (*vide supra*), a likely possibility for the EPR active product seems to be $[CpMoCl_3(dppe)]^+$, $\mathbf{7}^+$. For the $\mathbf{3}^+/Cl^-$ system, the initial product of CO substitution by Cl^-, namely $CpMoCl_2(dppe)$ ($E_{1/2} = -0.33$ V),[27] is able to reduce $\mathbf{3}^+$ to **3** ($E_{1/2} = -0.25$ V), being in turn oxidized to the Mo(IV) complex $[CpMoCl_2(dppe)]^+$. Unlike the corresponding Cp*/dppe system, $[CpMoCl_2(dppe)]^+$ can add another Cl^- to give the known neutral 18-electron, **7**, as already reported in the literature.[21] We have further confirmed this by generating $[CpMoCl_2(dppe)]^+$ from $CpMoCl_2(dppe)$ and Cp_2FePF_6, followed by addition of PPNCl. Identical ^1H and ^{31}P-NMR resonances with those reported[21] for **7** were immediately produced. Next, a cyclic voltammetric investigation of compound **7** was carried out, which showed two reversible oxidations at $E_{1/2} = -0.39$ and -0.02 V. Since two different isomers, eq−eq and ax−eq, are present in slow equilibrium for this compound,[21] it seems reasonable to assign each wave to the oxidation of a different isomer. The one isomer showing a reversible wave at -0.39 V is a sufficiently strong reductant to take $\mathbf{3}^+$ to **3**, becoming oxdized to $\mathbf{7}^+$ in the process, while the other isomer remains a neutral Mo(IV) species. As stated above, the ^{31}P NMR of the final products of the Cl^- addition showed the singlet resonance of the eq−eq isomer of **7**. Thus, the oxidation wave at $E_{1/2} = -0.02$ V can be assigned to the eq−eq isomer, which remains unoxidized during the Cl^- addition process, while the wave at $E_{1/2} = -0.39$ V is assigned to the ax−eq isomer. This also implies that, given the reversibility of the oxidation process, complex $\mathbf{7}^+$ should also adopt a pseudo-octahedral ax−eq configuration.

In order to confirm the identity of the EPR active material as $\mathbf{7}^+$, genuine samples were generated by two different pathways. The first one involved the interaction of $CpMoCl_4$ with dppe in THF. There was an immediate reaction with the precipitation of a light brown colored solid. This solid is insoluble in THF but dissolves in CH_2Cl_2, suggesting the ionic formulation $[CpMoCl_3(dppe)]^+Cl^-$ rather than the neutral adduct $CpMoCl_4(dppe)$, and showed the same EPR signal as the product of the Cl^- addition to $\mathbf{3}^+$. Compound $\mathbf{7}^+$ was also prepared without formulation ambiguities by chemical oxidation of **7** with $Cp_2Fe^+PF_6^-$ in THF . This product, unlike the corresponding Cl^- salt, was soluble in THF, and again showed the same EPR signal as the product of the $\mathbf{3}^+/Cl^-$ reaction, finally confirming the stoichiometry of eq 9. All of the results of the Cl^- addition to $\mathbf{1}^+$, $\mathbf{2}^+$, and $\mathbf{3}^+$ are summarized in Scheme 1.

$$(3 + 2n)[\mathrm{CpMoCl(dppe)(CO)}]^+ + (3 + 2n)\mathrm{Cl}^- \rightarrow (2 + n)\mathrm{CpMoCl(dppe)(CO)} + n\ eq,eq\text{-}\mathrm{CpMoCl_3(dppe)} + ax,eq\text{-}[\mathrm{CpMoCl_3(dppe)}]^+ + (1 + n)\mathrm{CO} \quad (9)$$

X-ray Analyses. An ORTEP diagram of $\mathbf{2}^+$, the first mononuclear Mo(III) carbonyl complex to be crystallographically characterized, is shown in Figure 3. The molecule exhibits a typical four-legged piano-stool geometry with an η^5-bound Cp* ring and the dppe ligand in the expected *cis* configuration, the other two positions being occupied by a chloride and a carbonyl ligand. The molecule is structurally similar to other known isoelectronic $CpMo^{III}$ complexes not containing a carbonyl ligand.[27] The Mo−CO distance (2.053(6) Å) is comparable with known diamagnetic Mo(III) dimers containing CO ligands, i.e. $[CpMo(CO)_2(\mu\text{-S-}t\text{-Bu})]_2(BF_4)$ (average 2.016(16) Å),[11] $[Cp_2Mo_2(CO)_3(MeCN)(\mu\text{-SPh})_2](BF_4)_2$ (average 2.01(4) Å),[12] and $[(CpMoCO)_2(\mu\text{-SMe})(S_2CH_2)]OTf$ (average 2.068(12) Å).[15] The Mo−Cl distance (2.473(2) Å) compares well with those in other half-sandwich Mo(III) complexes, e.g. 2.489-

Scheme 1



(1) Å (average) in $Cp^*MoCl_2(PMe_3)_2$,[23] 2.471(3) Å (average) in $CpMoCl_2(PMe_3)_2$,[32] and 2.427(9) Å in $[CpMoCl(PMe_3)_3]^+$.[33] The two Mo−P distances in [**2**]PF_6 differ by over 0.05 Å, with the P trans to the CO ligand having the longer distance, this being a possible manifestation of the stronger trans influence of the CO ligand compared to the Cl^- ligand. The average Mo−P distance (2.523 Å) is similar to the average Mo−P distances (2.51 Å) found in $Cp^*MoCl_2(PMe_3)_2$,[23] and slightly longer than the Mo−P bonds in $CpMoBr_2(dppe)$, which average 2.460(4) Å.[20] Another typical feature of the four-legged piano-stool Mo(III) molecules is the distinct "slip" of the ring with two of the C atoms distinctly closer than the other three, the difference between the longest and the shortest Mo−C bond being as much as 0.18 Å.[27] The structure of [**2**]PF_6 shows a similar phonemenon, the largest Δ(Mo−C) being 0.13 Å.

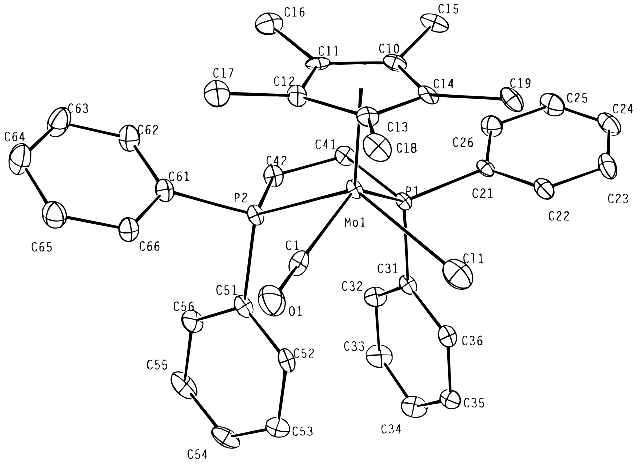


Figure 3. ORTEP view of the 2^+ ion. Ellipsoids are drawn at the 40% probability level.

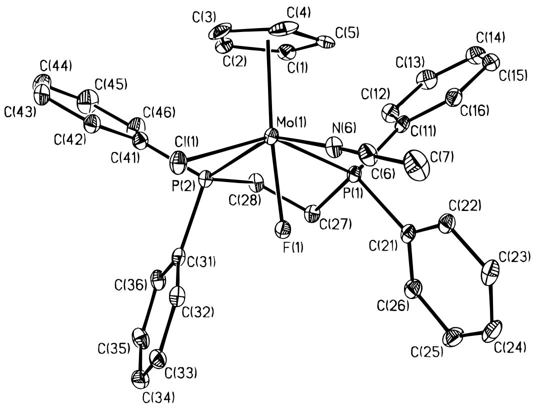


Figure 4. ORTEP view of the 4^+ ion. Ellipsoids are drawn at the 40% probability level.

An ORTEP view of 4^+ is shown in Figure 4. The molecule exhibits a pseudo-octahedral geometry when the η^5-Cp ring is considered to occupy a single coordination position. The F atom occupies the *trans* positions with respect to the ring, whereas the Cl atom, the MeCN molecule, and the dppe ligand occupy equatorial sites. All of the equatorial atoms are bent significantly away from the Cp ring, with values of the CNT−Mo−equatorial atom angles between 102.5° and 105.5°. This geometrical characteristic is also found for other 18-electron $CpMo^{IV}$ complexes, e.g. $CpMoCl_3(dppe)$,[21] $CpMoCl_3[P(OCH_2)_3CEt]_2$,[34] and $CpMoCl_3(PMe_2Ph)_2$.[30] The average Mo−P bond length (2.515(1) Å) in the title complex corresponds well with the $Mo-P_{eq}$ distance (2.521(2) Å) found in $CpMoCl_3(dppe)$[21] as well as the average distance (2.554(1) Å) found in $CpMoCl_3(PMe_2Ph)_2$.[30] The Mo−Cl distance (2.4984(10) Å) is similar to that found for the average $Mo-Cl_{eq}$ (2.527(1) Å) distance in $CpMoCl_3(PMe_2Ph)_2$ and the average Mo−Cl distance (2.476(3) Å) found for $CpMoCl_3(dppe)$. Very few $Mo^{IV}-F$ complexes have been crystallographically characterized. The Mo−F distance in the title complex (1.951(2) Å) is almost identical with that found in $[MoOF(Ph_2PCH{=}CHPPh_2)_2]^+$ (1.95(1) Å),[35] which has the F trans to the oxo ligand. The comparison seems reasonable due to the psuedo-octahedral geometry of the two molecules as well as the presence of strong trans-influencing ligands, Cp and O, in each of the compounds. A strong trans influence for the Cp ligand has also been observed in other compounds, e.g. $Cp^*WBr_3(CO)_2$.[36]

Discussion

While the electrochemical oxidation of compound $Cp^*MoCl(CO)_3$ is irreversible and occurs at the high potential of +0.55 V vs Fc/Fc^+, the isoelectronic complex $Cp^*MoCl(PMe_3)_3$ is oxidized reversibly at −1.32 V[27] (a stabilization of almost 2 V!) and the oxidation product, the 17-electron $[Cp^*MoCl(PMe_3)_3]^+$, has been isolated and crystallographically characterized.[28] We therefore reasoned that the mixed-ligand system $Cp^*MoCl(CO)(PMe_3)_2$, **1**, might undergo a reversible oxidation and generate a sufficiently stable Mo−CO compound. The results shown in this contribution show that our expectations have been fulfilled. The first stable 17-electron paramagnetic

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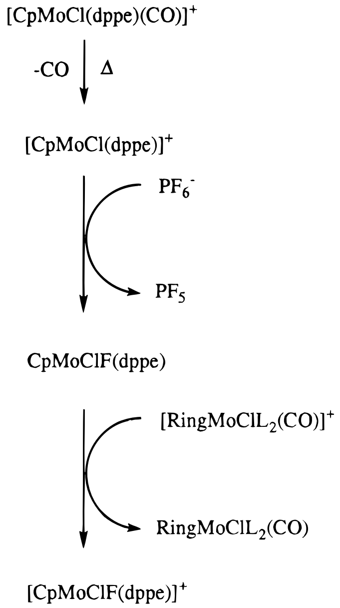
Mo(III) carbonyl complexes have been synthesized, spectroscopically and structurally characterized, and their thermal stability and reactivity toward Cl^- have been studied. Complexes **1**$^+$, **2**$^+$, and **3**$^+$ are easily prepared by chemical oxidation of the neutral parent molecules with 1 equiv of $Fc^+PF_6^-$. Thermal decomposition studies indicate that the stability of the carbonyl cation is directly related to the strength of the Mo−CO bond (i.e. the lower the ν_{CO}, the more stable the cation). Since weak Mo−CO bonds are expected for relatively high oxidation state metals, it seems reasonable to suggest that the electronic nature of the ancillary ligands helps stabilize these cationic complexes. The stability increase on going from **3**$^+$ to **2**$^+$ could be attributed to both the greater donor power and greater steric protection of the Cp* vs the Cp ligand.

One interesting aspect of the carbonyl cations is their reactivity toward nucleophiles. All three carbonyl cations react instantaneously with Cl^-, but the nature of the end products depends on the possibilities for the addition of more than one Cl^- as well as potential electron transfer processes. Scheme 1 shows that the pathways for the production of three different types of complexes (**5**, **6**$^+$, and **7**$^+$) are related to each other. As is shown, the first step always involves the attack of the Cl^- to the Mo center, replacing the CO ligand, and generating a neutral Mo(III) complex. A rapid electron transfer reaction occurs, involving the starting carbonyl cation, producing a Mo(IV) cation (**a**) and a neutral Mo(II) carbonyl complex. At this point the **2**$^+$ system stops due to the inability to add another Cl^- by either forming a very crowded 18-electron trichloride bis-phosphine complex or overcoming the chelate effect of the dppe ligand. The **1**$^+$ system does not have the barrier of the chelate effect to overcome and can easily displace a PMe_3 ligand in exchange for an additional Cl^-, producing the 16-electron complex, $Cp^*MoCl_3(PMe_3)$ (**b**). The followup chemistry has been fully rationalized with the independent studies presented in the Results section, and involves the ultimate formation of compound **5**. In the case of **3**$^+$, the smaller size of the Cp ligand with respect to Cp* allows a Cl^- ion to bind (**a**) and form the 18-electron $CpMoCl_3(dppe)$ (**c**). Cyclic voltammetric studies on $CpMoCl_3(dppe)$ showed that **7**$^+$ can be formed in the presence of a fair oxidant, i.e. **3**$^+$. For the same reason invoked to explain the stability of **6**$^+$ in the **2**$^+$ system, product **7**$^+$ remains a salt and does not add Cl^- due to the chelate effect of the dppe ligand and steric constraints. Thus, for all three systems, the products of Cl^- addition are the neutral parent carbonyl complex and one of the higher oxidation state complexes, **5**, **6**$^+$, or **7**$^+$.

Scheme 2



The first step of Scheme 1 deserves further discussion. This is a ligand exchange on a 17-electron organometallic complex, which is known to proceed in general by an associative pathway.[2] However, for Cp- and Cp*-containing Mo(III) organometallics, we have recently demonstrated the possible involvement of dissociative (e.g. 15-electron) intermediates.[37] This occurs, however, in the phosphine exchange process on the neutral $CpMoCl_2L_2$ complexes, i.e. a system in which the incoming ligand is relatively bulky (a condition disfavoring an associative path), the outgoing ligand is not strongly bound, and the unsaturated intermediate can be stablized by π-donor ancillary ligands and by the spin reorganization energy (both the latter two conditions favoring a dissociative path). A spin quartet ground state for the 15-electron $CpMoCl_2(PH_3)$ model compound has been recently calculated.[38] However, the halide exchange on the same system was shown to be associative.[29] For the process under consideration here, the coulombic effect of the opposite charges of complex and incoming nucleophile provides a strong bias in favor of the associative mechanism. It is, however, intriguing to consider the labilization of the CO ligand to give a cationic 15-electron complex, $[(ring)MoClL_2]^+$. This labilization could play an important role in the mechanism of thermal decomposition, since no strong nucleophilic reagent is present in that case. The formation of the same product by either thermal or photochemical decomposition of **3**$^+$ would seem to point toward a CO dissociation mechanism, since irradiation is known to promote CO dissociation processes.[39] At the same time, the much faster rate of the Cl^- addition reaction with respect to the thermal decomposition process indicates that the former *must* follow an associative pathway, because if this were a dissociative one, its rate would be regulated by the rate of CO dissociation and, consequently, should not be faster than the thermal decomposition process. To date, no stable $CpMo^{III}$ 15-electron complex has been isolated. Given the highly unsaturated nature of these hypothetical 15-electron complexes, their reactivity and tendency to reestablish a coordinately saturated system is expected to be quite high. This is manifested, during the decarbonylation of **3**$^+$, by the F^- abstraction from PF_6^-. Scheme 2 shows a possible pathway to the production of **4**$^+$. It is important to remember that the neutral complex **3** is also observed among the reaction products. The first step involves the formation of the highly reactive 15-electron intermediate, which quickly reacts with a molecule of PF_6^-, producing a neutral Mo(III) complex, CpMoClF(dppe). At this point, the system may enter the familiar electron transfer process seen in Scheme 1, producing $[CpMoClF(dppe)]^+$ as well as the neutral carbonyl complex, **3**. This process is expected because the effect of the fluoride ligand in the coordination sphere should be that of lowering the potential necessary for the oxidation of the 17-electron CpMoXY(dppe) (X,Y = halide). Although fluoride complexes are currently not known and it is therefore not possible to directly substantiate this hypothesis, it should be observed that the oxidation of $CpMoX_2(dppe)$ becomes more facile in the order I < Br < Cl, i.e. the lighter halide ligand increases the tendency of the metal to be oxidized.[20] This trend has been attributed to the better ability of the lighter halide to

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stabilize the higher oxidization state via π-donation. After formation of $[CpMoClF(dppe)]^+$ via electron transfer, the reaction ceases presumably because of the insolubility of the complex in THF as well as the unavailability of additional X^-. The insoluble red precipitate obtained from the thermal decomposition reaction indeed analyzes correctly for $[CpMoClF(dppe)]$-$[PF_6]$ (see Experimental Section). The addition of a molecule of MeCN occurs during the crystalization to finally produce $\mathbf{4}^+$.

Conclusion

We have reported in this contribution that mononuclear, paramagnetic Mo(III)−carbonyl compounds can be stabilized by strongly donating and sterically protecting phosphine and Cp ligands. Their structure and EPR properties are similar to those of an extensive class of half-sandwich Mo(III) complexes. The strength of the Mo−CO has been probed by thermal decompositions, indicating that the bond cleavage occurs more easily for the complex with the weakest CO bond. The results of the thermal and photochemical decomposition of $\mathbf{3}^+$ suggest the formation of an extremely reactive 15-electron intermediate that is able to abstract a fluoride ion from PF_6^-. Attack of the 17-electron carbonyl complexes by Cl^- probably occurs, on the other hand, associatively to afford products of CO substitution that further engage in redox processes with the unreacted Mo(III)−carbonyl compounds to ultimately lead to a variety of different products, whose nature and mechanism of formation has been fully elucidated.

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Supporting Information Available: X-ray structural determination of $[\mathbf{2}]PF_6\cdot THF$ and $[\mathbf{4}]PF_6\cdot MeCN$: complete crystallographic data, atomic coordinates, and full tables of distances and angle and anisotropic thermal parameters (30 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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