(Scheme III). The yield for each of the reactions is high. Since one can regenerate the acetonitrile starting material, it may be possible to develop a system which will produce chiral amines from nitriles utilizing this metal fragment. Use of the $[Tp'(CO)(RC_2Me)W]^+$ moiety as an electronically flexible Lewis acid with a high degree of stereocontrol appears promising for further research.

Acknowledgment. We thank the National Science Foundation for support of this research. Helpful discussions with Professor M. S. Brookhart are gratefully acknowledged.

Four-Legged Piano Stool Molybdenum(II) Compounds without Carbonyl Ligands. 1. Synthesis, Properties, and Chloride Substitution Reactions of $(\eta^5\text{-}C_5R_5)MoCl(PMe_3)_3$ (R = H, Me) and X-ray Crystal Structure of $[CpMoCl(PMe_3)_3]^+PF_6^-$

Fatima Abugideiri, Malcolm A. Kelland, and Rinaldo Poli*

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received September 19, 1991

The synthesis, solution structure, and redox properties of a series of cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp*) molybdenum-trimethylphosphine complexes is reported. $(\eta^5\text{-}C_5R_5)MoCl(PMe_3)_3$ (R = H (1), Me (1*)) compounds are prepared by sodium amalgam reduction of $CpMoCl_2$ or Cp^*MoCl_4, respectively, in the presence of PMe_3 and under an argon atmosphere. 1 is reversibly oxidized at $E_{1/2} = -1.46$ V with respect to $Cp_2Fe^{0/+}$. $[1]^+$ has been isolated as the PF_6^- salt and crystallographically characterized. Crystal data: orthorhombic, space group $P2_12_12_1$, $a = 11.008$ (4) Å, $b = 15.195$ (4) Å, $c = 13.843$ Å, $V = 2315.7$ (14) Å^3, $Z = 4$, $R = 0.0884$, and $R_w = 0.0876$. Interaction between $CpMoCl_4$ and Zn, followed by addition of PMe_3, produces a compound of formula $[CpMoCl(PMe_3)_3]\cdot ZnCl_3$ (2), which displays EPR properties identical with those of $[1]^+$. Treatment of 1 with either $LiEt_3BH$ or K in heptane affords pure $CpMoH(PMe_3)_3$ (3), whereas 1* and $LiEt_3BH$ give a mixture of $Cp^*MoH(PMe_3)_3$ (3*) and $Cp^*MoH_3(PMe_3)_2$ (4*). Alkylation with MeLi affords the methyl derivatives, $(\eta^5\text{-}C_5R_5)MoCH_3(PMe_3)_3$ (R = H (5), Me (5*)), which are stable at room temperature for R = H and at $T = -20$ °C for R = Me. At higher temperatures, both compounds eliminate CH_4, but while 5 undergoes metalation of a PMe_3 ligand to form the compound $CpMo(\eta^2\text{-}CH_2PMe_2)(PMe_3)_2$ (6), compound 5* undergoes metalation at a Cp* methyl group, to form compound $(\sigma{:}\eta^5\text{-}CH_2C_5Me_4)Mo(PMe_3)_3$ (7*). Treatment of 1 with PhLi proceeds directly to compound 6 without detection of an intermediate containing the Mo–Ph linkage. The reaction of 1 and 1* with allylmagnesium bromide affords the allyl derivatives $(\eta^5\text{-}C_5R_5)Mo(\eta^3\text{-}C_3H_5)(PMe_3)_2$ (R = H (8), Me (8*)).

Introduction

We have recently been investigating the chemistry of paramagnetic molybdenum(III) monocyclopentadienyl derivatives,[1-3] which exhibit interesting electrochemical, EPR, structural, and bonding properties, as well as a peculiar halide exchange reactivity.[4-6] We have also attempted to replace the halide ligands with methyl groups, only to discover that the resulting $CpMo(CH_3)_2L_2$ (L = phosphine) derivatives are unstable and decompose with metal reduction to four-legged piano stool complexes of Mo(II). Of these products, $CpMo(o\text{-}C_6H_4PMe_2)(PMe_2Ph)_2$, which contains an ortho-metalated phenyl ring, has been structurally characterized.[7] The reaction of $CpMoCl_2(PMe_3)_2$ with MeLi, which ultimately gives $CpMo(CH_3)(PMe_3)_3$ in the presence of excess PMe_3, was proposed to occur through the intermediacy of $CpMoCl(PMe_3)_3$.[7] We were thus interested in synthesizing this Mo(II) material and verifying that it can be transformed into the methyl product. In this contribution, we report the synthesis of the $CpMoCl(PMe_3)_3$ compound (1) and its Cp* analogue (1*) and their transformation to the corresponding methyl derivatives, as well as a few other compounds obtained by exchanging the chloride ligand with other anionic ligands. In the following paper,[8] we report other derivatives obtained by replacing one or more of the PMe_3 ligands in 1 and 1* with other neutral ligands.

There is another interest in this cyclopentadienyl-containing Mo(II) chemistry, which is of a more structural nature. While comparing the structural features of 17-electron four-legged piano stool Mo(III) molecules synthesized in our laboratory with those of similar compounds, we discovered some general trends in the angle between bonds to the "basal" ligands and to the center of the ring (the θ angle), which depend on the metal electron count

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0276-7333/92/2311-1303$03.00/0

Table I. NMR Spectroscopic Data (δ) for All New Compounds

compd	solvent	^1H	$^{31}P\{^1H\}$	^{13}C or $^{13}C\{^1H\}$
1	C_6D_6	4.33 (d, 5 H, J_{PH} = 2 Hz, Cp), 1.41 (vt,[a] 18 H, J_{PH} = 7 Hz, 2 PMe_3), 0.94 (d, 9 H, J_{PH} = 6.5 Hz, PMe_3)	25.8 (t, 1 P, J_{PP} = 52 Hz), 10.1 (d, 2 P, J_{PP} = 52 Hz)	
5	C_6D_6	4.06 (d, 5 H, J_{PH} = 2 Hz, Cp), 1.23 (vt,[a] 18 H, J_{PH} = 5 Hz, 2 PMe_3), 1.07 (d, 9 H, J_{PH} = 5.5 Hz, PMe_3), −0.10 (td, 3 H, J_{PH}(t) = 11.5 Hz, J_{PH}(d) = 2.5 Hz, Me)	19.2 (m, 1 P, J_{PP} = 20 Hz),[b] 17.3 (m, 2 P, J_{PP} = 20 Hz)[b]	83.5 (s, Cp), 27.0 (d, J_{PC} = 18 Hz, PMe_3), 25.1 (vt,[a] J_{PC} = 18 Hz, 2 PMe_3), −8.56 (s, CH_3)
6	C_6D_6 (20 °C)	4.33 (t, 5 H, J_{PH} = 1 Hz, Cp), 1.25 (d, 6 H, J_{PH} = 9 Hz, PMe_2), 1.16 (dd, 18 H, J_{PH} = 3 Hz, J_{PH} = 1 Hz, 2PMe_3), −0.38 (br s, 2 H, CH_2)	26.9 (d, 2 P, J_{PP} = 40 Hz), −40.6 (t, 1 P, J_{PP} = 40 Hz)	82.63 (s, Cp), 26.71 (br s, 2 PMe_3), 19.79 (dd, J_{PC} = 14 Hz, J_{PC} = 6 Hz, PMe_2), −21.00 (q, J_{PC} = 4.5 Hz, CH_2)
	$C_6D_5CD_3$ (−60 °C)	4.28 (br s, 5 H, Cp), 1.24 (br d, 3 H, PMe),[d] 1.19 (br d, 3 H, PMe),[d] 1.14 (br d, 9 H, J_{PH} = 9 Hz, PMe_3), 1.01 (br d, 9 H, J_{PH} = 9 Hz, PMe_3), 0.12 (br, 1 H, CH), −0.92 (dd, 1 H, J_{HH} = 20 Hz, J_{PH} = 8 Hz, CH)	29.9 (m, 1 P),[c] 26.9 (m, 1 P),[c] −39.6 (d, 1 P, J_{PP} = 80 Hz)	
8	C_6D_6	4.29 (t, 5 H, J_{PH} = 1 Hz, Cp), 2.99 (m, 1 H, CH_2–*CH*–CH_2), 1.43 (m, 2 H, *CH*H–CH–*CH*H, endo or exo), 1.30 (m, 2 H, *CH*H–CH–*CH*H, exo or endo), 0.88 (vt,[a] 18 H, J_{PH} = 6.5 Hz, 2 PMe_3)	20.8 (s)	83.9 (d, J_{HC} = 172 Hz, Cp), 66.6 (d, J_{HC} = 158 Hz, C–*C*–C), 32.1 (t, J_{HC} = 134 Hz, *C*–C–*C*), 22.2 (d or vt, J_{HC} = 122 Hz, J_{PC} = 10.5 Hz, 2 PMe_3)
1*	C_6D_6	1.66 (s, 15 H, Cp*), 1.32 (vt,[a] 18 H, J_{PH} = 6 Hz, 2 PMe_3), 1.10 (d, 9 H, J_{PH} = 6 Hz, PMe_3)	28.9 (t, 1 P, J_{PP} = 49 Hz), 9.2 (d, 2 P, J_{PP} = 49 Hz)	
3*	C_6D_6 (20 °C)	1.90 (s, 15 H, Cp*), 1.31 (vq,[e] 27 H, J_{PH} = 2 Hz, 3 PMe_3), −8.56 (q, 1 H, J_{PH} = 55 Hz, Mo–*H*)	18.9 (s)	
	$C_6D_5CD_3$ (−63 °C)	1.95 (s, 15 H, Cp*), 1.36 (d, 18 H, J_{PH} = 5 Hz, 2 PMe_3), 1.21 (d, 9 H, J_{PH} = 5 Hz, PMe_3), −8.66 (td, 1 H, J_{PH} = 13 Hz, J_{PH} = 77 Hz, Mo–*H*)	17.8 (m, 2 P),[c] 21.1 (m, 1 P)[c]	
4*	C_6D_6	2.04 (s, 15 H, Cp*), 1.18 (d, 18 H, 2 PMe_3, J_{PH} = 6.5 Hz), −5.14 (t, 3 H, J_{PH} = 53 Hz, Mo–*H*)	17.0 (s)	
5*	$C_6D_5CD_3$ (−15 °C)	1.63 (s, 15 H, Cp*), 1.25 (d, 9 H, J_{PH} = 5 Hz, PMe_3), 1.15 (d, 18 H, J_{PH} = 5 Hz, 2 PMe_3), −0.32 (t, 3 H, J_{PH} = 11 Hz, CH_3)	23.7 (t, 1 P, J_{PP} = 22 Hz), 19.0 (d, 2 P, J_{PP} = 22 Hz)	
7*	C_6D_6	2.58 (m, 2 H, CH_2), 1.88 (s, 6 H, 2 CH_3), 1.86 (s, 6 H, 2 CH_3), 1.21 (d, 18 H, J_{PH} = 5 Hz, 2 PMe_3), 1.15 (d, 9 H, J_{PH} = 5 Hz, PMe_3)	6.1 (d, 2 P, J_{PP} = 28 Hz), 1.2 (t, 1 P, J_{PP} = 28 Hz)	98.3 (s, *C*–CH_2), 95.0 (s, 2 *C*–CH_3), 93.8 (s, 2 *C*–CH_3), 48.1 (t, J_{PC} = 9 Hz, CH_2), 27.4 (vt,[a] J_{PC} = 18 Hz, 2 PMe_3), 26.8 (d, J_{PC} = 15 Hz, PMe_3), 14.4 (s, 2 CH_3), 13.8 (s, 2 CH_3)
8*	C_6D_6	2.86 (m, 1 H, CH_2–*CH*–CH_2), 1.66 (s, 15 H, Cp*), 1.37 (m, 2 H, *CH*H–CH–*CH*H, endo or exo), 0.91 (vt,[a] 18 H, J_{PH} = 6 Hz, 2 PMe_3), 0.22 (m, 2 H, *CH*H–CH–*CH*H, exo or endo)	18.3 (s)	94.4 (s, Cp*), 69.9 (s, C–*C*–C), 39.7 (s, *C*–C–*C*), 21.6 (vt, J_{PC} = 11 Hz, 2 PMe_3), 12.0 (s, Cp*)

[a] Intermediate pattern between doublet and virtual triplet. Coupling constant is given on the basis of the two outer peaks. [b] Second-order pattern; for the simulation, see Figure 1S (supplementary material). [c] Second-order pattern; not simulated. [d] Accurate values for the coupling constants could not be obtained due to overlap. [e] vq = virtual quartet.

and on whether the ligands are π-acids or π-bases.[9] One of the conclusions emerging from this analysis was that phosphine ligands behave as π-acids. The limited data on the subject seemed to suggest that the π-accepting ability of the phosphine ligands is enhanced when strong π-acceptor ligands (e.g. CO) are not present to compete for metal electron density. Our recent structure of the ortho-metalated $CpMo(o\text{-}C_6H_4PMe_2)(PMe_2Ph)_2$ compound[7] seems to confirm the validity of these considerations. In order to gather more information on this topic, it was therefore of interest to investigate other four-legged piano stool complexes of Mo(II) containing only phosphines and other ligands with weak or no π-acceptor properties.

Experimental Section

All operations were conducted under an atmosphere of argon unless otherwise stated. Solvents were dried by conventional methods and distilled under dinitrogen, followed by thorough degassing and saturation with argon prior to use. Instruments used were as follows: NMR, Bruker AF200, WP200, and AM400; EPR, Bruker ER200; MS, VG 7070E. For the electron impact mass spectra, the samples were introduced into the spectrometer with a desorption chemical ionization probe. For the fast atom bombardment mass spectra, a xenon ion source was used. The cyclic voltammograms were obtained by using an EG&G scanning potentiostat equipped with oscilloscope and square-wave generator for *IR* correction. The data were analyzed with MacLab hardware/software. The measurements were carried out in a cell which was equipped with two screw-threaded joints at top for fitting the flat surface working Pt electrode and the Ag/AgCl reference electrode, a stopcock, and a Pt auxiliary electrode, which was fitted at the bottom through Pt/uranium glass/Pyrex glass seals. Tetra-*n*-butylammonium hexafluorophosphate was used as supporting electrolyte, and the potentials were calibrated against the ferrocene–ferrocenium couple, which was introduced into the cell at the end of each experiment.

Elemental analyses were by Galbraith Laboratories, Knoxville, TN. The following compounds were prepared as described in the literature: $CpMoCl_4$,[2] Cp^*MoCl_4,[10] $CpMoCl_2$,[6] and $CpMoCl_2(PMe_3)_2$.[6] PMe_3 was purchased from Aldrich and trap-to-trap distilled prior to use. C_3H_5MgBr (1.0 M in Et_2O), $LiEt_3BH$ (1.0 M in THF), LiMe (1.4 M in Et_2O), LiPh (1.8 M in 70/30 cyclohexane/Et_2O), and $LiAlH_4$ were purchased from Aldrich and were used as received. All the NMR spectra of the new compounds are reported in Table I.

Preparation of $CpMoCl(PMe_3)_3$ (1). PMe_3 (1.29 mL, 12.5 mmol) was added to a stirred slurry of $CpMoCl_2$ (0.97 g, 4.2 mmol) in THF (30 mL). After formation of $CpMoCl_2(PMe_3)_2$ had oc-

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curred,[6] the solution was filtered from minor amounts of a yellow sticky solid, transferred onto sodium amalgam (100 mg, 4.3 mmol, 0.5% wt), and stirred for 6 h at room temperature. The resulting dark violet solution was evaporated to dryness, the residue was extracted with *n*-heptane (3 × 20 mL), and the solution was filtered and concentrated to 10 mL. Cooling to −80 °C overnight gave dark violet needles, which were filtered off and dried in vacuo. Yield: 1.10 g, 62%. Various attempts at obtaining elemental analytical data on this compound (operations carried out under argon) always gave low C, H content. Formulation of this compound as $CpMoCl(PMe_3)_3$ is confirmed by ^{1}H-NMR spectroscopy (see Table I), by MS [EI, 70 eV; envelope corresponding to $(M + H)^+$; % intensity of highest peak (m/e 427) = 1.4], and by the chemical transformations described below. The compound is very soluble in hydrocarbons and decomposes in CH_2Cl_2 with quantitative formation of its precursor, compound $CpMoCl_2(PMe_3)_2$.

Preparation of $Cp^*MoCl(PMe_3)_3$ (1*). PMe_3 (2.6 mL, 26 mmol) was added to a slurry of Cp^*MoCl_4 (3.15 g, 8.44 mmol) in THF (100 mL) at 0 °C. Na/Hg (580 mg, 1% solution, 25.3 mmol) was added and the solution brought to 20 °C with vigorous stirring. After 5 h the initially orange-brown solution had become dark brown-green (dark red through transmitted light). The solution was filtered and evaporated to dryness. The residue was extracted with 80 mL of pentane, followed by washings with 3 × 30 mL of pentane. The combined filtered extracts were concentrated to ca. 120 mL and cooled to −78 °C. After 2 days the large black crystals of the product were filtered off, washed with cold pentane, and dried. Yield: 3.05 g, 73%. Anal. Calcd for $C_{19}H_{42}ClMoP_3$: C, 46.10; H, 8.60. Found: C, 46.03; C, 8.42.

Oxidation of Compound 1. Preparation of $[1]^+PF_6^-$. Compound 1 (214 mg, 0.50 mmol) was dissolved in THF (20 mL), and $AgPF_6$ (129 mg, 0.50 mmol) was added while the solution was stirring. After 1 h the resulting pale brown solution was filtered from a dark brown precipitate and the precipitate washed with THF (2 × 5 mL). The combined filtrates were evaporated to dryness, and the residue was extracted with CH_2Cl_2 (10 mL). After filtration and removal of ca. 5 mL of solvent by evaporation, the yellow-orange solution was layered with Et_2O (20 mL) and stored for 1 week. Orange crystals slowly deposited. These were filtered off and dried. Yield: 45 mg, 15%. EPR (CH_2Cl_2): doublet of triplet, g = 2.006; a_P(d) = 25 G, a_P(t) = 20 G, a_{Mo} = 37 G. A single crystal selected from this batch was used for the X-ray analysis.

Preparation of $[CpMoCl(PMe_3)_3 \cdot ZnCl_3]$ (2). $CpMoCl_4$ (199 mg, 0.657 mmol) was treated with Zn powder (49 mg, 0.749 mg) in THF (20 mL) with vigorous stirring. The formation of golden-brown insoluble $CpMoCl_2$ took place as described earlier.[6] After 3 h, PMe_3 (0.25 mL, 2.5 mmol) was added and stirring at room temperature was continued. A microcrystalline brown precipitate slowly deposited. This was filtered off, washed with THF, and dried. Yield: 269 mg, 69%. EPR inspection (CH_2Cl_2) showed minor contamination by compound $CpMoCl_2(PMe_3)_2$. The compound was purified by washing with 10 mL of hot THF, followed by dissolution in CH_2Cl_2 (5 mL), and reprecipitation by slow diffusion of *n*-heptane, which had been layered on top of the solution. The EPR spectrum of this material is identical to that of $[1]^+PF_6^-$. Anal. Calcd for $C_{14}H_{32}Cl_4MoP_3Zn$: C, 28.2; H, 5.4. Found: C, 28.6; H, 5.7.

Reaction of Compound 2 with PPN^+X^- (X = Cl, I). EPR Monitoring. An aliquot of a CH_2Cl_2 solution of 2 and excess PPN^+Cl^- were transferred into a 3-mm o.d. glass tube which was sealed under dinitrogen. The progress of the reaction was monitored by EPR spectroscopy. The EPR spectrum slowly changed to the characteristic spectrum of $CpMoCl_2(PMe_3)_2$.[1] Complete conversion was achieved in ca. 24 h.

An aliquot of a solution of 2 (8.0 mg, 1.3 × 10^{-2} mmol) and PPN^+I^- (28 mg, 4.3 × 10^{-2} mmol) in CH_2Cl_2 (5 mL) was transferred in a 3-mm o.d. glass tube which was sealed under dinitrogen. The progress of the reaction was monitored by EPR spectroscopy. Slow growth of new peaks that could be assigned to $CpMoCl_2(PMe_3)_2$ was observed, and the final spectrum (ca. 24 h) contained a distribution of compounds $CpMoI_2(PMe_3)_2$, $CpMoClI(PMe_3)_2$, and $CpMoCl_2(PMe_3)_2$ in the proportion of 1:29:70. Quantitative determination of relative concentrations from EPR intensities was carried out as described elsewhere.[4]

Reaction of $(\eta^5\text{-}C_5R_5)MoCl(PMe_3)_3$ with $LiEt_3BH$. (a) R = H. Preparation of $CpMoH(PMe_3)_3$ (3). The stoichiometric amount of $LiEt_3BH$ (1.0 M in THF) was added to a stirred solution of 1 made in situ as described above from $CpMoCl_2$ (100 mg, 0.43 mmol). The violet THF solution changed color immediately to brown-yellow. The solution was evaporated to dryness, extracted with heptane, filtered, and evaporated to dryness again to give the pure (by NMR) compound 3 as a waxy yellow solid. ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopic properties are in agreement with those reported in the literature.[11]

Compound 3 is also the sole hydrocarbon-soluble product of the reaction between $CpMoCl_2(PMe_3)_2$, PMe_3, and excess $LiEt_3BH$ in THF.

(b) R = Me. Formation of $Cp^*MoH(PMe_3)_3$ (3*) and $Cp^*MoH_3(PMe_3)_2$ (4*). Compound 1* (100 mg, 0.20 mmol) was dissolved in Et_2O (10 mL) and treated with an excess of a 1.0 M THF solution of $LiEt_3BH$ (1.5 mL, 1.5 mmol). A dark orange solution forms immediately. Evaporation to dryness, followed by extraction with pentane, filtration, and evaporation to dryness gave a residue which consisted (by NMR in C_6D_6) of a 75:25 mixture of 3* and 4*. Treatment of this solution with PMe_3 did not change the relative ratio of compounds 3* and 4*. A mass spectrometric investigation of the residue (FAB, glycerol) showed envelopes corresponding to $(3^*)^+$ [% intensity of highest peak (m/e 462) = 7.5] and $(3^* - PMe_3 - 2H)^+$ and/or $(4^* - 4H)^+$ [% intensity of highest peak (m/e 384) = 100].

Reaction of Compound 1 with K in *n*-Heptane. Compound 1 (50 mg, 0.12 mmol) was dissolved in 10 mL of *n*-heptane and the resulting solution transferred into a Schlenk containing an excess of K mirror. The initial violet solution turned brown-yellow after a few hours of stirring at room temperature. The solution was filtered and evaporated to dryness. Inspection by ^{1}H-NMR spectroscopy in C_6D_6 showed $CpMoH(PMe_3)_3$ as the only Mo-containing species.

Reaction of $(\eta^5\text{-}C_5R_5)MoCl(PMe_3)_3$ with MeLi. (a) R = H. Formation of $CpMo(CH_3)(PMe_3)_3$ (5). Excess LiMe (1.4 M solution in Et_2O) was added to a stirred solution of 1 (ca. 20 mg, 0.05 mmol) in pentane (5 mL) at 0 °C. The solution turned yellow over a few minutes. After evaporation to dryness at 0 °C, the residue was extracted with cold (0 °C) pentane (10 mL), followed by filtration of the resulting solution and evaporation to dryness. A yellow solid was obtained. The ^{1}H-NMR spectrum of this material is identical to that reported earlier for compound 5.[7] The ^{31}P{^{1}H}-NMR spectrum shows second-order behavior and is reported in Figure 1S. The compound is stable in solution at 20 °C for several days, although the heat of the NMR probe when the broad band decoupler is used for the ^{31}P{^{1}H}-NMR experiment converts it smoothly to compound 6 (vide infra). MS (EI, 70 eV): $(M - 3H)^+$ [% intensity of highest peak (m/e 401) = 2.0].

(b) R = Me. Formation of $Cp^*Mo(CH_3)(PMe_3)_3$ (5*). LiMe (0.05 mL of a 1.4 M solution in Et_2O, 0.07 mmol) was added to a stirred solution of 1* (20 mg, 0.04 mmol) in Et_2O (3 mL) at −30 °C. The solution turned orange-yellow in a few minutes. After evaporation at −30 °C, the residue was extracted with pentane (5 mL) at −30 °C, followed by filtration and evaporation to dryness at −30 °C. A yellow solid was obtained. Elemental and mass spectrometric analyses could not be carried out because of thermal decomposition above 0 °C. Solutions of the compound also decompose above 0 °C to afford deep red solutions of compound 7*; see below.

Preparation of $CpMo(\eta^2\text{-}CH_2PMe_2)(PMe_3)_2$ (6). (a) By Thermal Decomposition of Compound 5. The NMR sample of compound 5 in C_6D_6 was maintained in the warm probe of the NMR instrument (warming was due to the broad band decoupler used for the ^{31}P{^{1}H}-NMR experiment). Periodic monitoring by ^{1}H-NMR spectroscopy showed clean conversion to compound 6. The growth of a singlet at δ 0.15 indicated the quantitative formation of CH_4.

(b) From Compound 1 and LiPh. LiPh (0.31 mL of a 1.8 M solution in Et_2O/cyclohexane, 0.55 mmol) was added to a stirred solution of compound 1 (0.235 g, 0.554 mmol) in *n*-heptane (20 mL). The solution turned orange-brown instantly. After $^1/_2$ h, the solution was filtered and evaporated to dryness to leave compound 6 as a waxy brown solid. Attempts to crystallize the

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Table II. Crystallographic Data for $[CpMoCl(PMe_3)_3]PF_6$

		(a) Crystal Parameters	
formula	$C_{14}H_{32}ClF_6P_4Mo$	Z	4
fw	569.69	cryst dimens, mm	0.25 × 0.34 × 0.36
cryst system	orthorhombic	cryst color	orange
space group	$P2_12_12_1$	D(calc), g cm^3	1.634
a, Å	11.008 (4)	μ(Mo Kα), cm^{-1}	9.87
b, Å	15.195 (4)	temp, K	296
c, Å	13.843 (4)	T(max)/T(min)	1.106
V, Å^3	2315.7 (14)		
		(b) Data Collection	
diffractometer	Nicolet R3m	no. of reflns collcd	3088
monochromator	graphite	no. of indpt rflns	2813
radiation (λ, Å)	Mo Kα (0.71073)	no. of indpt obsvd rflns [$F_o \geq n\sigma(F_o)$ (n = 5)]	1608
2θ scan range, deg	4–44	std rflns	3 std/197 rflns
data collcd (h,k,l)	±12,+17,+15	var in stds.	~5
		(c) Refinement	
$R(F)$, %	8.84	$\Delta(\rho)$, e Å^{-3}	2.084
$R_w(F)$, %	8.76	N_o/N_v	6.9
Δ/σ(max)	0.006	GOF	1.507

compound from pentane at −78 °C were unsuccessful. The NMR properties of this material are identical to those of the material obtained by thermal decomposition of compound **5**.

Preparation of (η^5:σ-$C_5Me_4CH_2$)Mo(PMe_3)$_3$ (7*). A solution of compound **5*** was prepared in situ as described above from **1*** (50 mg, 0.1 mmol) and LiMe (0.07 mL, 1.4 M, 0.1 mmol). The Et_2O solution was warmed to 20 °C with stirring, during which time the yellow solution turned deep red. After evaporation to dryness, the residue was extracted with pentane (10 mL), and the resulting solution was filtered, concentrated to 3 mL, and cooled to −78 °C for 3 days. The dark red crystals that formed were filtered off and dried. Yield: 28 mg. From the mother liquor, an additional 7 mg of product was recovered by further concentration and cooling to −80 °C. Total yield: 76%. Anal. Calcd for $C_{19}H_{41}MoP_3$: C, 49.79; H, 9.01. Found: C, 49.63; H, 8.74.

Reaction of (η^5-C_5R_5)MoCl(PMe_3)$_3$ with C_3H_5MgBr. Formation of (η^5-C_5R_5)Mo(η^3-C_3H_5)(PMe_3)$_2$ (R = H (8), Me (8*)). **(a) R = H.** Allylmagnesium bromide (0.16 mL, 1 M, 0.16 mmol) was added to a stirred solution of compound **1** (60 mg, 0.14 mmol) in THF (10 mL) at −40 °C. An immediate color change to dark green was observed, and on warming to 20 °C over $^1/_2$ h, the solution turned yellow. After evaporation to dryness, the residue was extracted with pentane (10 mL), and the resulting solution was filtered, concentrated to 4 mL, and cooled to −78 °C for 2 days to produce yellow crystals. These were filtered off, washed with a small amount of cold pentane, and dried under vacuum. Yield: 40 mg (80%). Anal. Calcd for $C_{14}H_{28}MoP_2$: C, 47.50; H, 7.90. Found: C, 47.14; H, 7.59.

In a separate experiment, the reaction was carried out with a larger excess of C_3H_5MgBr. The known[12] CpMo(η^3-C_3H_5)$_2$ was also isolated as a yellow solid, less soluble in pentane than compound **8**.

(b) R = Me. Allylmagnesium bromide (0.18 mL, 1 M, 0.18 mmol) was added to a stirred solution of compound **1*** (80 mg, 0.16 mmol) in THF (5 mL) at 0 °C. The solution rapidly turned green and then orange-yellow over the next 15 min. After evaporation to dryness, the residue was extracted with pentane (10 mL), and the resulting solution was filtered, concentrated to 5 mL, and cooled to −78 °C. The yellow-orange crystals of compound **8*** (44 mg, 64% yield) were filtered off and dried under vacuum. Anal. Calcd for $C_{19}H_{38}MoP_2$: C, 53.77; H, 9.02. Found: C, 53.46; H, 8.76.

X-ray Crystallography for $[1]^+PF_6^-$. Data Collection. Crystal, data collection, and refinement parameters are collected in Table II. An orange crystal, suitable for data collection, was mounted on a fine glass fiber with epoxy cement. The unit-cell parameters were obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). Preliminary photographic characterization showed *mmm* Laue symmetry, and the systematic absences in the diffraction data uniquely established the space group as $P2_12_12_1$. The result of the refinement of a multiplicative term (0.757) for $\Delta f''$ indicated that the enantiomorph reported is correct. No absorption correction was applied to the data (low μ, T_{max}/T_{min} = 1.106).

Structure Solution and Refinement. The structure was solved by heavy-atom methods, which located the Mo atom. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses. The hydrogen atoms were included

(12) Jolly, P. W.; Krüger, C.; Romão, C. C.; Romão, M. J. *Organometallics* **1984**, *3*, 936.

Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[1]^+PF_6^-$

	x	y	z	U^a
Mo	687.2 (19)	5935.7 (12)	3157.4 (16)	51.3 (7)
P(1)	2197 (7)	6557 (4)	4359 (5)	57 (2)
P(2)	407 (6)	4623 (4)	4227 (5)	62 (3)
P(3)	−1508 (7)	5766 (4)	2584 (6)	76 (3)
P(4)	4745 (9)	8299 (6)	1367 (7)	100 (4)
Cl	−152 (7)	7372 (5)	3536 (8)	125 (4)
F(1)	4537 (25)	9095 (13)	814 (17)	300 (24)
F(2)	3690 (23)	7894 (20)	916 (24)	606 (62)
F(3)	4955 (22)	7492 (13)	1915 (19)	265 (22)
F(4)	5509 (26)	7957 (16)	594 (16)	264 (21)
F(5)	5800 (25)	8696 (18)	1820 (21)	447 (37)
F(6)	3977 (28)	8629 (18)	2137 (17)	477 (40)
C(1)	811 (29)	5697 (15)	1442 (20)	85 (12)
C(2)	1234 (26)	4999 (17)	2041 (21)	72 (12)
C(3)	2269 (25)	5186 (20)	2564 (19)	80 (12)
C(4)	2497 (30)	6113 (18)	2258 (18)	82 (12)
C(5)	1540 (31)	6415 (16)	1631 (21)	97 (14)
C(6)	2738 (24)	7717 (15)	4087 (19)	76 (12)
C(7)	3666 (25)	5981 (18)	4555 (21)	100 (13)
C(8)	1634 (29)	6714 (16)	5641 (19)	93 (14)
C(9)	1729 (28)	4095 (21)	4608 (28)	136 (18)
C(10)	−303 (49)	4852 (26)	5364 (26)	214 (29)
C(11)	−480 (37)	3750 (19)	3836 (23)	137 (18)
C(12)	−2630 (20)	5745 (16)	3478 (25)	110 (16)
C(13)	−1981 (30)	6700 (17)	1801 (24)	116 (15)
C(14)	−1908 (29)	4753 (18)	1896 (29)	127 (16)

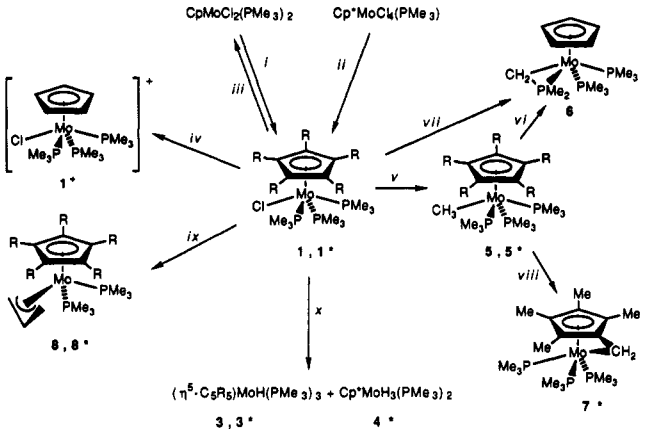
[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Selected Bond Distances and Bond Angles for $[1]^+PF_6^-$

	Bond Distance (Å)		
Mo–P(1)	2.534 (7)	Mo–P(2)	2.504 (7)
Mo–P(3)	2.557 (8)	Mo–Cl	2.427 (9)
Mo–CNT[a]	1.986 (18)		
	Bond Angles (deg)		
P(1)–Mo–P(2)	89.4 (2)	P(1)–Mo–P(3)	149.3 (3)
P(2)–Mo–P(3)	89.2 (2)	P(1)–Mo–Cl	76.9 (3)
P(2)–Mo–Cl	122.8 (3)	P(3)–Mo–Cl	78.3 (3)
P(1)–Mo–CNT	104.5 (8)	P(2)–Mo–CNT	113.3 (8)
P(3)–Mo–CNT	104.0 (8)	Cl–Mo–CNT	123.9 (8)

[a] CNT = centroid of atoms C(1)–C(5).

Scheme I[a]



[a] Unstarred numbers refer to R = H; starred numbers refer to R = Me. Key: (i) PMe_3, Na/Hg, THF, rt, 6 h; (ii) 2 PMe_3, 3 Na/Hg, THF, rt, 5 h; (iii) CH_2Cl_2, rt; (iv) $AgPF_6$, THF, rt, 1 h; (v) LiMe, Et_2O, T = 0 °C (R = H), -20 °C (R = Me); (vi) THF, 40 °C; (vii) LiPh, Et_2O/heptane, rt; (viii) Et_2O, 20 °C; (ix) C_3H_5MgBr, THF, rt; (x) $LiEt_3BH$, THF (R = H, Me) or K, heptane (only R = H).

as idealized isotropic contributions (d_{CH} = 0.960 Å, U = 1.2U for attached C). All non-hydrogen atoms were refined with anisotropic thermal parameters. Disorder and/or high thermal motion in the anion required the creation of a rigid octahedron model. Table III contains positional parameters, and Table IV contains relevant bond distances and angles.

All computer programs and the sources of the scattering factors are contained in the SHELXTL program library (5.1).[13]

Results

Syntheses, Characterization, and Reactivity. The reactions described in this paper are summarized in Scheme I.

The starting materials $(\eta^5\text{-}C_5R_5)MoCl(PMe_3)_3$ (R = H (1), Me (1*)) have been prepared by sodium amalgam reduction of suitable precursors ($CpMoCl_2$ and Cp^*MoCl_4, respectively) in the presence of the proper amount of PMe_3. The interaction of the above precursors with PMe_3 is known to afford the adducts $CpMoCl_2(PMe_3)_2$[6] and $Cp^*MoCl_4(PMe_3)$,[10] respectively. It is worth pointing out that these reductions have been carried out under an atmosphere of argon. Under dinitrogen, Baker has reported that the Cp* system forms a different derivative of Mo(II), i.e. $Cp^*MoCl(PMe_3)_2(N_2)$.[14] The reactions of compounds 1 and 1* with N_2 will be described in the following paper.[8] Compounds 1 and 1* are unstable in chlorinated solvents, where they are oxidized to the Mo(III) species $(\eta^5\text{-}C_5R_5)MoCl_2(PMe_3)_2$ (R = H, Me, respectively). We have not been able to obtain crystals of compounds 1 or 1* suitable for an X-ray analysis. However, the four-legged piano stool structure of these complexes is suggested by the NMR characterization (see Table I) and by the oxidation chemistry.

The $^{31}P\{^1H\}$-NMR spectrum shows a doublet and a triplet for both compounds. The possible alternative pseudo-tbp structure with axial chloride is excluded because it would contain equivalent phosphine ligands. The possibility of a pseudo-tbp structure with axial phosphine is not excluded by the data, although we observe that pseudo-tbp structures of the $CpML_4$ type have not been observed before as the ground state for 18-electron systems[15] and a theoretical investigation shows that they should be unstable with respect to the four-legged piano stool geometry.[16] In compound 1, the Cp protons couple significantly (J = 2 Hz) with only one phosphorus, that is, the one which is located trans to the chloride ligand. No corresponding phosphorus coupling is observed for the methyl groups in the Cp* ligand of compound 1*. Another characteristic feature of compounds 1 and 1* (and of many more compounds shown later in this and the following paper) is the intermediate coupling pattern (between a doublet and a virtual triplet) shown by the protons of the two equivalent PMe_3 ligands. Although exceptions are sometimes observed (vide infra), this typically occurs for those phosphines that are located in a relative trans position in the base of the pseudo-square pyramid and therefore form P–Mo–P angles greater than 90° (a situation in which virtual coupling is not observed, giving rise to a doublet pattern) but smaller than 180° (where virtual coupling is strong, giving rise to a triplet pattern). The unique PMe_3 ligand in compounds 1 and 1*, which is located at a <90° angle with respect to the other two phosphine ligands, shows a clean doublet in the ^1H-NMR spectrum.

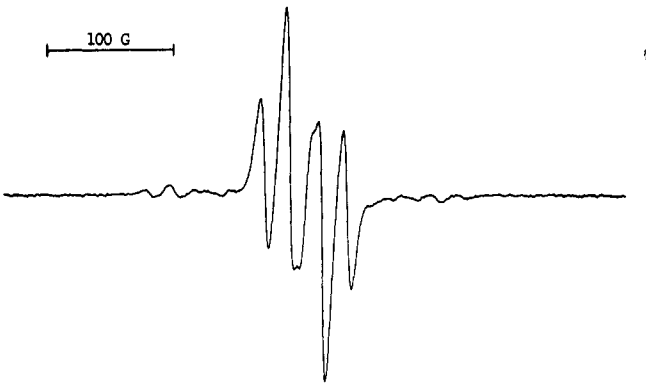


Figure 1. EPR spectrum of $[1^+]PF_6^-$ (solvent = CH_2Cl_2; room temperature).

Compound 1 exhibits a reversible oxidation wave in the cyclic voltammogram at $E_{1/2}$ = -1.46 V with respect to ferrocene, to produce the corresponding $[CpMoCl(PMe_3)_3]^+$ cation, $[1]^+$. The one-electron nature of this process is demonstrated by the chemical generation of the same species by oxidation of 1 with $AgPF_6$ and by a crystallographic study of the resulting PF_6^- salt, which shows a four-legged piano-stool structure (see below). The reversibility of the oxidation process in the cyclic voltammetric experiment is consistent with the four-legged piano structure for the precursor 1. Unlike 1, $[1]^+$ is quite stable in CH_2Cl_2 and single crystals of the PF_6^- salt were obtained by diffusion of Et_2O into a solution in this solvent. Solutions of $[1]^+$ exhibit a doublet of triplets in the EPR spectrum at room temperature centered at g = 2.006 with a_{Mo} = 36.5 G, a_P (doublet) = 26.0 G, and a_P (triplet) = 19.5 G (see Figure 1).

An identical EPR spectrum is observed for a solution obtained from $CpMoCl_4$ after reduction with Zn in THF

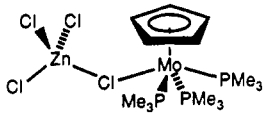
(13) Sheldrick, G. Nicolet (Siemens), Madison, WI.

(14) Baker, R. T.; Morton, J. R.; Preston, K. F.; Williams, A. J.; Le Page, Y. *Inorg. Chem.* **1991**, *30*, 113.

(15) (a) A pseudo-tbp $CpML_4$ compound is the 14-electron $[Cp^*WMe_4]^+$ complex: Liu, A. H.; Murray, R. C.; Dewan, J. C.; Santasiero, B. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 4282. (b) At low temperature, the fluxional 18-electron complexes $CpMX(CO)L_2$ [M = Mo, W; X = Cl, Br, I; L = $PMePh_2$, $P(OMe)Ph_2$] have been shown to exist as mixtures of isomers which include several ones with a pseudo-tbp geometry: Nickias, P. N.; Selegue, J. P. Presented at the 192nd National Meeting of the American Chemical Society, Anaheim, CA, Sept 7–12, 1986; abstract INOR 26. We thank one of the reviewers for bringing this reference to our attention.

(16) Kubacek, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

(which produces insoluble $CpMoCl_2$ and soluble $ZnCl_2$) followed by treatment in situ with PMe_3. The compound that was isolated from this solution analyzes correctly for $CpMoCl(PMe_3)_3 \cdot ZnCl_3$, compound **2**. We propose that the structure of this complex is either $[1]^+_2[Zn_2Cl_6]^{2-}$ or the zwitterionic molecular isomer illustrated in I. The $Zn_2Cl_6^{2-}$ ion has been described before.[17] The compound is quite soluble in CH_2Cl_2 but not soluble in hydrocarbons and THF.



I

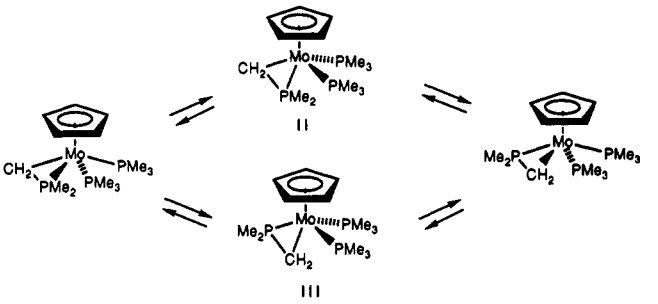
When PMe_3 is added to *isolated* $CpMoCl_2$, the product is $CpMoCl_2(PMe_3)_2$,[6] which does not react with excess PMe_3. Thus, it seems that the Lewis acidity of $ZnCl_2$ favors the replacement of one chloride ligand with PMe_3 in $CpMoCl_2(PMe_3)_2$. Addition of PPN^+Cl^- to a CH_2Cl_2 solution of compound **2** induces a smooth conversion to $CpMoCl_2(PMe_3)_2$. Upon addition of PPN^+I^- (4 equiv) to the same solution, $CpMoCl_2(PMe_3)_2$ is still formed as the predominant product, but the final solution also contains the known[1,6] $CpMoClI(PMe_3)_2$ and $CpMoI_2(PMe_3)_2$ complexes (see eq 1). The final ratio of the three complexes (Cl_2:ClI:I_2 = 70:29:1) is consistent with the higher thermodynamic stability of the chloride complex.[4,5]

$$2 + 4I^- \rightarrow \underset{n = 0\text{–}2}{CpMoCl_nI_{2-n}(PMe_3)_2} + \underset{m = 0\text{–}4}{[ZnCl_mI_{4-m}]^{2-}} \quad (1)$$

The reaction of **1** and **1*** with $LiEt_3BH$ has been briefly investigated. In both cases, substitution of the chloride with a hydride ligand occurs to afford compounds $YMoH(PMe_3)_3$ (Y = Cp (**3**), Cp* (**3***)). Compound **3** had been previously reported.[11] Both complexes show a diagnostic quartet resonance in the ^{1}H-NMR spectrum (δ = −8.40 (**3**), −8.59 (**3***)) at room temperature, which is attributable to the single hydride ligand coupled equivalently with the three phosphorus nuclei, indicating fluxional behavior. The fluxionality of these monohydride complexes is evidenced not only by the hydride resonance but also by the virtual quartet observed for the PMe_3 protons in compound **3*** at δ 1.31. While compound **3** remains fluxional at the lowest temperature we could reach in toluene-d_8, compound **3*** has the exchange process frozen on the NMR time scale at 210 K, as clearly shown by the triplet of doublets for the hydride resonance at that temperature. The PMe_3 resonances (both in ^{1}H- and ^{31}P{^{1}H}-NMR spectra) are also decoalesced at 210 K. This observation puts on a firmer footing the idea that (ring)-$MH(PMe_3)_3$ complexes have a fluxional four-legged piano stool structure, rather than a static pseudo-trigonal bipyramidal structure.[18a]

Compound **3** also forms from $CpMoCl_2(PMe_3)_2$ and excess $LiEt_3BH$ or by reacting compound **1** with a potassium mirror in THF. The reaction of **1*** with $LiEt_3BH$ also gave minor proportions of the trihydride complex $Cp^*MoH_3(PMe_3)_2$ (**4***) identified by the triplet resonance centered at δ −5.14 (J = 53 Hz) in the ^{1}H-NMR spectrum and by the other spectral data reported in Table I. The analogous

Scheme II



II III

complex $(C_5H_4$-*i*-Pr$)MoH_3(PMe_3)_2$ has similar NMR properties,[18b] with a triplet feature for the hydride protons centered at δ −5.60 (J = 40.5 Hz). The relative amount of **3*** and **4*** seemed somewhat dependent on the excess amount of $LiEt_3BH$ and the reaction time. The use of stoichiometric amounts of the boron reagent and immediate workup increased the amount of **3*** relative to **4*** (up to ca. 88:12), but we could never completely eliminate the formation of the latter complex. The source of the extra hydride ligands is unknown. Analogous reactions, which proceed to the formation of more hydride-rich products than expected, are not unprecedented.[19]

The interaction of **1** and **1*** with methyllithium affords the expected methyl derivatives, compounds **5** and **5***. Compound **5** has also been obtained from the reaction of methyllithium with $CpMoCl_2(PMe_3)_2$.[7] The ^{1}H-NMR spectrum of **5** has been discussed before.[7] While the two equivalent PMe_3 ligands show an intermediate coupling pattern between a doublet and virtual triplet in compound **5**, only a doublet is observed in compound **5***, suggesting that the steric bulk of the Cp* ligand reduces the *trans*-PMe_3–Mo–PMe_3 angle to a smaller value than allowed in the Cp complex. As discussed above, virtual coupling is generally negligible at angles close to 90° and gradually increases as the angle opens up toward 180°. The protons of the Mo-bound methyl group in **5*** resonate as a triplet (J_{PH} = 11 Hz) at δ −0.32, which compares with δ −0.10 for compound **5**. Coupling to the unique, trans PMe_3 ligand is not observed. The ^{31}P{^{1}H}-NMR spectrum of compound **5** displays second-order behavior. The coupling constants as obtained from the simulated spectrum are reported in Table I. The ^{31}P{^{1}H}-NMR spectrum of compound **5***, on the other hand, shows the expected doublet and triplet.

Compounds **5** and **5*** are thermally unstable and decompose to afford products of C–H bond activation with elimination of methane in both cases. The two complexes, however, differ in the nature of the C–H bond which is activated. Complex **5** undergoes oxidative addition of a PMe_3 C–H bond and converts into the η^2-CH_2PMe_2 complex **6**. This occurs at temperatures higher than room temperature. Complex **5*** is less stable and decomposes at $T \geq 0$ °C to give the product of oxidative addition of a Cp* C–H bond, compound **7***.

NMR investigations of compound **6** on an instrument that utilizes a 200-MHz frequency for ^{1}H resonances show fluxional behavior at room temperature: the two PMe_3 ligands are equivalent to each other both in the ^{1}H- and in the ^{31}P-NMR spectra, as are the two Me groups and the two CH_2 protons of the η^2-CH_2PMe_2 ligand. The static structure, consistent with a four-legged piano stool geometry, could be observed upon cooling to −60 °C. The fluxional process presumably involves rocking of the η^2-CH_2PMe_2 ligand, which could occur through either in-

(17) (a) Cotton, F. A.; Duraj, S. A.; Extine, M. W.; Lewis, G. E.; Roth, W. J.; Schmulbach, C. D.; Schwotzer, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1377. (b) Bouma, R. J.; Teuben, J. H.; Beukema, W. R.; Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 2715. (c) Hubertus, J.; Müller, U. *Z. Naturforsch.* **1989**, *44b*, 1037.

(18) (a) Green, M. L. H.; O'Hare, D.; Mountford, P.; Watkin, J. G. *J. Chem. Soc., Dalton Trans.* **1991**, 1705. (b) Grebenik, P. D.; Green, M. L. H.; Izquierdo, A.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1987**, 9.

(19) Arliguie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989**, *8*, 1308 and references therein.

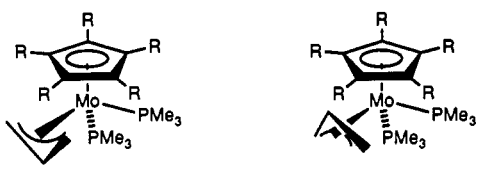
termediates II or III as indicated in Scheme II, although the entire rotation around the Mo–η^2-CH_2PMe_2 axis (i.e. the possibility that *both* intermediates II and III are involved) or the dissociation/reassociation of the PMe_2 arm of the ligand are alternative mechanistic possibilities.

Compound **7*** is static at room temperature. Metalation at a Cp* methyl group is shown by the 2:6:6 pattern for the Cp* protons in the ^{1}H-NMR spectrum and the 1:2:2 pattern for the Cp* methyl carbons in the $^{13}C\{^1H\}$-NMR spectrum. The metalated carbon nucleus is observed as a triplet due to coupling to the two equivalent phosphorus nuclei.

Compound **1** has been reacted with phenyllithium in an attempt to form the phenyl derivative $CpMoPh(PMe_3)_3$. Since the methyl complex **5** is thermally unstable and extremely soluble in saturated hydrocarbons, we had hoped that the substitution of the methyl with a phenyl group would increase the thermal stability and decrease the solubility of the compound. On the other hand, the expected phenyl product was not observed and the reaction proceeded directly to the metalated compound **6**, presumably with elimination of benzene.

The interaction of **1** and **1*** with allylmagnesium bromide afforded the corresponding $YMo(\eta^3\text{-}C_3H_5)(PMe_3)_2$ derivatives, yellow **8** (Y = Cp) and orange-yellow **8*** (Y = Cp*). In both reactions, the immediate formation of green intermediates took place. We were not able to obtain NMR characterization for these intermediates, but we think it likely that they are the corresponding η^1-allyl complexes, $YMo(\eta^1\text{-}C_3H_5)(PMe_3)_3$, which slowly lose PMe_3 to afford the final products. In the Cp system, the use of a large excess of the Grignard reagent afforded minor amounts of the known[12] paramagnetic $CpMo(\eta^3\text{-}C_3H_5)_2$ as a byproduct.

Compounds **8** and **8*** have a single resonance in the $^{31}P\{^1H\}$-NMR spectrum. The PMe_3 protons exhibit an intermediate pattern between a doublet and a virtual triplet, which is a situation typical of trans rather than cis PMe_3 ligands in four-legged piano stool geometry as discussed above. It is possible that the small steric bulk of the η^3-allyl group allows the PMe_3–Mo–PMe_3 angle to open up with respect to those found between cis ligands in structures where all the four "leg" ligands are monodentate (one might even consider **8** and **8*** as three-legged piano stools), although such an angle is not expected to become much larger than 90°. Concerning the orientation of the allyl moiety, both configurations IV (supine allyl group)



IV

V

and V (prone allyl group) are possible in principle. The observation of three independent allyl proton resonances (1:2:2 ratio) which are in similar positions for **8** and **8*** indicates that the two compounds are similar, but we cannot distinguish between configurations IV, V, and a fast equilibrium between the two.

A number of other allyl–Cp–Mo(II) complexes have been investigated before, and in general a dynamic equilibrium between the two orientations is found. The equilibrium is frozen out at low temperature on the NMR time scale for $(\eta^5\text{-}C_9H_7)Mo(\eta^3\text{-}C_3H_5)(CO)_2$[20] and for $(\eta^5\text{-}C_9H_7)Mo(\eta^3\text{-}1\text{-}C_3H_4Me)[P(OMe)_3]_2$,[21] whereas the two forms are still in rapid equilibrium at low temperature for $CpMo(\eta^3\text{-}1\text{-}C_3H_4Me)[P(OMe)_3]_2$.[21] For compound $CpMo(dppe)(\eta^3\text{-}1\text{-}MeC_3H_4)$, two different isomeric forms have been isolated.[22] Compounds **8** and **8*** have a temperature-independent ^{1}H-NMR spectrum in the temperature range 188–298 K, which shows that the compounds are either fluxional at 188 K or static and present as a single isomer at all temperatures. A ^{1}H-NOE-difference NMR experiment, which was carried out on both compounds **8** and **8***, suggests that, in each case, isomer IV represents at least a major proportion of the complex in solution: saturation of the Cp or Cp* ring Me resonance enhanced the resonances due to both endo and exo CH_2 protons, whereas the CH proton was not affected. Other isoelectronic Mo(II)–allyl complexes that have been reported are $[(\eta^6\text{-}C_6H_6)Mo(\eta^3\text{-}C_3H_5)(L\text{-}L)]^+$ (L-L = bidentate phosphorus- or nitrogen-based ligand)[23] and $(\eta^6\text{-}C_6H_6)Mo(\eta^3\text{-}C_3H_5)Cl(PR_3)$.[24] Structural studies have also been reported for a few isostructural (although not isoelectronic) zirconium derivatives: $CpZr(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_4H_6)$ has a *supine* allyl moiety in the most stable isomer, whereas the allyl group is *prone* in compound $CpZr(\eta^3\text{-}C_3H_5)(CH_3)_2$.[25a,b] $Cp^*ReH(CO)(\eta^3\text{-}C_3H_4R)$ complexes have been identified in both isomeric conformations, which mutually interconvert at measurable rates only above room temperature.[25c]

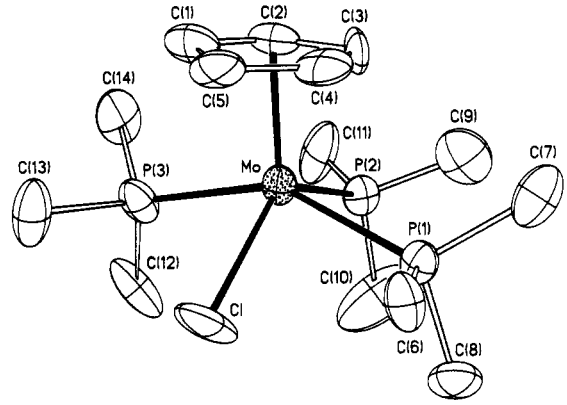


Figure 2. ORTEP drawing and labeling scheme for $[1]^+$. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at 35% probability.

Molecular Structure of $[CpMoCl(PMe_3)_3]^+PF_6^-$. The oxidation product of compound **1** with $AgPF_6$, $[1]^+PF_6^-$, crystallizes as orange crystals in the orthorhombic space group $P2_12_12_1$. The ions are well separated in the crystal lattice. A view of the cation is shown in Figure 2. Although it is located on a general position in the unit cell (no crystallographically imposed symmetry), the ion has ideal C_s symmetry, the mirror plane passing through the Mo, Cl, C(5), P(2), and C(10) atoms. The geometry of the ion is a typical four-legged piano stool. The θ angles[9] (angles between the bonds of molybdenum to the center

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of the Cp ring and to a specific monodentate ligand) are as follows: Cl, 123.9 (8)°; P(1), 104.0 (8)°, P(2), 113.3 (8)°, P(3), 104.0 (8)°. This trend of angles is in accord with our recent analysis of the distortions in the "legs" of four-legged piano stool structures.[9] For 17-electron compounds, potential π-acids (such as PMe_3) are not significantly distorted from the typical value of ca. 110° for π-neutral ligands, whereas π-donor ligands (such as Cl) experience a distortion to higher θ angles. In this particular case, a steric effect due to the presence of three PMe_3 ligands might be responsible for the slight distortion of P(1) and P(3) toward smaller θ values.

The bond distances in this ion can be compared with those of the isoelectronic $CpMoCl_2(PMe_3)_2$ molecule.[1] The Mo–Cl distance is shorter in $[1]^+$ [2.427 (9) Å vs 2.471 (3) Å (average) in $CpMoCl_2(PMe_3)_2$], probably because of the positive charge which reduces the effective ionic radius of molybdenum and/or favors a stronger Cl–Mo π-bonding [the latter could also be the cause of the larger θ angle in $[1]^+$:[9] 123.9 (8)° vs 117.4° (average) for $CpMoCl_2(PMe_3)_2$]. The Mo–P distances are, on the other hand, longer in $[1]^+$, probably because the positive charge on the complex disfavors Mo–P π-back-donation, which was present in compound $CpMoCl_2(PMe_3)_2$.[1] The Mo–P distances found in $[1]^+$ are more comparable with those of most of the other Mo(III)–phosphine complexes that do not contain the Cp ligand (in the 2.54–2.59-Å range).[26] The small difference between the Mo-P(2) distance [2.504 (7) Å] and those involving the other two phosphine ligands [average 2.54 (2) Å] is probably due to steric compression as reflected also by the θ angles for these ligands (vide supra). The Mo–C(Cp) distances are spread in the wide 2.19–2.42-Å range and have an average of 2.32 (3) Å, which is only slightly longer than the corresponding parameter for $CpMoCl_2(PMe_3)_2$, that is 2.282 (8) Å.[2] Although the significance of this slippage effect may be in question given the high final R factor, we observe that an identical distortion was found for the dichloride complex.[2] The distortion pattern (two shorter and three longer bonds) is also similar in the two structures and was interpreted for the dichloride complex as due to Mp–Cp δ back-bonding according to a published theoretical analysis.[16] The possibility that steric compression by the PMe_3 ligands is the cause of the distortion of the Cp ring does not seem likely since the longer Mo–C bond is the one to C(5), which is located directly above the Cl ligand, which is the smallest ligand and has the highest θ angle.

Discussion

Four-legged piano stool derivatives of molybdenum(II) containing the cyclopentadienyl ring are very common, although only a small fraction of these do not contain CO in the coordination sphere. Examples of these are CpMo(allyl)(dppe),[27] $[CpMo(butadiene)(dppe)]^+$,[27] $CpMoH(PMe_3)_3$,[11] and $Cp^*MoCl(PMe_3)_2(N_2)$.[14] In this paper, we describe the new starting materials $YMoCl(PMe_3)_3$ (Y = Cp, Cp*), which are easily prepared from $CpMoCl_2$ and Cp^*MoCl_4, respectively, and a number of other CO-free derivatives that have been obtained from them (see Scheme I). The facile transformation of compound 1 to the methyl derivative 5 is consistent with 1 being an intermediate in the transformation of $CpMoCl_2(PMe_3)_2$ to compound 5 upon interaction with MeLi, as earlier suggested.[7] The versatility of these compounds in organometallic synthesis is also shown by the results illustrated in the following companion paper.[8] Our interest in the analysis of distortions for non-carbonyl four-legged piano stools of Mo(II) (see Introduction) does not gain much information from the investigations reported here, due to the high solubility of most of the compounds which prevented their crystallization in a suitable form for an X-ray investigation to be carried out. Compound 1 forms crystals from cold (−78 °C) heptane, in which it is very soluble at room temperature, but these were small and were not found to diffract X-rays sufficiently well. Compound 1*, as well as the other Cp* derivatives that form suitable single crystals, were not investigated crystallographically since the steric bulk of the Cp* ring can introduce steric effects which may mask the sought electronic distortions.[9] The structure of the oxidation product of 1, compound $[1]^+PF_6^-$, besides suggesting an analogous four-legged piano stool structure for compound 1 (in conjunction with the cyclic voltammetric experiment; see Results), shows consistency with the qualitative MO analysis of the distortions reported earlier.[9]

The reactions reported in this paper (Scheme I) show little dependence on the steric bulk and electronic effect of the η^5-ring. The only major difference concerns the thermal decomposition of the unstable methyl derivatives 5 and 5*. Both compounds lose methane, but while the Cp derivative saturates the electronic demand of the metal by oxidatively adding a phosphine C–H bond, the Cp* derivative uses a Cp* methyl C–H bond for the same purpose instead. Each reaction is selective, and no other decomposition product is observed by ^{1}H-NMR spectroscopy. Systems where PMe_3 and Cp* ligands oxidatively add to an unsaturated transition metal center are quite common, especially for early transition metals.[28] In one case (Cp^*TaCl_4 + PMe_3 + reducing agent), the activation of either PMe_3 or Cp* occurs on the same system depending on reaction conditions: $[\eta^5{:}\sigma{:}\sigma\text{-}C_5Me_3(CH_2)_2]$-$Ta(H)_2(PMe_3)_2$ and $Cp^*Ta(H)_2(\eta^2\text{-}CHPMe_2)(PMe_3)$ are obtained in THF and PMe_3 as solvent, respectively.[29]

The formation of compounds 6 (Cp system) and 7* (Cp* system) is probably taking place via either preliminary PMe_3 dissociation or ring slippage, which creates a vacant coordination site and allows the oxidative addition process to take place prior to CH_4 reductive elimination. The PMe_3 dissociation mechanism requires that PMe_3 recoordinates after the methane elimination has occurred. The formation of compound 6 from 5 is reminiscent of the formation of the ortho-metalated $CpMo(o\text{-}C_6H_4PMe_2)(PMe_2Ph)_2$ complex, which was obtained from $CpMoCl_2(PMe_2Ph)_2$ and MeLi (2 equiv). Since the corresponding reaction of $CpMoCl_2(PMe_3)_2$ produced compound 5,[7] it is conceivable that the mechanism for the formation of these two ortho-metalated materials (compound 6 and $CpMo(o\text{-}C_6H_4PMe_2)(PMe_2Ph)_2$) is identical in the last steps.

The direct formation of compound 6 from the interaction of 1 and PhLi shows that reductive elimination of benzene from an intermediate of type $(\eta^{5-2x}\text{-}C_5H_5)Mo(H)(Ph)(\eta^2\text{-}CH_2PMe_2)(PMe_3)_{1+x}$ (x = 0, 1) is faster than elimination of methane from the analogous methyl–hydride intermediate and/or the phenyl group induces the faster generation of the $(\eta^2\text{-}CH_2PMe_2)$-hydrido intermediate with respect to the methyl group.

It is interesting to compare the reactivity of this presumed phenyl–hydride intermediate with known C–H

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activation chemistry of the late transition metals. Compounds such as $Cp^*M(PMe_3)(H)(R)$ (M = Rh, Ir; R = alkyl) are thermodynamically less stable than the corresponding phenyl–hydrido derivatives, and their thermal treatment in C_6D_6 proceeds to the formation of the more stable $Cp^*M(PMe_3)(D)(C_6D_5)$ product.[30] In our case, the methyl derivatives **5** and **5*** can be isolated (although they thermally decompose at mild temperatures) and the corresponding phenyl derivative (for the Cp system) cannot. This does not necessarily mean that the order of thermodynamic stability of phenyl vs methyl derivatives is reversed for the molybdenum system (M–Ph bonds are stronger than M-R(sp^3) bonds also for early transition metals, for instance for scandium[31]). A possible rationalization for the observed reactivity is that the cyclometalated forms (**6** and **7***) are thermodynamically more stable than the corresponding non-cyclometalated forms (**5**, **5***, or the corresponding phenyl derivatives), and although the phenyl derivatives probably are *thermodynamically more stable* than those containing the methyl group, they are also (in analogy to the Rh and Ir chemistry mentioned above)[30] *kinetically more labile*.

Acknowledgment. We thank the Camille and Henry Dreyfus Foundation and the National Science Foundation for awards (to R.P.) and for support.

Supplementary Material Available: A figure showing observed and simulated second-order $^{31}P\{^1H\}$-NMR spectra for compound **5** (Figure 1S) and tables of complete bond distances and angles, anisotropic thermal parameters, and positional parameters of hydrogen atoms for compound $[1]^+PF_6^-$ (5 pages); a table of observed and calculated structure factors for compound $[1]^+PF_6^-$ (5 pages). Ordering information is given on any current masthead page.

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Four-Legged Piano Stool Molybdenum(II) Compounds without Carbonyl Ligands. 2. Reactions of $(\eta^5\text{-}C_5R_5)MoCl(PMe_3)_3$ (R = H, Me) with Neutral Donors

Fatima Abugideiri, Malcolm A. Kelland, and Rinaldo Poli*

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

Received September 19, 1991

Substitution of a PMe_3 ligand of compound $CpMoCl(PMe_3)_3$ (**1**) with L affords $CpMoCl(PMe_3)_2L$ molecules (L = N_2 (**2**), C_2H_4 (**3**)). No analogous products are obtained with propene or butene. Neither does $Cp^*MoCl(PMe_3)_3$ (**1***) react in an analogous fashion with ethylene. NMR investigations show that the dinitrogen complex has a trans configuration of the monodentate ligands in the four-legged piano stool geometry, whereas the ethylene complex is present in solution as a mixture of cis and trans isomers, the cis isomer being the prevalent one (10:1 in benzene-d_6; 33:1 in acetone-d_6). The olefin ligand in the cis isomer does not freely rotate around the Mo–C_2H_4 bond on the NMR time scale, and its conformation has been established by a combination of selective decoupling, NOE, and ^1H–^{13}C COSY-NMR experiments. Interaction of **1** with butadiene affords $CpMoCl(PMe_3)(\eta^4\text{-}C_4H_6)$ (**4**), which can also be obtained directly from $CpMoCl_2$, butadiene, PMe_3, and Na/Hg. No analogous reactions occur with 2,3-dimethylbutadiene or cycloheptatriene. The corresponding Cp* compound, **4***, has been obtained by reduction of $Cp^*MoCl_4(PMe_3)$ with Na/Hg in the presence of butadiene. Compound **1** interacts with diphenylacetylene to afford the salt $[CpMo(PMe_3)_2(PhCCPh)]^+Cl^-$ (**5**). Compound **3** reacts with $LiEt_3BH$ or EtMgBr to afford $CpMoH(C_2H_4)(PMe_3)_2$ (**6**), which is fluxional at room temperature and decoalesces into a 47:53 mixture of cis and trans isomers at low temperature. Compound **6** was also obtained from **1** and EtMgBr. Interaction of **6** with PMe_3 results in C_2H_4 substitution rather than insertion into the Mo–H bond. Alkylation of **3** with MeLi generates $CpMo(CH_3)(C_2H_4)(PMe_3)_2$ (**7**), which is stable at $T \leq 60$ °C and is present exclusively as the cis isomer. Warming transforms the latter compound into $CpMo(\eta^2\text{-}CH_2PMe_2)(C_2H_4)(PMe_3)$ (**8**) with elimination of methane.

Introduction

In the preceding paper[1] we have reported the preparation of $YMoCl(PMe_3)_3$ (Y = Cp (**1**), Cp* (**1***)), a few substitution reactions of the chloro ligand with hydrido, alkyl, and allyl reagents, and the electrochemical and chemical oxidation of **1** to the 17-electron $[CpMoCl(PMe_3)_3]^+$ ion, including the X-ray structure of its PF_6^- salt. In this paper we report the preparation, characterization, and reactivity of derivatives of compounds **1** and **1*** where one or more PMe_3 ligands have been replaced by other neutral donors.

Experimental Section

All operations were conducted under an atmosphere of argon unless otherwise stated. Solvents were dried by conventional methods and distilled under dinitrogen, followed by thorough degassing and saturation with argon prior to use. Instruments used were as follows: NMR, Bruker AF200 and WP200 for routine ^1H, ^{13}C, ^{31}P, and variable-temperature analyses, Bruker AM400 for NOE studies, and Bruker AMX500 for the ^1H–^{13}C COSY investigation; EPR, Bruker ER200; MS, VG 7070E. For the

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0276-7333/92/2311-1311$03.00/0