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New Phosphine-Containing Cyclopentadienylmolybdenum(IV) Complexes with an 18- and a 16-Electron Count. X-ray Structure of $\text{CpMoCl}_3(\text{PMe}_2\text{Ph})_2$ and $\text{Cp}^*\text{MoCl}_3\text{L}$ ($\text{L} = \text{PMe}_3, \text{PMePh}_2$)

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Molybdenum(IV) complexes of the general formula $\text{CpMoCl}_3\text{L}_n$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $n = 1, 2$) and $\text{Cp}^*\text{MoCl}_3\text{L}$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) have been synthesized by addition of L to CpMoCl_3 and by reduction of Cp^*MoCl_4 with amalgamated Na in the presence of L. For the Cp system, although both mono- and bis-L adducts can be obtained when $\text{L} = \text{PMe}_3$ and PMe_2Ph , only the mono-adduct has been observed when the bulkier PMePh_2 ligand is used. For the Cp^* system only mono-adducts were obtained ($\text{L} = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2$), and no tendency of these to add additional L was observed. All 16-electron mono-adducts show paramagnetically shifted $^1\text{H-NMR}$ spectra in accord with the observed spin triplet ground state. A variable-temperature study on $\text{Cp}^*\text{MoCl}_3(\text{PMe}_3)$ and the analogous tribromide complex indicates the rapid equilibration between two isomeric species, each one showing paramagnetically shifted proton resonances. The crystal structure of three of these complexes has been determined. $\text{CpMoCl}_3(\text{PMe}_2\text{Ph})_2$: triclinic, $P\bar{1}$, $a = 10.807(2) \text{ \AA}$, $b = 11.621(2) \text{ \AA}$, $c = 11.644(2) \text{ \AA}$, $\alpha = 89.72(1)^\circ$, $\beta = 70.61(1)^\circ$, $\gamma = 83.15(1)^\circ$, $V = 1368.6(4) \text{ \AA}^3$, $Z = 2$, $d_{\text{calcd}} = 1.494 \text{ g}\cdot\text{cm}^{-3}$. $\text{Cp}^*\text{MoCl}_3(\text{PMe}_3)$: orthorhombic, $P2_12_12_1$, $a = 8.178(2) \text{ \AA}$, $b = 13.186(3) \text{ \AA}$, $c = 15.206(3) \text{ \AA}$, $V = 1764.1(7) \text{ \AA}^3$, $Z = 4$, $d_{\text{calcd}} = 1.557 \text{ g}\cdot\text{cm}^{-3}$. $\text{Cp}^*\text{MoCl}_3(\text{PMePh}_2)$: monoclinic, $P2_1/a$, $a = 16.062(2) \text{ \AA}$, $b = 15.335(2) \text{ \AA}$, $c = 19.914(3) \text{ \AA}$, $\beta = 103.90(1)^\circ$, $V = 4761(2) \text{ \AA}^3$, $Z = 8$, $d_{\text{calcd}} = 1.50 \text{ g}\cdot\text{cm}^{-3}$. The two Cp^* compounds adopt a pseudo-square pyramidal geometry with the Cp^* ring in the apical position, whereas the $\text{CpMoCl}_3(\text{PMe}_2\text{Ph})$ complex has a pseudooctahedral geometry with a *mer,trans* relative arrangement of the ligands.

Introduction

We have only recently developed synthetic routes to cyclopentadienylmolybdenum trihalides, $\{\text{CpMoX}_3\}_n$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)¹ and $[\text{Cp}^*\text{MoX}_3]_2$ ($\text{X} = \text{Cl}, \text{Br}$).² Adducts of the cyclopentadienyl system with neutral donors have been known for a longer time, e.g., $\text{CpMoX}_3(\text{CO})_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$),³ $\text{CpMoX}_3(\text{dppe})$ ($\text{X} = \text{Cl}, \text{Br}$),⁴ $\text{CpMoCl}_3(\text{dmppe})$,⁵ and $\text{CpMoX}_3[\text{P}(\text{OCH}_2)_3\text{CET}]_2$ ($\text{X} = \text{Cl}, \text{Br}$).¹ All these neutral donors either have a small cone angle or are chelating didentate ligands and therefore stabilize saturated, 18-electron geometries. As part of a recent investigation of the electron-transfer-chain catalyzed halide exchange on the 17-electron $\text{CpMoX}_2(\text{PMe}_3)_2$ ($\text{X} = \text{Cl}, \text{I}$) system, whereby the ligand exchange is catalyzed by oxidation to the corresponding 16-electron cationic complexes, we discovered that the interaction between $[\text{CpMoCl}_2-$

$(\text{PMe}_3)_2]^+$ and Cl^- affords the unstable 18-electron complex $\text{CpMoCl}_3(\text{PMe}_3)_2$ which establishes an equilibrium with 16-electron, paramagnetic $\text{CpMoCl}_3(\text{PMe}_3)$.⁶ This finding prompted us to examine adducts of $\{\text{CpMoCl}_3\}_n$ or $[\text{Cp}^*\text{MoCl}_3]_2$ with bulkier monodentate phosphine ligands.

Experimental Section

All operations were carried out under an atmosphere of dinitrogen with standard Schlenk-line and glovebox techniques. Solvents were purified by conventional methods and distilled under dinitrogen prior to use. NMR spectra were obtained with Bruker WP200 and AF200 spectrometers; the peak positions are reported downfield of TMS as calculated from the residual solvent peaks (^1H), or downfield of external 85% H_3PO_4 (^{31}P). EPR spectra were recorded on a Bruker ER200 spectrometer equipped with an X-band microwave generator. The elemental analyses were by Midwest Microlab, Indianapolis, IN, or Galbraith Laboratories, Inc., Knoxville, TN. $\{\text{CpMoCl}_3\}_n$ and Cp^*MoCl_3 were prepared as described in the literature.^{1,7}

Reaction between $\{\text{CpMoCl}_3\}_n$ and PMe_2Ph . Formation of $\text{CpMoCl}_3(\text{PMe}_2\text{Ph})_2$ and $\text{CpMoCl}_3(\text{PMe}_2\text{Ph})$. $[\text{CpMoCl}_3]_n$ (203 mg, 0.759 mmol of CpMoCl_3) was slurried in THF (25 mL) and to the resulting mixture PMe_2Ph (108 μL , 0.76 mmol) was added. Within 15 min of stirring at room temperature, all the

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Table I. Crystal Data

compound	Cp*MoCl ₃ (PMe ₂ Ph) ₂	Cp*MoCl ₃ (PMe ₃)	Cp*MoCl ₃ (PMePh ₂)
formula	C ₂₅ H ₃₅ Cl ₃ MoOP ₂	C ₁₃ H ₂₄ Cl ₃ MoP	C ₂₃ H ₂₈ Cl ₃ MoP
fw	615.8	413.6	537.75
space grp	P $\bar{1}$	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /a
a, Å	10.807(2)	8.178(2)	16.062(2)
b, Å	11.621(2)	13.186(3)	15.335(2)
c, Å	11.644(2)	15.206(3)	19.914(3)
α, deg	89.72(1)		
β, deg	70.61(1)		103.90(1)
γ, deg	83.15(1)		
V, Å ³	1368.6(4)	1764.1(7)	4761(2)
Z	2	4	8
d _{calcd} , g/cm ³	1.494	1.557	1.50
μ(Mo Kα), cm ⁻¹	9.05	12.59	9.50
temp, K	233	243	298
T _{max} /T _{min}	N/A	1.33	1.15
diffractometer	Siemens P4	Siemens P4	Enraf-Nonius CAD4
monochromator		graphite	
radiation		Mo Kα (λ = 0.71073 Å)	
2θ scan range, deg	4–65	4–52	2–45
data collected (hkl)	±16, ±17, +17	+10, +17, +18	+17, +16, ±21
no. of rflns collected	10 322	2016	6772
no. of indpt rflns	9903	1995	6501
no. of indpt obsd rflns (F _o ≥ 4σ(F _o))	7938	1553	2853
std rflns	3 std/197 rflns	3 std/197 rflns	3 std/2 h
var in stds, %	<1	<1.5	<1
R(F), %	4.04	4.18	4.3
R(wF), %	5.55	4.09	5.1
Δ/σ (max)	0.005	0.001	0.11
Δ(ρ), e Å ⁻³	1.08	0.58	0.35
N _o /N _v	27.5	9.5	5.6
GOF	1.18	1.02	1.05

starting material dissolved to yield an orange-brown solution. The solution was filtered and evaporated at reduced pressure to ca. half volume. Slow diffusion of a *n*-heptane layer (50 mL) afforded 126 mg of brown crystals. Yield: 30.5%. Elemental analysis and ¹H-NMR are consistent with the presence of loosely packed lattice THF. Anal. Calcd for C₂₃H₃₁Cl₃MoO_{0.5}P₂ (CpMoCl₃(PMe₂Ph)₂·1/2THF): C, 47.65; H, 5.39; Cl, 18.35. Found: C, 47.4; H, 5.6; Cl, 20.4. ¹H-NMR (CDCl₃, δ) of this material does not show evidence for CpMoCl₃(PMe₂Ph): 7.39, 7.24 (br, 10H, Ph), 4.47 (br, 5H, Cp), 3.60 (m, THF), 1.85 (br, 12H, Me), 1.69 (m, THF). ³¹P-NMR (CDCl₃, δ): -6.55 (br). The relative proportion of Mo compound and THF from the integration is ca. 1:0.66, in close agreement with the result of the elemental analysis. A single crystal from this batch was used for the X-ray analysis.

An identical reaction was run with similar quantities of all the materials. An aliquot of the solution was evaporated to dryness and redissolved in CDCl₃. ¹H-NMR inspection of this solution was consistent with a mixture of CpMoCl₃(PMe₂Ph)₂ and CpMoCl₃(PMe₂Ph). ¹H-NMR for CpMoCl₃(PMe₂Ph): 150.0 (br, Cp), 14.5, 10.6 (br, Ph), -10.7 (br, Me). The solid that was crystallized out of this solution also showed evidence (¹H-NMR) of the presence of CpMoCl₃(PMe₂Ph).

Reaction between CpMoCl₃(PMe₂Ph)₂ and MeI. CpMoCl₃(PMe₂Ph)₂ (41 mg, 0.071 mmol) was dissolved in THF (5 mL), and to the resulting solution was added MeI (4.4 μL, 0.071 mmol). The orange-brown solution was stirred at room temperature overnight, during which time a white crystalline precipitate deposited. The color of the final solution was similar to the initial one. The solution was evaporated to dryness, and the residue was examined by ¹H-NMR in CDCl₃, confirming the presence of CpMoCl₃(PMe₂Ph) (see previous section).

Preparation of CpMoCl₃(PMePh₂). {CpMoCl₃}_n (301 mg, 1.13 mmol of CpMoCl₃) was slurried in THF (40 mL), and to the resulting mixture PMePh₂ (210 μL, 1.13 mmol) was added. The insoluble starting material rapidly dissolved to afford a green-brown solution. After overnight stirring at room temperature, the solution was filtered and evaporated at reduced pressure to about half of its original volume. Slow diffusion of a *n*-heptane layer (45 mL) yielded 267 mg of brown crystals (50.5%). ¹H-NMR and elemental analyses showed that the compound

crystallizes with loosely bound THF. Anal. Calcd for C₂₂H₂₆Cl₃MoOP₂ (CpMoCl₃(PMePh₂)·THF): C, 48.96; H, 4.86; Cl, 19.71. Found: C, 48.6; H, 4.6; Cl, 20.1. ¹H-NMR (CDCl₃, δ): 149.5 (br, Cp), 10.5, 10.1 (br, Ph), 3.7 (m, THF), 1.8 (m, THF), -25.5 (br, 3H, Me).

A different batch obtained from an identical preparation showed THF peaks of reduced intensity in the ¹H-NMR and had the following elemental analysis: C, 47.1; H, 4.6; Cl, 20.7. Calcd for CpMoCl₃(PMePh₂)·1/2THF: C, 47.69; H, 4.40; Cl, 21.12.

Preparation of Cp*MoCl₃(PMe₃). Cp*MoCl₃ (374 mg, 1.00 mmol) was suspended in THF (35 mL) and reacted with PMe₃ (104 μL, 1.04 mmol). EPR investigation of the resulting mixture confirmed the presence of Cp*MoCl(PMe₃).⁷ The mixture was transferred via cannula into a Schlenk tube containing amalgamated sodium (23 mg, 1.0 mmol, in 4.5 g Hg), followed by stirring at room temperature overnight. The resulting brown solution was filtered through Celite and evaporated to dryness, and the residue was extracted into toluene (40 mL). Cooling this solution to -20 °C produced 203 mg of brown crystals, which were filtered off and dried in vacuo. Yield: 49.1%. Anal. Calcd for C₁₃H₂₄Cl₃MoP: C, 37.75; H, 5.85; Cl, 25.71. Found: C, 37.7; H, 5.9; Cl, 25.6. ¹H-NMR (C₆D₆, δ): 2.9. μ_{eff} = 2.65 μ_B (CD₂Cl₂ solution, 278 K); 2.77 μ_B (CD₂Cl₂ solution, 215 K); 2.26 μ_B (CD₃CN solution, room temperature). A single crystal from this batch was used for the X-ray analysis.

Preparation of Cp*MoCl₃(PMe₂Ph). By a procedure analogous to that described above for the preparation of Cp*MoCl₃(PMe₃), Cp*MoCl₃ (1.106 g, 2.97 mmol), PMe₂Ph (422 μL, 2.97 mmol), and Na amalgam (68 mg, 2.96 mmol, in 21.2 g Hg) afforded 764 mg of Cp*MoCl₃(PMe₂Ph) (yield: 53%). After the addition of PMe₂Ph and before the addition of Na/Hg to the molybdenum complex, the solution showed the following EPR signal: *g* = 1.989; *a_P* = 26 G; *a_{Mo}* = 44 G. Anal. Calcd for C₁₈H₂₆Cl₃MoP: C, 45.45; H, 5.51; Cl, 22.36. Found: C, 45.4; H, 5.5; Cl, 20.9. ¹H-NMR (acetone-*d*₆, δ): 13.4 (br, 2H, *o*-Ph), 7.9 (br, 1H, *p*-Ph), 6.4 (br, 2H, *m*-Ph), 0.6 (br, 15H, Cp*), -19.1 (br, 6H, Me).

Preparation of Cp*MoCl₃(PMePh₂). By a procedure analogous to that described above for the preparation of Cp*MoCl₃(PMe₃), Cp*MoCl₃ (227 mg, 0.609 mmol), PMePh₂ (227 μL, 1.22 mmol), and Na amalgam (42 mg, 1.83 mmol, in 12.0 g Hg) afforded

103 mg of Cp*MoCl₃(PMePh₂) (yield: 31.4%). After the addition of PMePh₂ and before the addition of Na/Hg to the molybdenum complex, the solution showed the following EPR signal: $g = 1.987$; $a_p = 24$ G; $a_{Mo} = 44$ G. Anal. Calcd for C₂₃H₂₈Cl₃MoP: C, 51.37; H, 5.25; Cl, 19.78. Found: C, 51.8; H, 5.4; Cl, 17.6. ¹H-NMR (acetone-*d*₆, δ): 10.7, 10.3, 7.9, 7.8 (all br, 10H, Ph), -2.5 (br, 15H, Cp*), -13.4 (br, 3H, Me). A single crystal obtained by diffusion of a heptane layer into a toluene solution was used for the X-ray analysis.

X-ray Crystallography for Cp*MoCl₃(PMe₂Ph)₂, Cp*MoCl₃(PMe₃) and Cp*MoCl₃(PMePh₂). Crystals suitable for X-ray structural determination were mounted on glass fibers with epoxy cement. Crystal data collection and refinement parameters for all compounds are collected in Table I. The unit-cell parameters were obtained from the least-squares fit of 25 reflections ($20^\circ \leq 2\theta \leq 25^\circ$). Photographic evidence and cell reduction routines indicated $\bar{1}$ symmetry for Cp*MoCl₃(PMe₂Ph)₂. The chemically sensible results of refinement established the space group as $P\bar{1}$. Although elemental analysis and ¹H-NMR on the sample from which the crystal was chosen indicated the presence of THF (vide supra), no interstitial solvent molecule was found in the crystal structure. Our conclusion is that the compound, although chemically pure, probably crystallizes as a mixture of solvated and unsolvated species, and the better-looking crystal which was selected belonged to the latter category. No correction factor for absorption was applied to the data set (low μ , well-shaped crystal). The space group for Cp*MoCl₃(PMe₃) was uniquely established to be $P2_12_12_1$ through systematic absences in the diffraction data. A semiempirical absorption correction was applied to the data set (216 ψ -scans, $T_{max}/T_{min} = 1.33$). Analogously, the systematic absences uniquely established the space group for Cp*MoCl₃(PMePh₂) as $P2_1/a$ (nonstandard setting for $P2_1/c$, No. 14). An absorption correction based on the analysis of 259 ψ -scans was applied ($T_{max}/T_{min} = 1.15$). For this compound, two independent but chemically equivalent molecules were present in the asymmetric unit.

The structures were solved by direct methods which located the Mo and Cl atoms. The remaining non-hydrogen atoms were located through subsequent Fourier syntheses. All hydrogen atoms were included 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. For Cp*MoCl₃(PMe₃), refinement of a multiplicative term 0.8(3) for $\Delta f'$ indicated that the enantiomer reported is correct. Positional parameters are collected in Tables II–IV, and selected bond distances and angles are listed in Tables V–VII for Cp*MoCl₃(PMe₂Ph)₂, Cp*MoCl₃(PMe₃), and Cp*MoCl₃(PMePh₂), respectively. All software and the sources of the scattering factors are contained in the SHELXTLPLUS (4.2) program library.⁸

Results

Syntheses and Equilibria. The cyclopentadienylmolybdenum(IV) adducts with PMe₂Ph and PMePh₂ have been prepared by direct interaction of the phosphine with {Cp*MoCl₃}_{*n*} (eqs 1 and 2). Thus, these reactions do not suffer from the complications found for the corresponding reaction with PMe₃, which produces a variety of decomposition products including MoCl₃(PMe₃)₃.^{1a}

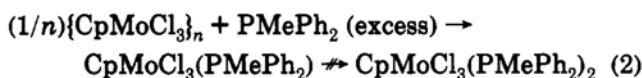
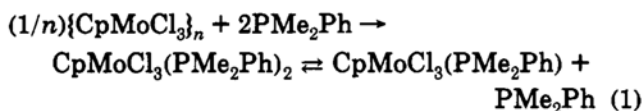


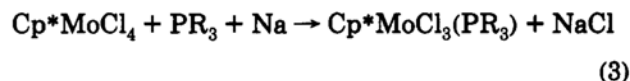
Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for Cp*MoCl₃(PMe₂Ph)₂

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Mo	180.4(2)	2363.6(2)	2159.1(2)	23.3(1)
Cl(1)	862.6(7)	3316.9(6)	3694.9(7)	39.9(2)
Cl(2)	1791.8(8)	3702.2(7)	933.2(8)	45.2(3)
Cl(3)	-1150.5(7)	1435.7(7)	4046.3(6)	40.9(2)
P(1)	-1550.8(7)	4126.2(6)	2984.2(7)	34.7(2)
P(2)	2102.7(6)	942.3(6)	2319.9(6)	27.3(2)
O	5716(6)	8074(5)	2102(5)	139(3)
C(1)	452(3)	2150(3)	25(3)	40(1)
C(2)	-854(3)	2582(3)	704(3)	39(1)
C(3)	-1379(3)	1743(3)	1555(3)	37(1)
C(4)	-359(3)	800(2)	1409(3)	37(1)
C(5)	766(3)	1074(2)	461(2)	36(1)
C(6)	-954(4)	5483(3)	2432(5)	71(2)
C(7)	-2149(4)	4366(4)	4639(3)	66(2)
C(8)	-3112(3)	4184(2)	2690(3)	33(1)
C(9)	-4081(3)	3536(3)	3377(3)	43(1)
C(10)	-5286(3)	3579(3)	3184(4)	52(1)
C(11)	-5537(3)	4269(3)	2309(4)	58(1)
C(12)	-4597(4)	4897(3)	1619(4)	53(1)
C(13)	-3384(3)	4859(3)	1789(3)	40(1)
C(14)	2281(3)	863(3)	3822(3)	41(1)
C(15)	3709(3)	1278(3)	1353(3)	42(1)
C(16)	2131(3)	-595(2)	1979(3)	32(1)
C(17)	2958(3)	-1152(3)	900(3)	41(1)
C(18)	3009(3)	-2351(3)	719(4)	53(1)
C(19)	2239(4)	-2978(3)	1603(4)	57(2)
C(20)	1393(4)	-2438(3)	2668(4)	56(2)
C(21)	1326(3)	-1245(3)	2869(3)	42(1)
C(22)	5217(6)	7803(4)	3396(5)	83(2)
C(23)	5838(9)	8533(6)	3988(6)	140(5)
C(24)	6455(8)	9318(7)	3033(7)	158(5)
C(25)	6243(6)	9084(4)	2000(5)	92(3)

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

It is interesting to note that the PMe₂Ph adduct behaves in a similar way to the previously investigated PMe₃ compound,⁶ the mono- and bis-adducts being in equilibrium in solution, whereas the slightly larger phosphine PMePh₂ only affords the mono-adduct. The Cp*MoCl₃(PMe₂Ph)₂ complex was isolated in the crystalline state, and its solid-state structure was verified by X-ray methods (vide infra). Its solution ¹H-NMR showed no immediate conversion to the corresponding mono-adduct. This is in contrast with the PMe₃ system, for which the immediate formation of a mixture of mono- and bis-adducts from [Cp*MoCl₂(PMe₃)₂]⁺ and Cl⁻ indicates a fast equilibrium. However, when the bis-PMe₂Ph compound is reacted with the phosphine scavenger MeI, the mono-PMe₂Ph compound slowly forms. Evidence for the formation of the 16-electron mono-adduct is also obtained when the bis-PMe₂Ph complex is kept for a long period of time in CDCl₃, although in this case the reaction is more complex and other decomposition products are also observed.

The pentamethylcyclopentadienyl system, Cp*MoCl₃, only forms mono-adducts with tertiary phosphines, including the relatively small PMe₃ ligand. Although we now know that these compounds can also be made by adding the phosphine directly to [Cp*MoCl₃]₂,² for the purpose of this investigation they were prepared by reduction of Cp*MoCl₄ in the presence of the appropriate phosphine (eq 3).



Addition of PR₃ to Cp*MoCl₄ affords the corresponding adducts Cp*MoCl₃(PR₃), which can be identified by EPR

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for $\text{Cp}^*\text{MoCl}_3(\text{PMe}_3)$

	x	y	z	$U(\text{eq})^a$
Mo(1)	2405.0(8)	1446.8(4)	7668.2(4)	32.0(2)
Cl(1)	4535(3)	1585(2)	8746(2)	63(1)
Cl(2)	4630(3)	1055(2)	6685(2)	76(1)
Cl(3)	1140(4)	107(2)	6991(2)	72(1)
P(1)	1220(3)	564(2)	8968(2)	49(1)
C(1)	2612(12)	3044(5)	7303(7)	59(3)
C(2)	1744(16)	2602(7)	6618(6)	63(4)
C(3)	262(13)	2290(7)	6985(7)	55(3)
C(4)	222(10)	2536(6)	7869(5)	40(3)
C(5)	1679(10)	3003(6)	8073(6)	41(3)
C(6)	4234(13)	3526(8)	7174(12)	139(8)
C(7)	2214(23)	2587(9)	5677(7)	153(9)
C(8)	-1180(17)	1850(9)	6511(11)	145(8)
C(9)	-1234(14)	2520(9)	8458(9)	103(6)
C(10)	2062(15)	3502(8)	8916(7)	90(5)
C(11)	1315(14)	1089(8)	10040(6)	72(4)
C(12)	2379(16)	-500(6)	9111(7)	90(5)
C(13)	-870(14)	142(7)	8900(9)	93(5)

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

in comparison with the previously reported and fully characterized PMe_3 compound.⁷ These adducts are promptly reduced by 1 equiv of amalgamated sodium to afford the Mo(IV) materials. X-ray structures of the PMe_3 and PMePh_2 complexes have been obtained (vide infra). Previous investigations have shown that the reduction of $\text{Cp}^*\text{MoCl}_4(\text{PMe}_3)$ with excess sodium in the presence of PMe_3 affords $\text{Cp}^*\text{MoCl}_2(\text{PMe}_3)_2$, $\text{Cp}^*\text{MoCl}(\text{PMe}_3)_2(\text{N}_2)$, or $\text{Cp}^*\text{MoCl}(\text{PMe}_3)_3$ depending on the amount of sodium, phosphine, and other conditions.^{9,10} The addition of excess PMe_3 to a solution of $\text{Cp}^*\text{MoCl}_3(\text{PMe}_3)$ did not perturb the appearance of the ^1H spectrum, and the ^{31}P -NMR spectrum showed the resonance of free PMe_3 which was not significantly shifted by chemical exchange with the paramagnetic complex.

X-ray Structures. Compounds $\text{CpMoCl}_3(\text{PMe}_2\text{Ph})_2$, $\text{Cp}^*\text{MoCl}_3(\text{PMe}_3)$, and $\text{Cp}^*\text{MoCl}_3(\text{PMePh}_2)$ have been characterized by X-ray diffraction methods. Views of the three molecules are shown in Figures 1–3. All molecules are located on a general position. Only one of the two independent $\text{Cp}^*\text{MoCl}_3(\text{PMePh}_2)$ molecules is shown in Figure 3, the other being provided as part of the supplementary material. The molecular symmetry is approximately C_s for the first two structures (locally C_{2v} for the $\text{MoCl}_3(\text{PMe}_2\text{Ph})_2$ moiety).

When considering the Cp ligand as formally occupying a single coordination position, the geometry of the $\text{CpMoCl}_3(\text{PMe}_2\text{Ph})_2$ compound can be described as a distorted octahedron with the ligands arranged in a *mer,trans* fashion. The distortion is caused by the greater bulk of the axial Cp ring, which pushes the equatorial PMe_2Ph and Cl ligands away from it and toward the axial Cl ligand [Cp(center-of-gravity)–Mo–L angles are $99.5(1)^\circ$ for Cl(2), $104.5(1)^\circ$ for Cl(3), $105.8(1)^\circ$ for P(1), and $103.4(1)^\circ$ for P(2)]. The $\text{Cp}^*\text{MoCl}_3\text{L}$ molecules (L = PMe_3 , PMePh_2), on the other hand, adopt the typical four-legged piano stool geometry.¹¹ Cp(center-of-gravity)–Mo–L an-

Table IV. Positional Parameters and $B(\text{eq})$ Values for $\text{Cp}^*\text{MoCl}_3(\text{PMePh}_2)$

atom	x	y	z	$B(\text{eq}),^a \text{\AA}^2$
Mo(1)	0.18064(6)	0.18776(7)	0.39865(5)	3.20(5)
Mo(2)	0.78020(6)	0.13149(6)	0.04441(5)	2.95(4)
Cl(1)	0.0943(2)	0.2962(2)	0.4342(2)	6.2(2)
Cl(2)	0.0448(2)	0.1213(3)	0.3469(2)	7.0(2)
Cl(3)	0.2202(2)	0.0398(2)	0.4263(2)	5.5(2)
Cl(5)	0.8066(2)	0.0119(2)	-0.0250(2)	4.4(1)
Cl(6)	0.7224(2)	0.0171(2)	0.1037(2)	5.7(2)
Cl(7)	0.6611(2)	0.2115(2)	0.0652(2)	5.6(2)
P(1)	0.2507(2)	0.2003(2)	0.5291(2)	3.4(1)
P(2)	0.7109(2)	0.1847(2)	-0.0795(2)	3.3(1)
C(1)	0.2914(7)	0.2738(8)	0.3725(6)	3.5(5)
C(2)	0.2990(8)	0.1875(8)	0.3488(7)	4.4(6)
C(3)	0.224(1)	0.1692(8)	0.2960(7)	4.6(7)
C(4)	0.1718(8)	0.2443(8)	0.2870(6)	3.9(6)
C(5)	0.2135(7)	0.3072(8)	0.3328(6)	3.9(6)
C(6)	0.362(1)	0.324(1)	0.4192(7)	6.7(8)
C(7)	0.376(1)	0.128(1)	0.370(1)	9(1)
C(8)	0.202(1)	0.089(1)	0.2547(9)	9(1)
C(9)	0.090(1)	0.259(1)	0.2332(7)	7.7(9)
C(10)	0.188(1)	0.401(1)	0.3368(8)	7.1(8)
C(11)	0.2551(9)	0.3104(8)	0.5668(7)	5.4(7)
C(12)	0.1865(8)	0.1416(8)	0.5793(6)	3.8(6)
C(13)	0.2180(8)	0.134(1)	0.6501(7)	5.2(7)
C(14)	0.169(1)	0.097(1)	0.6910(7)	5.7(8)
C(15)	0.091(1)	0.063(1)	0.6610(8)	5.2(7)
C(16)	0.0601(8)	0.0672(8)	0.5909(7)	4.7(7)
C(17)	0.1080(8)	0.1059(7)	0.5491(6)	4.1(6)
C(18)	0.3604(7)	0.1619(8)	0.5612(6)	3.4(6)
C(19)	0.4278(8)	0.2200(7)	0.5828(6)	4.1(6)
C(20)	0.5104(9)	0.187(1)	0.6017(8)	6.0(8)
C(21)	0.5296(8)	0.102(1)	0.5976(8)	5.5(8)
C(22)	0.4637(9)	0.0447(8)	0.5792(7)	5.1(7)
C(23)	0.3802(8)	0.0737(9)	0.5602(7)	4.8(7)
C(24)	0.8916(7)	0.2394(7)	0.0571(6)	3.5(5)
C(25)	0.8567(7)	0.2470(8)	0.1147(6)	3.3(5)
C(26)	0.8689(7)	0.1678(8)	0.1510(6)	3.5(5)
C(27)	0.9160(7)	0.1109(7)	0.1170(6)	3.5(5)
C(28)	0.9298(7)	0.1543(7)	0.0586(6)	3.5(5)
C(29)	0.905(1)	0.313(1)	0.0125(7)	6.0(7)
C(30)	0.8216(9)	0.3275(9)	0.1392(8)	6.0(7)
C(31)	0.8464(9)	0.151(1)	0.2182(7)	5.8(7)
C(32)	0.9489(8)	0.0214(8)	0.1413(7)	6.0(7)
C(33)	0.9833(9)	0.125(1)	0.0115(8)	7.1(8)
C(34)	0.6539(8)	0.2877(8)	-0.0881(6)	5.0(7)
C(35)	0.7797(8)	0.1949(8)	-0.1401(5)	3.5(5)
C(36)	0.809(1)	0.2780(9)	-0.1535(7)	5.2(7)
C(37)	0.867(1)	0.283(1)	-0.1938(7)	5.9(8)
C(38)	0.896(1)	0.213(1)	-0.2242(7)	5.9(8)
C(39)	0.867(1)	0.133(1)	-0.2111(7)	5.9(8)
C(40)	0.8104(8)	0.1223(8)	-0.1685(6)	4.5(6)
C(41)	0.6236(7)	0.1120(7)	-0.1207(6)	3.5(6)
C(42)	0.5990(9)	0.101(1)	-0.1918(8)	5.9(8)
C(43)	0.526(1)	0.047(1)	-0.2203(7)	6.5(8)
C(44)	0.483(1)	0.006(1)	-0.178(1)	6.6(9)
C(45)	0.5077(9)	0.0188(8)	-0.1105(8)	5.2(7)
C(46)	0.5781(9)	0.0681(8)	-0.0803(6)	4.5(6)

^a Equivalent isotropic B defined as one third of the trace of the orthogonalized B_{ij} tensor.

gles for these molecules are larger (in the 110 – 120° range), the largest one being associated with the bulkier PMePh_2 ligand.

The Mo–Cl distances are considerably longer in the compound $\text{CpMoCl}_3(\text{PMe}_2\text{Ph})_2$ [2.461(1) Å for the axial Cl(1) ligand; 2.512(1) and 2.542(1) Å for the equatorial Cl ligands] than in the 16-electron compounds $\text{Cp}^*\text{MoCl}_3\text{L}$ (averages 2.406(9) Å for L = PMe_3 ; 2.389(13) and 2.402(16) Å for the two independent molecules with L = PMePh_2). This difference can be rationalized either on the basis of the σ -only bonding model as due to the greater electron density on the metal in the Cp-bis(PMe_2Ph) compound (which in turn indicates that one Cp and two PMe_2Ph donate more electron density overall to the metal than

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Table V. Selected Bond Lengths and Angles for CpMoCl₃(PMe₂Ph)₂

(a) Bond Lengths (Å)			
Mo–Cl(1)	2.461(1)	Mo–Cl(2)	2.542(1)
Mo–Cl(3)	2.512(1)	Mo–P(1)	2.555(1)
Mo–P(2)	2.553(1)	Mo–CNT ^a	1.974(3)
(b) Bond Angles (deg)			
Cl(1)–Mo–Cl(2)	76.01(1)	Cl(1)–Mo–Cl(3)	80.0(1)
Cl(2)–Mo–Cl(3)	156.0(1)	Cl(1)–Mo–P(1)	74.4(1)
Cl(2)–Mo–P(1)	89.4(1)	Cl(3)–Mo–P(1)	84.0(1)
Cl(1)–Mo–P(2)	76.8(1)	Cl(2)–Mo–P(2)	90.4(1)
Cl(3)–Mo–P(2)	84.4(1)	P(1)–Mo–P(2)	150.4(1)
Cl(1)–Mo–CNT ^a	175.5(1)	Cl(2)–Mo–CNT ^a	99.5(1)
Cl(3)–Mo–CNT ^a	104.5(1)	P(1)–Mo–CNT ^a	105.8(1)
P(2)–Mo–CNT ^a	103.4(1)		

^a CNT = centroid of atoms C(1)–C(5).**Table VI. Selected Bond Lengths and Angles for Cp*MoCl₃PMe₃**

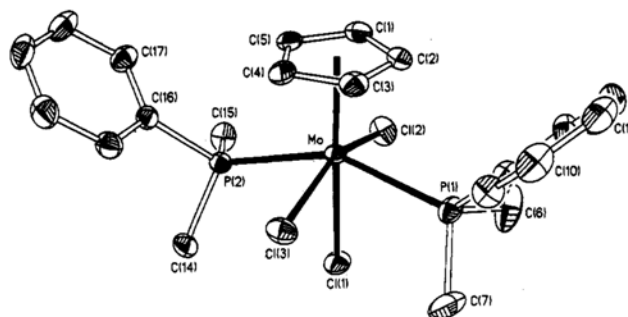
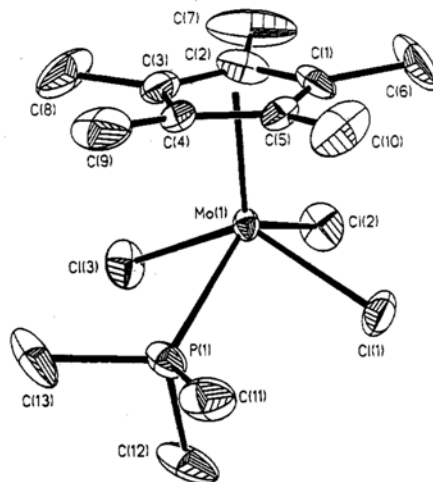
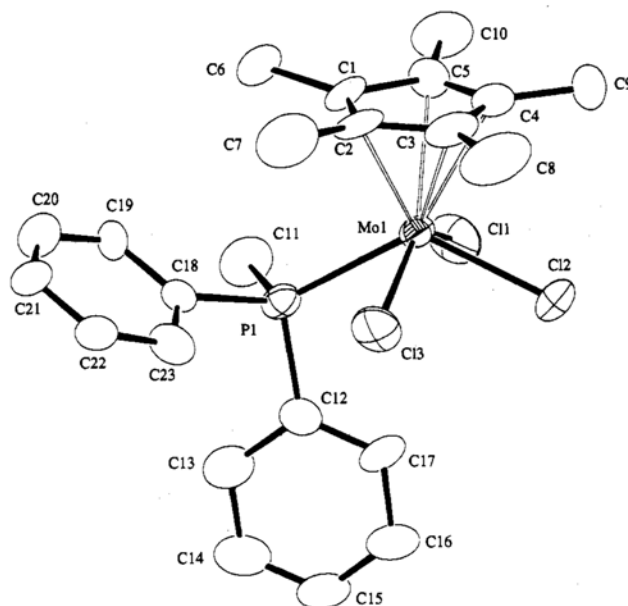
(a) Bond Lengths (Å)			
Mo(1)–Cl(1)	2.400(3)	Mo(1)–Cl(2)	2.420(3)
Mo(1)–Cl(3)	2.397(3)	Mo(1)–P(1)	2.533(3)
Mo(1)–CNT ^a	2.038(9)	P(1)–C(11)	1.794(10)
P(1)–C(12)	1.795(10)	P(1)–C(13)	1.814(12)
(b) Bond Angles (deg)			
Cl(1)–Mo(1)–Cl(2)	84.0(1)	Cl(1)–Mo(1)–Cl(3)	132.2(1)
Cl(2)–Mo(1)–Cl(3)	82.9(1)	Cl(1)–Mo(1)–P(1)	77.6(1)
Cl(2)–Mo(1)–P(1)	131.0(1)	Cl(3)–Mo(1)–P(1)	77.1(1)
Cl(1)–Mo(1)–CNT ^a	113.7(3)	Cl(2)–Mo(1)–CNT ^a	113.2(3)
Cl(3)–Mo(1)–CNT ^a	113.8(3)	P(1)–Mo(1)–CNT ^a	115.8(3)
Mo(1)–P(1)–C(11)	119.1(4)	Mo(1)–P(1)–C(12)	108.0(4)
Mo(1)–P(1)–C(13)	118.6(5)	C(11)–P(1)–C(12)	102.5(5)
C(11)–P(1)–C(13)	103.3(6)	C(12)–P(1)–C(13)	103.1(5)

^a CNT = centroid of atoms C(1)–C(5).**Table VII. Intramolecular Distances (Å) and Angles (deg) for Cp*MoCl₃(PMePh₂)^a**

Mo1–Cl1	2.380(4)	Mo2–Cl5	2.395(3)
Mo1–Cl2	2.405(4)	Mo2–Cl6	2.421(3)
Mo1–Cl3	2.384(3)	Mo2–Cl7	2.391(3)
Mo1–P1	2.578(3)	Mo2–P2	2.583(3)
Mo1–CNT1	2.03(1)	Mo2–CNT2	2.04(1)
P1–C18	1.82(1)	P2–C34	1.81(1)
P1–C12	1.84(1)	P2–C41	1.83(1)
P1–C11	1.84(1)	P2–C35	1.83(1)
Cl1–Mo1–Cl2	83.7(1)	Cl5–Mo2–Cl6	82.4(1)
Cl1–Mo1–Cl3	137.6(1)	Cl5–Mo2–Cl7	138.8(1)
Cl1–Mo1–P1	78.0(1)	Cl5–Mo2–P2	77.7(1)
Cl1–Mo1–CNT1	110.9(4)	Cl5–Mo2–CNT2	110.9(3)
Cl2–Mo1–Cl3	82.0(1)	Cl6–Mo2–Cl7	82.6(1)
Cl2–Mo1–P1	126.5(1)	Cl6–Mo2–P2	124.5(1)
Cl2–Mo1–CNT1	112.7(3)	Cl6–Mo2–CNT2	114.6(3)
Cl3–Mo1–P1	79.1(1)	Cl7–Mo2–P2	79.9(1)
Cl3–Mo1–CNT1	111.5(3)	Cl7–Mo2–CNT2	110.2(3)
P1–Mo1–CNT1	120.8(4)	P2–Mo2–CNT2	120.9(3)
Mo1–P1–C11	116.3(4)	Mo2–P2–C34	117.2(4)
Mo1–P1–C12	110.3(4)	Mo2–P2–C35	117.9(4)
Mo1–P1–C18	118.7(4)	Mo2–P2–C41	110.2(4)
C11–P1–C12	101.4(6)	C34–P2–C35	103.5(6)
C11–P1–C18	102.3(6)	C34–P2–C41	100.0(6)
C12–P1–C18	105.9(5)	C35–P2–C41	106.0(6)

^a CNT1 = centroid of atoms C1–C5. CNT2 = centroid of atoms C24–C28.

one Cp* and one PMe₃ or PMePh₂ ligand) or on the basis of the σ/π bonding model as involving also a contribution from active Mo–Cl π bonding in the unsaturated Cp* compound. Related Mo–Cl distances are in the 2.43–2.50-Å range for other CpMoCl₃L₂ complexes (L₂ = dmpe, dppe, [P(OCH₂)₃CET]₂)^{1a,4b,5b} and 2.371(13) Å (average) for [CpMoCl₂(PMe₃)₂]^{+,12} The Mo–P distances are similar for the three structures reported here and compare with those of other Mo(IV) complexes with monodentate

**Figure 1. ORTEP view of CpMoCl₃(PMe₂Ph)₂ with the atomic numbering scheme adopted. Ellipsoids are drawn at the 35% level.****Figure 2. ORTEP view of Cp*MoCl₃(PMe₃) with the atomic numbering scheme adopted. Ellipsoids are drawn at the 35% level.****Figure 3. ORTEP view of one of the two independent Cp*MoCl₃(PMePh) molecules with the atomic numbering scheme adopted. Ellipsoids are drawn at the 40% level.**

phosphines,¹² including complexes that do not contain cyclopentadienyl ligands.¹³ Finally, it is interesting to observe that, contrary to expectations, the Mo–ring(center-of-gravity) distance is longer for the unsaturated Cp* compounds. One possible rationalization is based on the greater steric bulk of Cp* because of the presence of the

five Me groups. The same effect was held responsible for the lengthening of the Mo-ring distance on going from $[\text{CpMoI}_2(\text{PMe}_3)_2]^+$ to $[\text{Cp}^*\text{MoI}_{1.5}\text{Cl}_{0.5}(\text{PMe}_3)_2]^+$.¹⁴

NMR and Magnetic Characterization. The 18-electron $\text{CpMoCl}_3(\text{PMe}_2\text{Ph})_2$ compound is diamagnetic, and its ^1H and ^{31}P -NMR spectra show no unusual features. They are consistent with the *mer,trans* solid-state structure in that they show chemically equivalent phosphorus atoms and phosphine methyl hydrogen atoms. Of the two alternative structures, the one having a *fac* arrangement of the three Cl atoms (found for the related complex $\text{CpMoCl}_3[\text{P}(\text{OCH}_2)_3\text{CEt}]_2$)^{1a} would have equivalent P atoms but inequivalent Me groups, and the *mer,cis* structure [found for the related $\text{CpMoCl}_3(\text{dppe})$ ^{4b} and $\text{CpMoCl}_3(\text{dmpe})$ ^{5b}] would have inequivalent P atoms and Me groups.

The 16-electron monophosphine adducts CpMoCl_3L ($\text{L} = \text{PMe}_2\text{Ph}, \text{PMePh}_2$) and $\text{Cp}^*\text{MoCl}_3\text{L}$ ($\text{L} = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2$) are all paramagnetic, as indicated by the paramagnetically shifted ^1H -NMR resonances and by the failure to observe a ^{31}P -NMR resonance. Several similar 16-electron Mo(IV) compounds have been reported earlier, for instance $[\text{CpMoX}_2(\text{PMe}_3)_2]^+$ ($\text{X} = \text{Cl}, \text{I}$) and $\text{CpMoCl}_3(\text{PMe}_3)$,⁶ which show similar paramagnetic shifts to those observed for the Cp compounds reported here. In particular, the Cp protons were reported at δ 179.5, 181.0, and 145.4 for $[\text{CpMoCl}_2(\text{PMe}_3)_2]\text{PF}_6$, $[\text{CpMoI}_2(\text{PMe}_3)_2]\text{PF}_6$, and $\text{CpMoCl}_3(\text{PMe}_3)$.⁶ The corresponding Cp resonances for CpMoCl_3L ($\text{L} = \text{PMe}_2\text{Ph}, \text{PMePh}_2$) are δ 150.0 and 149.5, respectively. The analogous Cp* compounds show methyl resonances at δ 0.6 and -2.5 at room temperature for the PMe_2Ph , and PMePh_2 adducts, respectively. All these resonances are broad ($w_{1/2} = \text{ca. } 100$ Hz) as would be expected of a paramagnetic system with relatively fast electronic relaxation. The phosphine methyl resonances appear as broad resonances at δ -11.6 for the previously reported $\text{CpMoCl}_3(\text{PMe}_3)$ compound,⁶ at δ -10.7 and -25.5 for the analogous PMe_2Ph and PMePh_2 derivatives, and at δ -19.1 and -13.4 for $\text{Cp}^*\text{MoCl}_3(\text{PMe}_2\text{Ph})$ and $\text{Cp}^*\text{MoCl}_3(\text{PMePh}_2)$. The phenyl proton resonances are somewhat more difficult to assign unambiguously, but they are typically found shifted downfield from their natural position in diamagnetic analogues (in the δ 15–6 range). This behavior (upfield paramagnetic shifts for phosphine Me protons and downfield paramagnetic shifts for phosphine Ph protons) is common to octahedral complexes of d^3 Mo(III).¹⁵

The ^1H -NMR spectrum of $\text{Cp}^*\text{MoCl}_3(\text{PMe}_3)$ shows a single broad resonance whose position is somewhat solvent dependent (δ 2.9 in C_6D_6 , 2.4 in CDCl_3 , 0.7 in CD_3CN). A variable-temperature ^1H -NMR study in acetone- d_6 shows a single broad resonance which slightly shifts upfield upon cooling (from δ 1.4 at 271 K to δ 0.1 at 199 K), and at ca. 215 K two broad bands start to appear at ca. δ 90 and -54 , which continue to shift away from the diamagnetic region on further cooling. The single broad resonance at ca. δ 0 remains, however, the major resonance in the spectrum.

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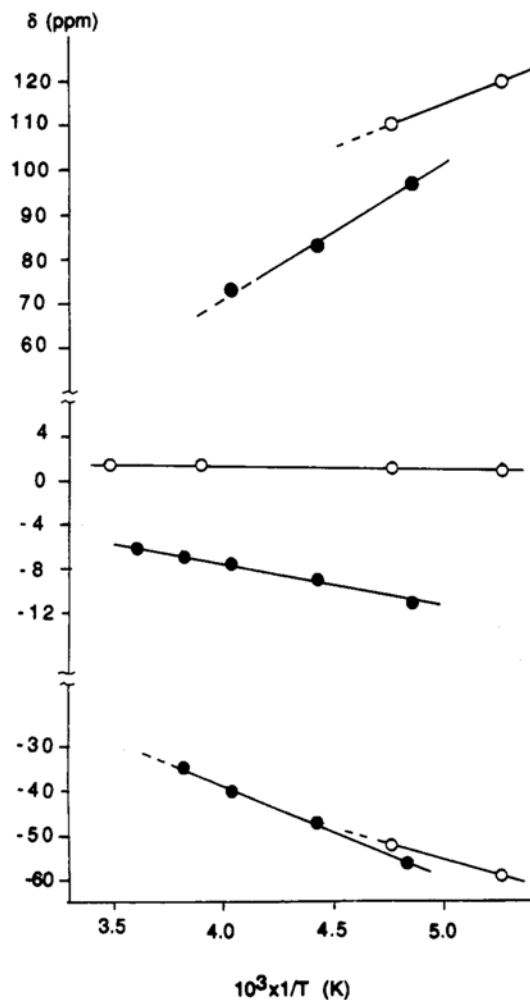


Figure 4. Position of ^1H -NMR resonances observed for $\text{Cp}^*\text{MoX}_3(\text{PMe}_3)$ as a function of temperature (O, $\text{X} = \text{Cl}$; ●, $\text{X} = \text{Br}$).

For comparison purposes, we have carried out an identical investigation on the previously reported² $\text{Cp}^*\text{MoBr}_3(\text{PMe}_3)$. The results are practically identical to those described above for the trichloride analogue. In this case, new broad and paramagnetically shifted peaks begin to appear at ca. 260 K. The temperature dependence of the peak position for both compounds is indicated in Figure 4. At the lowest temperature, the resonances of the bromide compound were sharp enough to allow an integration, which indicated that the two new resonances are in the correct relative intensity for the PMe_3 protons (downfield resonance) and Cp* protons (upfield resonance) of $\text{Cp}^*\text{MoBr}_3(\text{PMe}_3)$, and these two resonances combined represented 40% of the total intensity.

Compounds $\text{Cp}^*\text{MoX}_3(\text{PMe}_3)$ ($\text{X} = \text{Cl}, \text{Br}$) have also been investigated by magnetic susceptibility in solution (Evans' method). Both compounds show a moment close to the expected value for two unpaired electrons in CDCl_3 ($2.74 \mu_B$ for $\text{X} = \text{Br}$ at room temperature, $2.65 \mu_B$ for $\text{X} = \text{Cl}$ at 278 K). The moment measured for the trichloride compound does not substantially change upon cooling ($2.77 \mu_B$ at 215 K), but the moment is slightly lower when measured at room temperature in $\text{MeCN}-d_3$ ($2.26 \mu_B$).

Discussion

Adducts of $\{\text{CpMoCl}_3\}_n$ and Cp^*MoCl_3 with neutral donors have now been proven to adopt any of the following

structures: four-legged piano stool for the 16-electron mono-adducts and pseudooctahedral with either the *mer,trans*, the *mer,cis*, or the *fac* stereochemistry for the 18-electron bis-adducts. The choice between mono- and bis-adducts seems to be dictated solely by the steric requirements of the ligand system. Saturated bis-adducts are favored with small ligands such as CO^{2,3} and P(OCH₂)₃CET.¹ On the other hand, mono-adducts are formed by the Cp* system with phosphine ligands and by the Cp system with the bulkier phosphine PMePh₂. For the Cp derivatives with PMe₃⁶ and PMe₂Ph, either mono- or bis-adducts can be formed depending on the amount of available phosphine, and the bis-adducts can be transformed to mono-adducts in the presence of phosphine scavengers.

The *mer,trans* stereochemistry found for CpMoCl₃(PMe₂Ph)₂ (Figure 1) differs from those previously reported, that is, *mer,cis* [as in CpMoCl₃(dppe)^{4b} and CpMoCl₃(dmpe)^{5b}] or *fac* [as in CpMoCl₃[P(OCH₂)₃CET]₂^{1a}]. Compounds CpMoX₃(CO)₂ and Cp*MoX₃(CO)₂, although not crystallographically characterized, can also be assigned the *fac* geometry based on IR spectroscopy,^{2,3} and a *fac* geometry has been confirmed by X-ray crystallography on the related tungsten complex (η⁵-C₅H₄-i-Pr)WBr₃(CO)₂.¹⁶ Both steric and electronic effects probably influence the choice of stereochemistry for the bis-adducts. Small π acidic ligands (such as CO) probably induce the system to preferentially adopt the *fac* structure because they can so maximize the π back-bonding interaction. For the bulkier, poorer π accepting phosphine ligands, steric arguments become of primary importance. Although CpMoCl₃[P(OCH₂)₃CET]₂ still prefers to crystallize in the *fac* geometry^{1a} (the cage phosphite is a relatively small ligand with good π accepting capabilities), the more congested CpMoCl₃(PMe₂Ph)₂ exists as the *mer,trans* isomer where the two bulkier PMe₂Ph ligands are as far apart as possible. With the chelating dmpe and dppe ligands, the alternative *mer,cis* structure is probably favored by the better ability of this geometry to accommodate the small "bite angle" of the bidentate ligands.

For 16-electron mono-adducts, the four-legged piano stool structure previously proposed for CpMoCl₃(PMe₃) is now confirmed by the structure of the Cp* analogue (Figure 2). A four-legged piano stool compound with a 16-electron configuration (e.g., with a d² metal) can in principle be found in two different spin states: a diamagnetic state where the two metal electrons are coupled in the d_{xy} orbital and the d_{z²} orbital remains empty, or a triplet state where the two metal frontier orbitals hold one electron each.¹¹ According to pairing energy arguments,¹⁷ the low spin configuration should be preferred for low oxidation state systems where the pairing energy is low. Accordingly, Zr(II) systems such as (η⁶-arene)-ZrX₂(PMe₃)₂ (X = halogen) have been found to be diamagnetic,¹⁸ whereas the Nb(III) system Cp*NbCl₂(PMe₃)₂ is paramagnetic.¹⁹ On the basis of this trend, the Mo(IV)Cp and Cp*MoCl₃(PR₃) systems are also expected to be paramagnetic, and this is indeed what we find. The

structural parameters of Cp*MoCl₃L (L = PMe₃, PMePh₂), notably the ring centroid-M-Cl angles (θ), are also consistent with an S = 1 configuration. In case of a low-spin configuration, the π-donor ligands tend to distort by increasing the θ angle, thereby maximizing the π overlap with the empty d_{z²}.^{11b} In the low spin Zr(II) complexes mentioned above θ_X is in the 125–128° range,¹⁸ whereas for high spin complexes such as [CpMoX₂(PMe₃)₂]⁺ (X = Cl, I)^{12,14} and CpVCl₂(PMe₃)₂,²⁰ θ_X is always smaller than 120°.

For the compound Cp*MoCl₃(PMe₃), the moment measured by the NMR method is 2.65 μ_B in CD₂Cl₂ at 278 K, a value slightly lower than the spin-only value calculated for two unpaired electrons (2.83 μ_B), and is relatively temperature independent in the 278–215-K range. Magnetic moments for Mo(IV) compounds with this geometry have not been reported before to the best of our knowledge. Magnetic moments of Mo(IV) complexes with octahedral geometry are in the 2.2–2.5 μ_B range.²¹ However, the observed moment of Cp*MoCl₃(PMe₃) is lower in CD₃CN solution (2.26 μ_B at room temperature). On the basis of the comparison with the magnetic properties of isoelectronic Zr(II) and Nb(III) complexes (see above), we do not believe that this is indication of a solvent-dependent spin equilibrium with an S = 0 Cp*MoCl₃(PMe₃) structure. We rather prefer to suggest that there may be an equilibrium between the 16-electron structure and a 18-electron (therefore diamagnetic) solvent adduct which would have a structure similar to that of the crystallographically characterized CpMoCl₃(PMe₂Ph)₂ complex (Figure 1). The small size of the MeCN donor would seem to make a ligand addition possible to this system. On the other hand, we point out that the unsaturated compound CpMoCl₃(PMe₂Ph) does not strongly bind THF, since the two species are independently observed in the ¹H-NMR spectrum (CDCl₃ solution).

The variable-temperature ¹H-NMR investigation of Cp*MoX₃(PMe₃) (X = Cl, Br) was carried out to resolve the question of the missing second resonance. We believe the observed results are most consistent with the assignment of the more intense low-temperature absorption to the resonances of Cp* and PMe₃ protons in the four-legged piano stool structure which accidentally overlap, and the two paramagnetically more shifted resonances that are observed only at low temperature are assigned to a second paramagnetic (S = 1) isomeric form. The observed magnetic moment in solution and the high paramagnetic shifts rule out an equilibrium between a paramagnetic monomer and either a dinuclear (18-electron) species or a S = 0 monomer. Other four-legged piano stool Mo(IV) compounds, including the structurally characterized [CpMoX₂(PMe₃)₂]⁺ (X = Cl, I) species,^{12,14} show paramagnetically shifted PMe₃ resonances at ca. δ -10 at room temperature,⁶ which is in the range observed for the phosphine methyl protons of the other Cp*MoCl₃L (L = PMe₂Ph, PMePh₂) compounds reported here. The latter compounds show Cp* resonances in the δ 1 to -3 region. Furthermore, the structurally characterized Cp*₂Mo₂X₄(μ-X)₂ compounds with a four-legged piano stool configuration around the two weakly antiferromagnetically coupled Mo(IV) centers have a room-temperature Cp* resonance of ca. δ -4 and ca. δ -6 for X = Cl and X = Br,

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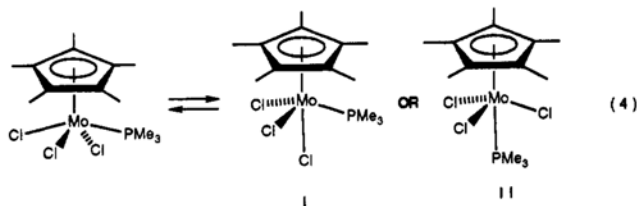
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respectively.² Thus, both Cp* and PCH₃ protons in four-legged piano stool Mo(IV) compounds resonate in the same region, that is, around or slightly upfield of 0 δ . The peaks observed for the other species are in completely different regions (values extrapolated to room temperature are in the δ 50 to 90 range for PMe₃ and in the δ -20 to -30 range for Cp*, see Figure 4). Only with a different geometry is it likely that a very different spin density is transmitted to the protons in the molecule. A possible alternative to the four-legged piano stool is the pseudo-tbp structure.^{11a} Thus, we propose an equilibrium as represented in eq 4.



It is not possible to distinguish between I and II on the basis of the ¹H-NMR. It is to be observed that although the four-legged piano stool, or pseudo-sp, is the ubiquitous structural type for CpML₄ compounds,¹¹ the pseudo-tbp arrangement is adopted by [Cp*WMe₄]⁺.²² Pseudo-sp/pseudo-tbp equilibria have been proposed before for 18-electron CpMX(CO)L₂ (M = Mo, W; X = Cl, Br, I; L = PMePh₂, P(OMe)Ph₂) compounds²³ and for the 17-electron

CpMoX₂L₂ (X = Cl, L₂ = dppe, L = PMePh₂ or PPh₃; X = I, L = PMePh₂) compounds²⁴ on the basis of low-temperature NMR and X- and Q-band EPR, respectively. The observations reported here are the first ones to indicate the same kind of equilibrium in a CpML₄ system with a 16-electron configuration.

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Supplementary Material Available: Full tables of bond distances and angles, anisotropic displacement parameters, and H-atom coordinates for compounds CpMoCl₃(PMe₂Ph)₂, Cp*MoCl₃(PMe₃), and Cp*MoCl₃(PMePh₂) and an ORTEP view of the second Cp*MoCl₃(PMePh₂) molecule in the asymmetric unit with numbering scheme (22 pages). Ordering information is given on any current masthead page.

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