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New Phosphine-Containing Cyclopentadienylmolybdenum(IV) Complexes with an 18- and a 16-Electron Count. X-ray Structure of $CpMoCl_3(PMe_2Ph)_2$ and Cp^*MoCl_3L (L = PMe_3, $PMePh_2$)

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Molybdenum(IV) complexes of the general formula $CpMoCl_3L_n$ ($Cp = \eta^5\text{-}C_5H_5$; $n = 1, 2$) and Cp^*MoCl_3L ($Cp^* = \eta^5\text{-}C_5Me_5$) 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 L = 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 (L = PMe_3, PMe_2Ph, $PMePh_2$), and no tendency of these to add additional L was observed. All 16-electron mono-adducts show paramagnetically shifted ^1H-NMR spectra in accord with the observed spin triplet ground state. A variable-temperature study on $Cp^*MoCl_3(PMe_3)$ 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. $CpMoCl_3(PMe_2Ph)_2$: triclinic, $P\bar{1}$, $a = 10.807(2)$ Å, $b = 11.621(2)$ Å, $c = 11.644(2)$ Å, $\alpha = 89.72(1)°$, $\beta = 70.61(1)°$, $\gamma = 83.15(1)°$, $V = 1368.6(4)$ Å^3, $Z = 2$, $d_{calcd} = 1.494$ g·cm^{-3}. $Cp^*MoCl_3(PMe_3)$: orthorhombic, $P2_12_12_1$, $a = 8.178(2)$ Å, $b = 13.186(3)$ Å, $c = 15.206(3)$ Å, $V = 1764.1(7)$ Å^3, $Z = 4$, $d_{calcd} = 1.557$ g·cm^{-3}. $Cp^*MoCl_3(PMePh_2)$: monoclinic, $P2_1/a$, $a = 16.062(2)$ Å, $b = 15.335(2)$ Å, $c = 19.914(3)$ Å, $\beta = 103.90(1)°$, $V = 4761(2)$ Å^3, $Z = 8$, $d_{calcd} = 1.50$ g·cm^{-3}. The two Cp* compounds adopt a pseudo-square pyramidal geometry with the Cp* ring in the apical position, whereas the $CpMoCl_3(PMe_2Ph)$ 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, $\{CpMoX_3\}_n$ (X = Cl, Br, I)[1] and $[Cp^*MoX_3]_2$ (X = Cl, Br).[2] Adducts of the cyclopentadienyl system with neutral donors have been known for a longer time, e.g., $CpMoX_3(CO)_2$ (X = Cl, Br, I),[3] $CpMoX_3(dppe)$ (X = Cl, Br),[4] $CpMoCl_3(dmpe)$,[5] and $CpMoX_3[P(OCH_2)_3CEt]_2$ (X = Cl, Br).[1] All these neutral donors either have a small cone angle or are chelating bidentate 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 $CpMoX_2(PMe_3)_2$ (X = Cl, I) system, whereby the ligand exchange is catalyzed by oxidation to the corresponding 16-electron cationic complexes, we discovered that the interaction between $[CpMoCl_2(PMe_3)_2]^+$ and Cl^- affords the unstable 18-electron complex $CpMoCl_3(PMe_3)_2$ which establishes an equilibrium with 16-electron, paramagnetic $CpMoCl_3(PMe_3)$.[6] This finding prompted us to examine adducts of $\{CpMoCl_3\}_n$ or $[Cp^*MoCl_3]_2$ 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. $\{CpMoCl_3\}_n$ and Cp^*MoCl_4 were prepared as described in the literature.[1,7]

Reaction between $\{CpMoCl_3\}_n$ and PMe_2Ph. Formation of $CpMoCl_3(PMe_2Ph)_2$ and $CpMoCl_3(PMe_2Ph)$. $\{CpMoCl_3\}_n$ (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	$CpMoCl_3(PMe_2Ph)_2$	$Cp^*MoCl_3(PMe_3)$	$Cp^*MoCl_3(PMePh_2)$
formula	$C_{25}H_{35}Cl_3MoOP_2$	$C_{13}H_{24}Cl_3MoP$	$C_{23}H_{28}Cl_3MoP$
fw	615.8	413.6	537.75
space grp	$P\bar{1}$	$P2_12_12_1$	$P2_1/a$
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 ($F_o \geq 4\sigma(F_o)$)	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
$\Delta(\rho)$, 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 ^{1}H-NMR are consistent with the presence of loosely packed lattice THF. Anal. Calcd for $C_{23}H_{31}Cl_3MoO_{0.5}P_2$ ($CpMoCl_3(PMe_2Ph)_2\cdot{}^1/_2THF$): C, 47.65; H, 5.39; Cl, 18.35. Found: C, 47.4; H, 5.6; Cl, 20.4. ^{1}H-NMR ($CDCl_3$, δ) of this material does not show evidence for $CpMoCl_3(PMe_2Ph)$: 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). ^{31}P-NMR ($CDCl_3$, 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 $CDCl_3$. ^{1}H-NMR inspection of this solution was consistent with a mixture of $CpMoCl_3(PMe_2Ph)_2$ and $CpMoCl_3(PMe_2Ph)$. ^{1}H-NMR for $CpMoCl_3(PMe_2Ph)$: 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 (^{1}H-NMR) of the presence of $CpMoCl_3(PMe_2Ph)$.

Reaction between $CpMoCl_3(PMe_2Ph)_2$ and MeI. $CpMoCl_3(PMe_2Ph)_2$ (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 ^{1}H-NMR in $CDCl_3$, confirming the presence of $CpMoCl_3(PMe_2Ph)$ (see previous section).

Preparation of $CpMoCl_3(PMePh_2)$. $\{CpMoCl_3\}_n$ (301 mg, 1.13 mmol of $CpMoCl_3$) was slurried in THF (40 mL), and to the resulting mixture $PMePh_2$ (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%). ^{1}H-NMR and elemental analyses showed that the compound crystallizes with loosely bound THF. Anal. Calcd for $C_{22}H_{26}Cl_3MoOP_2$ ($CpMoCl_3(PMePh_2)\cdot THF$): C, 48.96; H, 4.86; Cl, 19.71. Found: C, 48.6; H, 4.6; Cl, 20.1. ^{1}H-NMR ($CDCl_3$, 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 ^{1}H-NMR and had the following elemental analysis: C, 47.1; H, 4.6; Cl, 20.7. Calcd for $CpMoCl_3(PMePh_2)\cdot{}^1/_2THF$: C, 47.69; H, 4.40; Cl, 21.12.

Preparation of $Cp^*MoCl_3(PMe_3)$. Cp^*MoCl_4 (374 mg, 1.00 mmol) was suspended in THF (35 mL) and reacted with PMe_3 (104 μL, 1.04 mmol). EPR investigation of the resulting mixture confirmed the presence of $Cp^*MoCl_4(PMe_3)$.[7] The mixture was transferred via cannula into a Schlenck 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 $C_{13}H_{24}Cl_3MoP$: C, 37.75; H, 5.85; Cl, 25.71. Found: C, 37.7; H, 5.9; Cl, 25.6. ^{1}H-NMR (C_6D_6, δ): 2.9. μ_{eff} = 2.65 μ_B (CD_2Cl_2 solution, 278 K); 2.77 μ_B (CD_2Cl_2 solution, 215 K); 2.26 μ_B (CD_3CN solution, room temperature). A single crystal from this batch was used for the X-ray analysis.

Preparation of $Cp^*MoCl_3(PMe_2Ph)$. By a procedure analogous to that described above for the preparation of $Cp^*MoCl_3(PMe_3)$, Cp^*MoCl_4 (1.106 g, 2.97 mmol), PMe_2Ph (422 μL, 2.97 mmol), and Na amalgam (68 mg, 2.96 mmol, in 21.2 g Hg) afforded 764 mg of $Cp^*MoCl_3(PMe_2Ph)$ (yield: 53%). After the addition of PMe_2Ph 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 $C_{18}H_{26}Cl_3MoP$: C, 45.45; H, 5.51; Cl, 22.36. Found: C, 45.4; H, 5.5; Cl, 20.9. ^{1}H-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 $Cp^*MoCl_3(PMePh_2)$. By a procedure analogous to that described above for the preparation of $Cp^*MoCl_3(PMe_3)$, Cp^*MoCl_4 (227 mg, 0.609 mmol), $PMePh_2$ (227 μL, 1.22 mmol), and Na amalgam (42 mg, 1.83 mmol, in 12.0 g Hg) afforded

103 mg of $Cp^*MoCl_3(PMePh_2)$ (yield: 31.4%). After the addition of $PMePh_2$ 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 $C_{23}H_{28}Cl_3MoP$: 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 $CpMoCl_3(PMe_2Ph)_2$, $Cp^*MoCl_3(PMe_3)$ and $Cp^*MoCl_3(PMePh_2)$. 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 ($20° \leq 2\theta \leq 25°$). Photographic evidence and cell reduction routines indicated $\bar{1}$ symmetry for $CpMoCl_3(PMe_2Ph)_2$. 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 $Cp^*MoCl_3(PMe_3)$ 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 $Cp^*MoCl_3(PMePh_2)$ 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 $Cp^*MoCl_3(PMe_3)$, 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 $CpMoCl_3(PMe_2Ph)_2$, $Cp^*MoCl_3(PMe_3)$, and $Cp^*MoCl_3(PMePh_2)$, 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 PMe_2Ph and $PMePh_2$ have been prepared by direct interaction of the phosphine with $\{CpMoCl_3\}_n$ (eqs 1 and 2). Thus, these reactions do not suffer from the complications found for the corresponding reaction with PMe_3, which produces a variety of decomposition products including $MoCl_3(PMe_3)_3$.[1a]

$$(1/n)\{CpMoCl_3\}_n + 2PMe_2Ph \rightarrow CpMoCl_3(PMe_2Ph)_2 \rightleftarrows CpMoCl_3(PMe_2Ph) + PMe_2Ph \quad (1)$$

$$(1/n)\{CpMoCl_3\}_n + PMePh_2 \text{ (excess)} \rightarrow CpMoCl_3(PMePh_2) \not\rightarrow CpMoCl_3(PMePh_2)_2 \quad (2)$$

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 10^3$) for $CpMoCl_3(PMe_2Ph)_2$

	x	y	z	U(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 PMe_2Ph adduct behaves in a similar way to the previously investigated PMe_3 compound,[6] the mono- and bis-adducts being in equilibrium in solution, whereas the slightly larger phosphine $PMePh_2$ only affords the mono-adduct. The $CpMoCl_3(PMe_2Ph)_2$ 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 PMe_3 system, for which the immediate formation of a mixture of mono- and bis-adducts from $[CpMoCl_2(PMe_3)_2]^+$ and Cl^- indicates a fast equilibrium. However, when the bis-PMe_2Ph compound is reacted with the phosphine scavenger MeI, the mono-PMe_2Ph compound slowly forms. Evidence for the formation of the 16-electron mono-adduct is also obtained when the bis-PMe_2Ph complex is kept for a long period of time in $CDCl_3$, although in this case the reaction is more complex and other decomposition products are also observed.

The pentamethylcyclopentadienyl system, Cp^*MoCl_3, only forms mono-adducts with tertiary phosphines, including the relatively small PMe_3 ligand. Although we now know that these compounds can also be made by adding the phosphine directly to $[Cp^*MoCl_3]_2$,[2] for the purpose of this investigation they were prepared by reduction of Cp^*MoCl_4 in the presence of the appropriate phosphine (eq 3).

$$Cp^*MoCl_4 + PR_3 + Na \rightarrow Cp^*MoCl_3(PR_3) + NaCl \quad (3)$$

Addition of PR_3 to Cp^*MoCl_4 affords the corresponding adducts $Cp^*MoCl_4(PR_3)$, which can be identified by EPR

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[8] Sheldrick, G., Siemens XRD, Madison, WI.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Cp*MoCl$_3$(PMe$_3$)

	x	*y*	*z*	*U*(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 $\mathbf{U}_{ij}$ 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 Cp*MoCl$_4$(PMe$_3$) with excess sodium in the presence of PMe$_3$ affords Cp*MoCl$_2$(PMe$_3$)$_2$, Cp*MoCl(PMe$_3$)$_2$(N$_2$), or Cp*MoCl(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 Cp*MoCl$_3$(PMe$_3$) did not perturb the appearance of the ^{1}H 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 CpMoCl$_3$(PMe$_2$Ph)$_2$, Cp*MoCl$_3$(PMe$_3$), and Cp*MoCl$_3$(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 Cp*MoCl$_3$(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 MoCl$_3$(PMe$_2$Ph)$_2$ moiety).

When considering the Cp ligand as formally occupying a single coordination position, the geometry of the CpMoCl$_3$(PMe$_2$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$_2$Ph and Cl ligands away from it and toward the axial Cl ligand [Cp(center-of-gravity)–Mo–L angles are 99.5(1)° for Cl(2), 104.5(1)° for Cl(3), 105.8(1)° for P(1), and 103.4(1)° for P(2)]. The Cp*MoCl$_3$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 angles for these molecules are larger (in the 110–120° range), the largest one being associated with the bulkier PMePh$_2$ ligand.

Table IV. Positional Parameters and *B*(eq) Values for Cp*MoCl$_3$(PMePh$_2$)

atom	*x*	*y*	*z*	*B*(eq),^{a} Å^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 $\mathbf{B}_{ij}$ tensor.

The Mo–Cl distances are considerably longer in the compound CpMoCl$_3$(PMe$_2$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 Cp*MoCl$_3$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$_2$Ph) compound (which in turn indicates that one Cp and two PMe$_2$Ph donate more electron density overall to the metal than

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Table V. Selected Bond Lengths and Angles for $CpMoCl_3(PMe_2Ph)_2$

(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 $Cp^*MoCl_3PMe_3$

(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 $Cp^*MoCl_3(PMePh_2)$[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.

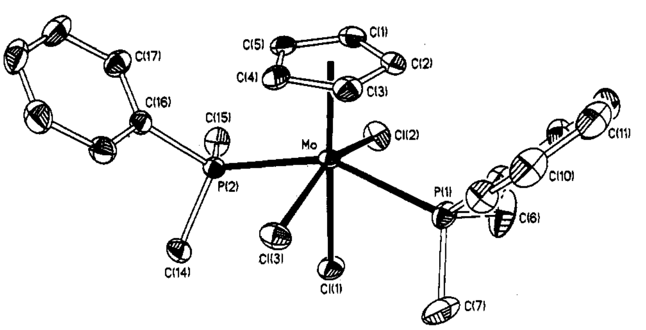

Figure 1. ORTEP view of $CpMoCl_3(PMe_2Ph)_2$ with the atomic numbering scheme adopted. Ellipsoids are drawn at the 35% level.

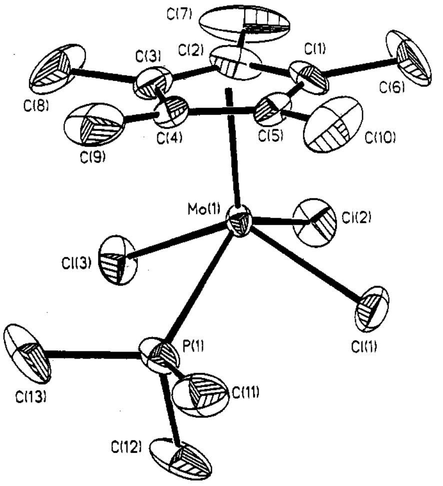

Figure 2. ORTEP view of $Cp^*MoCl_3(PMe_3)$ with the atomic numbering scheme adopted. Ellipsoids are drawn at the 35% level.

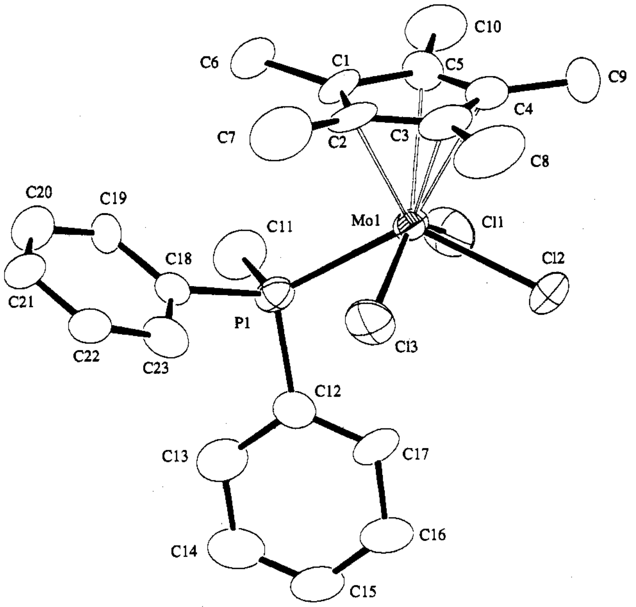

Figure 3. ORTEP view of one of the two independent $Cp^*MoCl_3(PMePh)$ molecules with the atomic numbering scheme adopted. Ellipsoids are drawn at the 40% level.

one Cp* and one PMe_3 or $PMePh_2$ 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 $CpMoCl_3L_2$ complexes (L_2 = dmpe, dppe, $[P(OCH_2)_3CEt]_2$)[1a,4b,5b] and 2.371(13) Å (average) for $[CpMoCl_2(PMe_3)_2]^+$.[12] The Mo–P distances are similar for the three structures reported here and compare with those of other Mo(IV) complexes with monodentate 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 $[CpMoI_2(PMe_3)_2]^+$ to $[Cp^*MoI_{1.5}Cl_{0.5}(PMe_3)_2]^+$.[14]

NMR and Magnetic Characterization. The 18-electron $CpMoCl_3(PMe_2Ph)_2$ 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 $CpMoCl_3[P(OCH_2)_3CEt]_2$)[1a] would have equivalent P atoms but inequivalent Me groups, and the *mer,cis* structure [found for the related $CpMoCl_3(dppe)$[4b] and $CpMoCl_3(dmpe)$[5b]] would have inequivalent P atoms and Me groups.

The 16-electron monophosphine adducts $CpMoCl_3L$ (L = PMe_2Ph, $PMePh_2$) and Cp^*MoCl_3L (L = PMe_3, PMe_2Ph, $PMePh_2$) 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 $[CpMoX_2(PMe_3)_2]^+$ (X = Cl, I) and $CpMoCl_3(PMe_3)$,[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 $[CpMoCl_2(PMe_3)_2]PF_6$, $[CpMoI_2(PMe_3)_2]PF_6$, and $CpMoCl_3(PMe_3)$.[6] The corresponding Cp resonances for $CpMoCl_3L$ (L = PMe_2Ph, $PMePh_2$) 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 ($w_{1/2}$ = 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 $CpMoCl_3(PMe_3)$ 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 $Cp^*MoCl_3(PMe_2Ph)$ and $Cp^*MoCl_3(PMePh_2)$. 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 $Cp^*MoCl_3(PMe_3)$ 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.

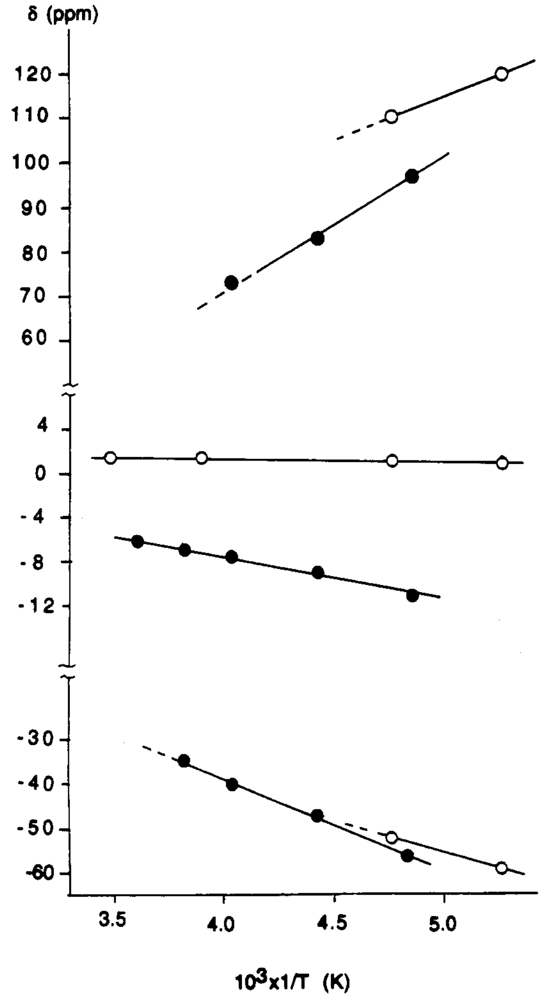

Figure 4. Position of ^1H-NMR resonances observed for $Cp^*MoX_3(PMe_3)$ as a function of temperature (○, X = Cl; ●, X = Br).

For comparison purposes, we have carried out an identical investigation on the previously reported[2] $Cp^*MoBr_3(PMe_3)$. 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 relatively intensity for the PMe_3 protons (downfield resonance) and Cp* protons (upfield resonance) of $Cp^*MoBr_3(PMe_3)$, and these two resonances combined represented 40% of the total intensity.

Compounds $Cp^*MoX_3(PMe_3)$ (X = Cl, 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 μ_B for X = Br at room temperature, 2.65 μ_B for X = Cl at 278 K). The moment measured for the trichloride compound does not substantially change upon cooling (2.77 μ_B at 215 K), but the moment is slightly lower when measured at room temperature in MeCN-d_3 (2.26 μ_B).

Discussion

Adducts of $\{CpMoCl_3\}_n$ and Cp^*MoCl_3 with neutral donors have now been proven to adopt any of the following

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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 $P(OCH_2)_3CEt$.[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 $PMePh_2$. For the Cp derivatives with PMe_3[6] and PMe_2Ph, 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 $CpMoCl_3(PMe_2Ph)_2$ (Figure 1) differs from those previously reported, that is, *mer,cis* [as in $CpMoCl_3(dppe)$[4b] and $CpMoCl_3(dmpe)$[5b]] or *fac* [as in $CpMoCl_3[P(OCH_2)_3CEt]_2$[1a]]. Compounds $CpMoX_3(CO)_2$ and $Cp^*MoX_3(CO)_2$, 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 (η^5-C_5H_4-*i*-Pr)$WBr_3(CO)_2$.[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 $CpMoCl_3[P(OCH_2)_3CEt]_2$ 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 $CpMoCl_3(PMe_2Ph)_2$ exists as the *mer,trans* isomer where the two bulkier PMe_2Ph 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 $CpMoCl_3(PMe_3)$ 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 d^2 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_{z^2} 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 (η^6-arene)$ZrX_2(PMe_3)_2$ (X = halogen) have been found to be diamagnetic,[18] whereas the Nb(III) system $Cp^*NbCl_2(PMe_3)_2$ is paramagnetic.[19] On the basis of this trend, the Mo(IV)Cp and $Cp^*MoCl_3(PR_3)$ systems are also expected to be paramagnetic, and this is indeed what we find. The structural parameters of Cp^*MoCl_3L (L = PMe_3, $PMePh_2$), 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_{z^2}.[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 $[CpMoX_2(PMe_3)_2]^+$ (X = Cl, I)[12,14] and $CpVCl_2(PMe_3)_2$,[20] θ_X is always smaller than 120°.

For the compound $Cp^*MoCl_3(PMe_3)$, the moment measured by the NMR method is 2.65 μ_B in CD_2Cl_2 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 $Cp^*MoCl_3(PMe_3)$ is lower in CD_3CN 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 $S = 0$ $Cp^*MoCl_3(PMe_3)$ 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 $CpMoCl_3(PMe_2Ph)_2$ 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 $CpMoCl_3(PMe_2Ph)$ does not strongly bind THF, since the two species are independently observed in the ^{1}H-NMR spectrum ($CDCl_3$ solution).

The variable-temperature ^{1}H-NMR investigation of $Cp^*MoX_3(PMe_3)$ (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 PMe_3 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 $[CpMoX_2(PMe_3)_2]^+$ (X = Cl, I) species,[12,14] show paramagnetically shifted PMe_3 resonances at ca. δ −10 at room temperature,[6] which is in the range observed for the phosphine methyl protons of the other Cp^*MoCl_3L (L = PMe_2Ph, $PMePh_2$) compounds reported here. The latter compounds show Cp* resonances in the δ 1 to −3 region. Furthermore, the structurally characterized $Cp^*{}_2Mo_2X_4(\mu$-$X)_2$ 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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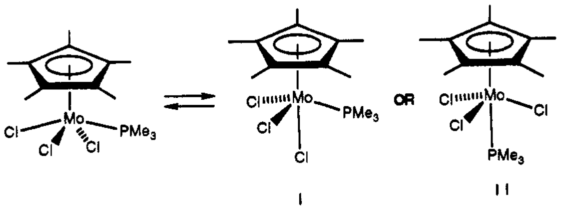
respectively.[2] Thus, both Cp* and PCH_3 protons in four-legged piano stool Mo(IV) compounds resonate in the same region, that is, around or slightly upfield of 0 δ. The peaks observed for the other species are in completely different regions (values extrapolated to room temperature are in the δ 50 to 90 range for PMe_3 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.



(4)

It is not possible to distinguish between **I** and **II** on the basis of the ^{1}H-NMR. It is to be observed that although the four-legged piano stool, or pseudo-sp, is the ubiquitous structural type for $CpML_4$ compounds,[11] the pseudo-tbp arrangement is adopted by $[Cp^*WMe_4]^+$.[22] Pseudo-sp/pseudo-tbp equilibria have been proposed before for 18-electron $CpMX(CO)L_2$ (M = Mo, W; X = Cl, Br, I; L = $PMePh_2$, $P(OMe)Ph_2$) compounds[23] and for the 17-electron $CpMoX_2L_2$ (X = Cl, L_2 = dppe, L = $PMePh_2$ or PPh_3; X = I, L = $PMePh_2$) compounds[24] 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 $CpML_4$ 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 coördinates for compounds $CpMoCl_3(PMe_2Ph)_2$, $Cp^*MoCl_3(PMe_3)$, and $Cp^*MoCl_3(PMePh_2)$ and an ORTEP view of the second $Cp^*MoCl_3(PMePh_2)$ molecule in the asymmetric unit with numbering scheme (22 pages). Ordering information is given on any current masthead page.

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