Organometallics **1991,** *10,* 3041–3046

Reactions of $CpMoCl_2L_2$ ($Cp = \eta^5$-C_5H_5; $L = PMe_3, PMe_2Ph$) with Methyllithium. Preparation and Structure of a Molybdenum(II) Compound Containing an Ortho-Metalated PMe_2Ph Ligand: $CpMo(o$-$C_6H_4PMe_2)(PMe_2Ph)_2$

Rinaldo Poli,*[,1a] Steven T. Krueger,[1a] Fatima Abugideiri,[1a] Brian S. Haggerty,[1b] and Arnold L. Rheingold[1b]

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, and Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received March 11, 1991

The reaction of $CpMoCl_2(PMe_3)_2$ with methyllithium in the presence of PMe_3 generates $CpMoMe(PMe_3)_3$. The intermediate 17-electron dimethyl derivative, $CpMoMe_2(PMe_3)_2$, can be identified by EPR. The analogous methylation of $CpMoCl_2(PMe_2Ph)_2$ generates low yields of the ortho-metalated complex, $CpMo(o$-$C_6H_4PMe_2)(PMe_2Ph)_2$, which has been structurally characterized. Crystal data: monoclinic, space group $P2_1/n$, $a = 14.855$ (3) Å, $b = 13.655$ (2) Å, $c = 15.174$ (2) Å, $\beta = 110.887$ (13)°, $V = 2875.8$ (8) Å^3, $Z = 4$, $R = 0.0393$, $R_w = 0.0437$. The four-legged piano stool structure shows variation in bond distances and angles that can be rationalized in terms of Mo–P π back-bonding. The instability and susceptibility to reduction of the 17-electron $CpMoX_2(PMe_3)_2$ (X = alkyl) with respect to the stability and susceptibility to oxidation of the same compounds with X = halogen is rationalized on the basis of the π-bonding properties of the ligands.

Introduction

We have recently investigated the class of stable 17-electron organometallic compounds $CpMoX_2L_2$ (X = Cl, Br, I; $L = PMe_3$[2] or L_2 = dppe[3]). We were interested in these materials, among other things, as potential synthons to other organometallic odd-electron compounds via the substitution of the ligands X and/or L. Odd-electron alkyl or aryl compounds constitute a class of materials whose reactivity is enhanced with respect to their electronically saturated counterparts,[4] and for this reason, they are potentially interesting for stoichiometric organic transformations and for catalysis. Several odd-electron alkyl derivatives have been isolated by taking advantage of steric hindrance, chelating effect, intertness of the electronic configurations, and thermodynamic stability of bonds to ancillary ligands, all factors that increase the activation energy of decomposition pathways. Among these derivatives, those with a 17-electron count are a relatively small number.[5] We tested our Mo(III) material as a possible precursor of 17-electron dimethyl species and report here the results of these studies. Stable compounds of formula $CpMo(CH_3)_2L_2$ were not obtained, although the one with $L = PMe_3$ was observed as intermediate, and products of metal reduction were obtained instead.

Experimental Section

Unless otherwise stated, all operations were carried out under an atmosphere of dinitrogen or argon. The solvents were dehydrated by conventional methods and distilled under dinitrogen prior to use. Instruments used were as follows: NMR, Bruker AF200, Bruker WP200, and Bruker AM400; EPR, Bruker ER200; FTIR, Nicolet 5DXC. Gas chromatographic analyses were carried out on a Hewlett-Packard 5890A instrument using a 6-ft packed column with Porapak Q as the stationary phase and N_2 as the carrier gas. Elemental analyses were by Galbraith Laboratories, Knoxville, TN. $CpMoCl_2$ was prepared as described in the literature.[6] Solutions of MeLi in Et_2O, $AlMe_3$ in THF, and MeMgBr in THF were purchased from Aldrich and used as received after titration. MeZnI was prepared from MeI and activated (with $BrCH_2CH_2Br$) zinc powder.

Methylation Reaction of $CpMoCl_2(PMe_3)_2$. (a) EPR Studies. A solution of $CpMoCl_2(PMe_3)_2$ was prepared in situ by allowing $CpMoCl_2$ to interact with 2 equiv of PMe_3 in a known volume of the appropriate solvent (THF or toluene).[6] Complete disappearance of the insoluble $CpMoCl_2$ indicated the completion of the reaction. For the reaction carried out in THF, a known aliquot of the solution was transferred to a 3-mm o.d. glass EPR tube, which was then cooled in a dry ice/acetone slush. A stoichiometric amount or an excess alkylating solution was introduced via a microsyringe, and after being further cooled to the liquid nitrogen temperature, the tube was flame-sealed under vacuum. The tube was then thawed to the dry ice temperature and maintained under these conditions until introduction into the precooled EPR probe for monitoring by the EPR technique. For the reaction carried out in toluene, the low solubility of methyllithium did not allow low-temperature monitoring of the reaction in the EPR tube. Rather, we carried out the reaction under vigorous stirring inside the Schlenk tube at room temperature and monitored it by withdrawing aliquots at different times for the EPR analysis.

(b) NMR Studies. No isolable material was obtained from the preparative scale reaction between $CpMoCl_2(PMe_3)_2$ and MeLi in THF. The color of the solution changed from red to yellow-

---

(1) (a) University of Maryland. (b) University of Delaware.

(2) Krueger, S. T.; Poli, R.; Rheingold, A. L.; Staley, D. L. *Inorg. Chem.* **1989**, *28*, 4599.

(3) Krueger, S. T.; Owens, B. E.; Poli, R. *Inorg. Chem.* **1990**, *29*, 2001.

(4) (a) Kochi, J. K. *Organometallic Mechanism and Catalysis*; Academic Press: New York, 1978. (b) Lappert, M. F.; Lednor, P. W. *Adv. Organomet. Chem.* **1976**, *14*, 345.

(5) (a) Brintzinger, H. H. *J. Am. Chem. Soc.* **1967**, *89*, 6871. (b) Siegert, F. W.; De Liefde Meijer, H. J. *J. Organomet. Chem.* **1970**, *23*, 177. (c) Elson, I. H.; Kochi, J. K.; Klabunde, U.; Manzer, L. E.; Parshall, G. W.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 7374. (d) Manzer, L. E. *Inorg. Chem.* **1976**, *15*, 2567. (e) Manzer, L. E.; Gearhart, R. C.; Guggenberger, L. J.; Whitney, J. F. *J. Chem. Soc., Chem. Commun.* **1976**, 942. (f) Manzer, L. E. *Inorg. Chem.* **1977**, *16*, 525. (g) Manzer, L. E. *J. Organomet. Chem.* **1977**, *135*, C6. (h) Manzer, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 8068. (i) Treichel, P. M.; Molzahn, D. C.; Wagner, K. P. *J. Organomet. Chem.* **1979**, *174*, 191. (j) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648. (k) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570. (l) Asaro, M. F.; Cooper, S. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1985**, *108*, 5187. (m) Becalska, A.; Hill, R. H. *J. Chem. Soc., Chem. Commun.* **1989**, 1626. (n) Aase, T.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 4974. (o) Roger, C.; Hamon, P.; Toupet, L.; Rabaâ, H.; Saillard, J.-Y.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1991**, *10*, 1045.

(6) Linck, R. G.; Owens, B. E.; Poli, R.; Rheingold, A. L. *Gazz. Chim. Ital.* **1991**, *121*, 163.

0276-7333/91/2310-3041$02.50/0

orange, and the residue could not be crystallized out of concentrated solutions in *n*-heptane at −80 °C. Its ^{1}H NMR spectrum (C_6D_6) exhibits a minor triplet of doublets centered at δ −0.10, consistent with the formation of $CpMoMe(PMe_3)_3$ among other products. The reaction was repeated in the presence of an extra 1 equiv of PMe_3. Again, the residue could not be crystallized from *n*-heptane, but the ^{1}H NMR was most consistent with the presence of $CpMoMe(PMe_3)_3$ as the major product (>90% yield by inspection of the resonances in the cyclopentadienyl region). ^{1}H NMR (C_6D_6, δ): 4.06 (d, 5 H, Cp, J_{HP} = 2.3 Hz), 1.24 (intermediate pattern between doublet and virtual triplet, 18 H, *c*-PMe_3, J_d = 5.3 Hz), 1.07 (d, 9 H, *t*-PMe_3, J_{HP} = 5.6 Hz), −0.10 (dt, 3 H, J_d = 2.3 Hz, J_t = 11.4 Hz). Gas chromatographic analysis of the volatile materials revealed the presence of methane.

In a separate experiment, $CpMoCl_2(PMe_3)_2$ was prepared in situ from 104 mg of $CpMoCl_2$ (0.448 mmol) and 93 μL of PMe_3 (0.93 mmol) in THF (10 mL). After this reaction was complete, the solvent was completely removed and replaced with 1 mL of THF-d_8. To this solution was added a 1.60 M solution of MeLi in Et_2O (0.56 mL, 0.90 mmol) at room temperature. The volatiles that formed during this reaction were trapped in ca. 1 mL of C_6D_6, and the resulting solution was investigated by ^{1}H NMR. A single peak at δ 0.153 indicates the presence of CH_4 and the absence of any CH_3D. A control experiment carried out under similar conditions shows that CH_3D (generated from MeLi and D_2O) appears in the ^{1}H NMR as a 1:1:1 triplet centered at δ 0.134 (J_{HD} = 1.93 Hz).

Reaction of $CpMoCl_2(PMe_2Ph)_2$ with Methyllithium. Preparation of $CpMo(o\text{-}C_6H_4PMe_2)(PMe_2Ph)_2$. To a suspension of $CpMoCl_2$ (0.252 g, 1.09 mmol) in THF (20 mL) was added PMe_2Ph (0.46 mL, 3.3 mmol). A clear red solution was obtained after ca. 20 min of stirring. EPR analysis of this solution revealed the formation of $CpMoCl_2(PMe_2Ph)_2$ (binomial triplet with Mo satellites, g = 1.994, a_P = 15.7 G, a_{Mo} = 42.6 G). Small amounts of a residual undissolved material were eliminated by filtration, and a 1.53 M solution of methyllithium in Et_2O (1.4 mL, 2.2 mmol) was added to the filtrate at room temperature. Gas evolved for ca. 2 min. Gas chromatographic analysis of the volatiles indicated the presence of methane in addition to Et_2O and THF vapors and the absence of hydrogen and ethane. The resulting solution was EPR silent. After complete removal of the solvent at reduced pressure, *n*-heptane (30 mL) was introduced and the resulting mixture filtered to give a red-orange solution. Partial evaporation to ca. 10 mL and cooling to −80 °C afforded 0.150 g (24% yield) of crystalline product. A single crystal for the X-ray analysis was obtained from this batch. Anal. Cald for $C_{29}H_{37}P_3Mo$: C, 60.6; H, 6.5; P, 16.2. Found, C, 60.3; H, 6.4; P, 15.5. ^{1}H NMR (C_6D_6, δ): 1.01, 1.20, 1.36, 1.39, 1.47, and 1.62 (3 H each, all doublets, P*Me*$_2$Ph, J_{HP} = 6.0, 6.9, 7.5, 6.8, 6.0, and 6.4 Hz, respectively), 4.58 (5 H, C_5H_5, d, J = 2.2 Hz), 6.66 (1 H, ddd, J_{1-3} = 1.0, 7.1, 11.7 Hz), 7.03 (1 H, tm, J_t = 7.2 Hz), 7.2–7.4 (12 H, m). ^{31}P NMR (C_6D_6, δ): −57.56 (dd, $J_{1,2}$ = 4.3, 65.1 Hz), 26.32 (dd, $J_{2,3}$ = 64.9, 35.2 Hz), 29.76 (dd, $J_{1,3}$ = 4.1, 35.5 Hz). IR (Nujol mull, cm^{-1}): 1435 m, 1415 m, 1280 m, 1270 w, 1105 w, 995 w, 940 s, 930 s, 900 s, 825 w, 785 s, 750 s, 740 s, 720 s, 705 s, 685 w, 675 m, 665 s, 500 m, 490 m, 410 s.

An identical reaction has been carried out with ^{1}H NMR monitoring as follows: $CpMoCl_2$ (93 mg, 0.40 mmol) was reacted with 114 μL of PMe_2Ph (0.80 mmol) in 3 mL of THF. After $^1/_2$ h, the solution was filtered and the solvent was completely removed under reduced pressure. To the residue was added at −80 °C a solution containing 0.80 mmol of MeLi in ca. 1 mL of THF-d_8 (prepared by placing in a separate Schlenk tube 520 μL of a 1.4 M solution of MeLi in Et_2O, removing the solvent under vacuum, and redissolving the residue in THF-d_8 at −80 °C). To the resulting solution was added an extra 1 equiv of PMe_2Ph (57 μL, 0.40 mmol), and then the mixture was rapidly transferred via cannula into a 5-mm NMR tube while both the Schlenk tube and the receiving NMR tube were kept immersed in the dry ice/acetone bath. The NMR tube was then further cooled to the liquid nitrogen temperature, sealed under vacuum, and warmed to room temperature. ^{1}H NMR analysis showed the formation of the product in 28.0 ± 0.2% yield (average of the Cp proton integrated intensity with respect to the total phenyl protons and the total methyl protons). The ^{31}P NMR showed only the presence of the ortho-metalated material and free PMe_2Ph.

Table I. Crystallographic Data for $CpMo(o\text{-}C_6H_4PMe_2)(PMe_2Ph)_2$

(a) Crystal Parameters	
formula	$C_{29}H_{37}MoP_3$
formula weight	574.44
crystal system	monoclinic
space group	$P2_1/n$
a, Å	14.855 (3)
b, Å	13.655 (2)
c, Å	15.174 (2)
β, deg	110.887 (13)
V, Å^3	2875.8 (8)
Z	4
cryst dimens, mm	0.26 × 0.28 × 0.34
cryst color	orange-red
D(calc), g·cm^{-3}	1.327
μ(Mo Kα), cm^{-1}	6.24
temp, K	297
(b) Data Collection	
diffractometer	Nicolet R3m
monochromator	graphite
radiation (λ, Å)	Mo Kα (0.71073)
2θ scan range, deg	4–64
data collected (*hkl*)	±23,+21,+23
no. of reflcns collected	10701
no. of indep reflcns	9997
R(merg), %	2.7
no. of indep reflcns obsd with $F_o \geq 4\sigma(F_o)$	6066
std reflcns	3 std/197 reflns
var in std, %	<2
(c) Refinement	
$R(F)$, %	3.93
$R(wF)$, %	4.37
Δ/σ (max)	0.02
$\Delta(\rho)$, e·Å^{-3}	0.70
N_o/N_v	22.14
GOF	1.096

X-ray Crystallography for $CpMo(o\text{-}C_6H_4PMe_2)(PMe_2Ph)_2$. A crystal suitable for the X-ray structural determination was mounted on a glass fiber with epoxy cement. In Table I crystal parameters and data collection and refinement parameters are collected. The unit cell parameters were obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). Systematic absences in the diffraction data uniquely established the space group as $P2_1/n$. No correction for absorption was required (low μ, well-shaped crystal, T_{max}/T_{min} = 1.112).

The structure was solved by heavy-atom methods that located the Mo atom. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions (d_{CH} = 0.960 Å, U = 1.2U for attached C), and the phenyl rings were constrained as rigid planar hexagons (d_{CC} = 1.396 Å). All non-hydrogen atoms were refined with anisotropic thermal parameters. All software and the sources of the scattering factors are contained in the SHELXTL program library.[7]

Selected bond distance and angles are collected in Table II. Additional crystallographic data are available as supplementary material.

Results

One of the starting materials used in this study, $CpMoCl_2(PMe_3)_2$, has been described previously.[2,6] The analogous $CpMoCl_2(PMe_2Ph)_2$ compound has been prepared in an analogous manner. As all our attempts to isolate this compound invariably gave an oily material, we always generated it in situ as described in eq 1. The identity of the product of eq 1 as the 17-electron bis(phosphine) adduct is confirmed by the EPR spectrum (triplet, g = 1.994, a_P = 15.7 G, a_{Mo} = 42.6 G), which is

---

(7) Sheldrick, G. Nicolet Corp., Madison, WI.

Table II. Selected Bond Distances and Angles for $CpMo(o\text{-}C_6H_4PMe_2)(PMe_2Ph)_2$

(a) Bond Distances (Å)

Mo-P(1)	2.486 (1)	P(1)-C(8)	1.781 (3)
Mo-P(2)	2.480 (1)	P(2)-C(14)	1.837 (3)
Mo-P(3)	2.399 (1)	P(2)-C(15)	1.829 (4)
Mo-C(9)	2.229 (3)	P(2)-C(26)	1.859 (3)
Mo-CNT[a]	1.981 (3)	P(3)-C(16)	1.831 (4)
Mo-C(1)	2.321 (3)	P(3)-C(17)	1.836 (4)
Mo-C(2)	2.280 (3)	P(3)-C(36)	1.849 (4)
Mo-C(3)	2.279 (3)	C(1)-C(2)	1.422 (6)
Mo-C(4)	2.328 (3)	C(1)-C(5)	1.392 (5)
Mo-C(5)	2.369 (3)	C(2)-C(3)	1.417 (5)
P(1)-C(6)	1.833 (3)	C(3)-C(4)	1.415 (5)
P(1)-C(7)	1.832 (5)	C(4)-C(5)	1.403 (5)

(b) Bond Angles (deg)

P(1)-Mo-P(2)	83.5 (1)	C(9)-Mo-CNT[a]	107.3 (1)
P(1)-Mo-P(3)	102.0 (1)	Mo-P(1)-C(6)	131.2 (2)
P(1)-Mo-C(9)	63.3 (1)	Mo-P(1)-C(7)	98.3 (2)
P(1)-Mo-CNT[a]	131.0 (1)	Mo-P(1)-C(8)	87.4 (1)
P(2)-Mo-P(3)	88.1 (1)	C(6)-P(1)-C(7)	98.3 (2)
P(2)-Mo-C(9)	140.5 (1)	C(6)-P(1)-C(8)	106.0 (2)
P(2)-Mo-CNT[a]	110.7 (1)	C(7)-P(1)-C(8)	105.1 (2)
P(3)-Mo-C(9)	79.3 (1)	P(1)-C(8)-C(9)	101.2 (2)
P(3)-Mo-CNT[a]	124.4 (1)	Mo-C(9)-C(8)	108.0 (2)

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

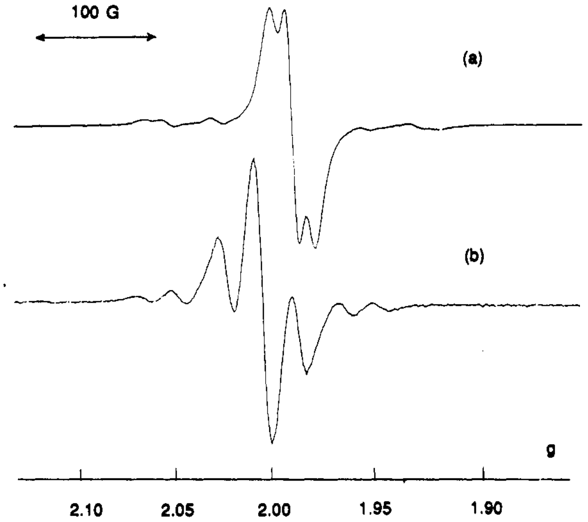


Figure 1. EPR spectrum of $CpMoCl_2(PMe_3)_2$: (a) solvent = THF, room temperature; (b) after reaction with 2 equiv of MeLi, T = 270 K.

similar to that of the characterized PMe_3 and dppe analogues.[2,3]

$$1/n\{CpMoCl_2\}_n + 2PMe_2Ph \rightarrow CpMoCl_2(PMe_2Ph)_2 \quad (1)$$

The interaction between $CpMoCl_2L_2$ and MeLi (2 equiv) was first investigated at low temperature with EPR monitoring. For L = PMe_3, no reaction was evident at temperatures lower than −20 °C. At T = −20 °C in THF as solvent, the characteristic triplet of the starting material at g = 1.982, a_P = 15.0 G, and a_{Mo} = 41.0 G decreased to leave a *much less intense* triplet signal at g = 2.003, a_P = 36.7 G and a_{Mo} = 27.6 G (see Figure 1). The latter signal broadens when the temperature is raised, and at room temperature, the hyperfine structure is no longer discernible. This change depends only upon the temperature and is not indicative of further reactivity: cooling the probe to 270 K restores the signal shown in Figure 1b. However, when the EPR tube is kept at room temperature for a long period of time, the EPR signal decreases in intensity and the solution eventually obtained is EPR silent. An analogous result was obtained when the same experiment was carried out in toluene. In this case, however, the increase of the EPR signal shown in Figure 1b was substantial.

From an analogous experiment carried out in a Schlenk tube, ^1H NMR analysis of the residue indicated the formation of the Mo(II) species $CpMo(CH_3)(PMe_3)_3$, among other unidentified products. The reaction was thus repeated in the presence of an extra 1 equiv of PMe_3, and under these conditions, $CpMo(CH_3)(PMe_3)_3$ was the prevalent product. We were not able to isolate this material due to it extreme solubility in aliphatic hydrocarbons, but its identity is clearly demonstrated by the ^1H NMR resonance at δ −0.10 corresponding to three protons. The shape of this resonance as a triplet of doublets is consistent with a four-legged piano stool geometry. The Cp resonance is found at δ 4.06, and its pattern as a doublet shows that the largest coupling is with the phosphorus atom that is trans to the methyl group, the other coupling to the two equivalent cis phosphorus atoms being too small to be detected. The PMe_3 resonances are found at δ 1.07 (doublet, 9 protons) and at δ 1.24 (18 protons). The latter resonance appears as a doublet with a third broader peak in the middle, indicating a situation of intermediate virtual coupling in accord with two phosphine ligands at an angle between 90 and 180°. Gas chromatographic analysis and ^1H NMR analysis of the volatile materials indicated the formation of CH_4. We thus propose that the product forms according to the stoichiometry illustrated in eq 2.

$$CpMoCl_2(PMe_3)_2 + 2LiMe + PMe_3 \rightarrow CpMoMe(PMe_3)_3 + 2LiCl + Me^\bullet \quad (2)$$

The methyl radical would turn into methane by hydrogen atom abstraction. The hydrogen atom could be donated by either the THF solvent, the diethyl ether that comes with the methyllithium, or a coordinated phosphine. The formation of only CH_4 and no CH_3D when the reaction is conducted in THF-d_8 points toward one of the latter two substances as the hydrogen atom source.

Other methylating agents did not prove as effective as MeLi in the reaction shown in eq 2. MeMgCl and $AlMe_3$ in THF react only very slowly (over several days) at room temperature as shown by EPR monitoring. The nature of the EPR-silent products of these reactions was not investigated. MeZnI reacts to produce sequentially the known[2,6] $CpMo(Cl)(I)(PMe_3)_2$ and $CpMoI_2(PMe_3)_2$ and no major decrease of EPR intensity due to a reaction such as eq 2 is detected over 2 days.

The interaction between $CpMoCl_2(PMe_2Ph)_2$ and MeLi in THF did not result in the observation of any EPR-active intermediate. An EPR-silent solution was obtained at room temperature over ca. 3 h, while NMR analysis of the residue obtained upon evaporation of the solvent indicated the presence of a compound containing three phosphorus atoms. As $CpMoCl_2(PMe_2Ph)_2$ had been prepared in situ from $CpMoCl_2$ and the phosphine, a little excess of the latter over the required stoichiometry could account for this result. When the reaction was carried out in the presence of an extra 1 equiv of PMe_2Ph, the compound containing three phosphorus atoms was obtained in 28% yields (by NMR) and could be isolated by recrystallization from heptane in 15–24% yields. The rest of the reaction seems to afford paramagnetic products that we have not yet been able to characterize.

The diamagnetic product was characterized by NMR and X-ray crystallography as the ortho-metalated $CpMo(o\text{-}C_6H_4PMe_2)(PMe_2Ph)_2$ compound. The ^1H NMR spectrum shows the Cp protons and the phenyl and methyl protons of the phosphine ligands consistent with a ratio of 1:3 Cp to PMe_2Ph. The methyl region consists of six

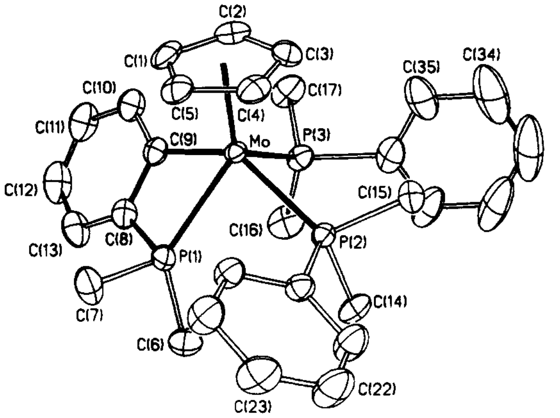


Figure 2. ORTEP view of the $CpMo(o\text{-}C_6H_4PMe_2)(PMe_2Ph)_2$ molecule.

doublets of equivalent intensity, showing that the six methyl groups of the phosphine ligands are all inequivalent. The presence of three phosphine ligands is confirmed by the $^{31}P\{^1H\}$ NMR, which shows three doublets of doublets (AMX system). One of the three resonances is shifted upfield by ca. 80 ppm with respect to the others, a clear signature feature of the participation of the phosphorus atom in a four-membered ring.[8] The phenyl region in the ^1H NMR spectrum shows two resonances at higher field (δ 7.03 and 6.66) with intensities corresponding to one proton each. We assign these to the two protons in the 3- and 4-positions of the ortho-metalated ring, which more strongly feel the effect of the diamagnetic anisotropy of the Cp ring.

The structure of the $CpMo(o\text{-}C_6H_4PMe_2)(PMe_2Ph)_2$ molecule has been determined by X-ray crystallography. A view of the molecule is shown in Figure 2. Although four-legged piano stool Mo(II) compounds are quite common,[9] only a few of these do not contain CO in the coordination sphere. Among these, structurally characterized examples are $(\eta^6\text{-arene})Mo(CH_3)_2(PMe_2Ph)_2$ (arene = benzene, toluene),[10] $CpMo(OCOCF_3)(CF_3COOH)[P(OMe)_3]_2$,[11] and $[CpMo(dmpe)_2]^+$ [dmpe = bis(dimethylphosphino)ethane].[12] Ortho-metalated phenylphosphine complexes are also quite common, but not many have been characterized crystallographically and among these none has a four-legged piano stool structure or molybdenum as the central atom. Examples are $[Ru(o\text{-}C_6H_4PPh_2)H_2(PPh_3)_2]^-$, $Mn(o\text{-}C_6H_3(CH_3)P\text{-}p\text{-}Tol_2)(CO)_4$, $Ir(o\text{-}C_6H_4PPh_2)(PPh_3)L_2$ (L = C_2H_4, CO), and $Ir(o\text{-}C_6H_4PPh_2)_2H(PPh_3)$.[13]

The most interesting features of the structure are the variations of Mo–P distances and Cp(center of gravity)–Mo–P angles, which we define as θ angles.[9] As discussed in a previous paper,[9] the θ value in 18-electon four-legged piano-stool complexes correlates with the extent of M–L π back-donation. The typical θ angles for π-neutral ligands are near 110°, whereas higher values are found when the M–L bond has a π back-bonding component, the deviation being higher the stronger π acceptor the ligand and the stronger π donor the metal. CO has a θ angle in the 120–130° range when trans to another CO and in the 115–122° range when trans to a weaker π-acceptor or to a π-neutral ligand. The latter phenomenon has been termed "angular trans influence", which remains, so far, without a theoretical interpretation. It has also been observed[9] that phosphine ligands can exhibit large θ angles in compounds that are void of stronger π-acceptor ligands like CO and contain strong σ-donor ligands (e.g., alkyls) and that these large angles cannot be solely the result of steric repulsions between the phosphines and the cyclopentadienyl ring. These observations were taken to suggest substantial metal–phosphorus π back-bonding in these complexes. The structure illustrated here serves to reinforce all the concepts put forward in the earlier paper.[9] The P(3) donor atom has a large θ angle (124.4 (1)°) and a short Mo–P distance (2.399 (1) Å). This is one of the shortest Mo(II)–P distances ever found. A recent survey of crystallographic bond distances[14] reports an average of 2.532 (17) or 2.468 (22) Å for all $Mo–PMe_2Ph$ bonds trans to, respectively, good and weak σ-donor ligands. Of more relevance to the structural type of concern here, such distance has been found to be 2.470 (7) and 2.472 (6) Å in *trans*-$(\eta^6\text{-}C_5H_5R)MoMe_2(PMe_2Ph)_2$ (R = H and Me, respectively),[10] 2.451 (2) and 2.453 (2) Å in $Mo(OC_6H_3Ph\text{-}\eta^6\text{-}C_6H_5)H(PMePh_2)_2$,[15] 2.50 (1) Å in *cis*-$CpMoI(CO)_2[P(n\text{-}Bu)_3]$,[16] 2.481 (5) Å in *trans*-$CpMoI(CO)_2(PPh_3)$,[17] 2.496 (4) and 2.439 (5) Å in CpMoCl(CO)(dppe),[17] 2.473 (3) Å in *trans*-$CpMo(COMe)(CO)_2(PPh_3)$,[18] and 2.462 (2) Å in $Cp^*Mo(CHO)(CO)_2(PMe_3)$.[19] The Mo–P(3) distance in the compound reported here compares more favorably with compounds containing phosphites or fluorinated phosphines, which are conceivably better π acids than PMe_2Ph (for instance, 2.406 (9) and 2.388 (8) Å for *trans*-$(\eta^5\text{-}C_5H_4R)MoI(CO)_2[P(OMe)_3]$ (R = H and Me, respectively)[20] and 2.402 (1) and 2.437 (2) Å for *trans*-$CpMoCl(CO)[(C_6F_5)_2PCH_2CH_2(C_6F_5)_2]$.[21] On the other hand, P(2) has a smaller θ value (110.7 (1)°) and, correspondingly, a longer Mo–P bond (2.480 (1) Å). The difference in distance and angle of these two phosphine ligands can be attributed to the angular trans influence:[9] P(3) is trans to another phosphorus donor, whereas P(2) is trans to a π-neutral ligand. The θ angle of C(9) is 107.3 (2)°, which agrees with the values typically found for other π-neutral ligands.[9] As expected, P(1) has a large θ angle (131.0 (1)°), but the Mo–P(1) distance (2.468 (1) Å) is longer than the Mo–P(3) distance (although still shorter than the Mo–P(2) distance!), as a probable result of strain in the four-membered cycle. Strain in the Mo–P(1)–C(8)–C(9) cycle is also indicated by several other structural features. The Mo–C(9) distance of 2.229 (3) Å is longer than the average of 2.172 (16) Å quoted in a recent review[14] for distances involving σ-aryls in complexes of Mo(II) and Mo(IV). The P(1)–C(8) distance, on the other hand, is compressed at 1.781 (3) Å versus the chemically analogous P(2)–C(26) and P(3)–C(36) distances of 1.859 (3) and 1.849 (4) Å, respectively. The ring angles subtended at P(1), C(8), and C(9) of 87.4 (1),

---

[8] Garrou, P. *Chem. Rev.* **1981**, *81*, 229.

[9] Poli, R. *Organometallics* **1990**, *9*, 1892, and references therein.

[10] Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans* **1979**, 1519.

[11] Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1982**, 493.

[12] Owens, B. E.; Poli, R. *Inorg. Chim. Acta* **1991**, *179*, 229.

[13] (a) Pez, G. P.; Grey, R. A.; Corsi, J. *J. Am. Chem. Soc.* **1981**, *103*, 7528. (b) McKinney, R. J.; Knobler, C. B.; Huie, B. T.; Kaesz, H. D. *J. Am. Chem. Soc.* **1977**, *99*, 2988. (c) Perego, G.; Del Piero, G.; Cesari, M.; Clerici, M. G.; Perrotti, E. *J. Organomet. Chem.* **1973**, *54*, C51. (d) Del Piero, G.; Perego, G.; Zazzetta, A.; Cesari, M. *Cryst. Struct. Commun.* **1974**, *3*, 725.

[14] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

[15] Kerschner, J. L.; Torres, E. M.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1989**, *8*, 1424.

[16] Fenn, R. H.; Cross, J. H. *J. Chem. Soc. A* **1971**, 3312.

[17] Bush, M. A.; Hardy, A. D. U.; Manojlovic-Muir, L.; Sim, G. A. *J. Chem. Soc. A* **1971**, 1003.

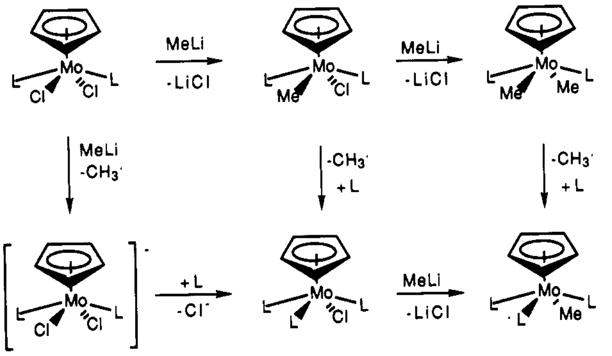
[18] Churchill, M. R.; Fennessey, J. P. *Inorg. Chem.* **1968**, *7*, 953.

[19] Asdar, A.; Lapinte, C.; Toupet, L. *Organometallics* **1989**, *8*, 2708.

[20] Hardy, A. D. U.; Sim, G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1900.

[21] Ernst, M. F.; Roddick, D. M. *Inorg. Chem.* **1990**, *29*, 3627.

Scheme I



101.2 (2), and 108.0 (2)° are all smaller than the ideal 109.4, 120, and 120° values. The four-membered ring is perfectly coplanar, with the sum of the four angles at Mo, P(1), C(8), and C(9) being 159.9 (3) Å. The Mo–Cp carbon atom distances show a spread and the Cp distortion from the perfect η^5 conformation is as expected for a substantial Mo–Cp δ back-bonding.[22]

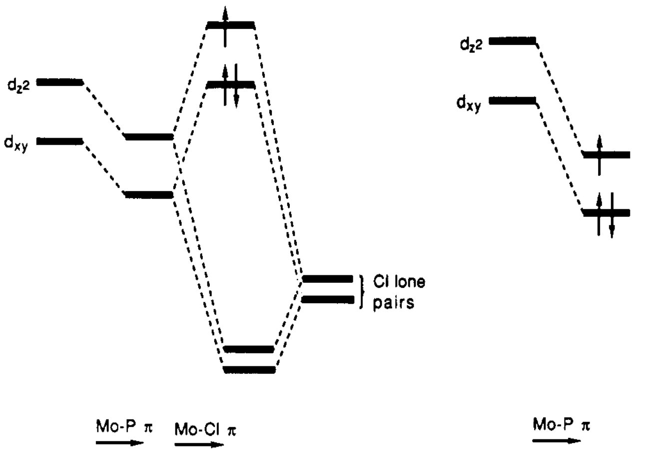
Discussion

The interaction between CpMoCl$_2$(PMe$_3$)$_2$ and MeLi at low temperature produces a derivative whose EPR spectrum shows coupling to two equivalent $I = {}^1/_2$ nuclei (Figure 1b). However, qualitative analysis of the EPR intensities shows that only a small fraction (<10%) of the starting material is transformed into the EPR-active product when the reaction is carried out in THF. The remaining 90% or more of the initial interaction between CpMoCl$_2$(PMe$_3$)$_2$ and MeLi could occur via direct reduction of the starting material or the CpMoClMe(PMe$_3$)$_2$ intermediate to the 16-electron CpMoCl(PMe$_3$)$_2$, followed by trapping by free PMe$_3$, as shown in Scheme I. We have independently generated and isolated CpMoCl(PMe$_3$)$_3$ by Na/Hg reduction of CpMoCl$_3$(PMe$_3$)$_2$ in the presence of PMe$_3$ and converted it to CpMoMe(PMe$_3$)$_3$ by reaction with MeLi.[23]

The involvement of alkyllithium reagents in single electron transfer (SET) reactions is well-known. It is also known that basic solvents favor the SET pathway relative to the simple nucleophilic type reactivity.[24] Consistent with this, changing the solvent to toluene causes a much greater increase of the EPR triplet signal due to the dimethylmolybdenum(III) derivative. Eventually, however, an EPR-silent solution is still obtained.

The intermediate that gives rise to the EPR triplet shown in Figure 1b could be either CpMoCl(CH$_3$)(PMe$_3$)$_2$ or CpMo(CH$_3$)$_2$(PMe$_3$)$_2$. We believe this spectrum is due to the dimethyl derivative, based on the fact that the same spectral changes are observed when a larger excess of MeLi is used. In addition, using only 1 equiv of MeLi in either toluene or THF causes less than 50% reduction of the EPR intensity for the triplet of the starting material.

The 17-electron CpMoMe$_2$(PMe$_3$)$_2$ complex is not a stable species at room temperature. This is not surprising since 17-electron transition-metal alkyl complexes are notoriously unstable and only few have been isolated.[5] It is interesting, however, to compare the stability and reactivity of CpMoMe$_2$(PMe$_3$)$_2$ with that of its dichloride precursor. The dichloride compound can be easily oxidized to the corresponding 16-electron cation, but reduction is difficult and the corresponding 18-electron anion is not a stable species.[2] The dimethyl derivative, on the other hand, decomposes with metal reduction. Thus, replacement of the two chlorine atoms with methyl groups makes the system less stable and more susceptible to reduction.



(a) CpMoCl$_2$(PMe$_3$)$_2$ (b) CpMoMe$_2$(PMe$_3$)$_2$

Figure 3. Qualitative MO interactions in HOMO and SHOMO of (a) CpMoCl$_2$(PMe$_3$)$_2$ and (b) CpMoMe$_2$(PMe$_3$)$_2$.

It has been shown earlier that the dichloride complex exhibits significant Mo–P π back-donation and Cl–Mo π donation.[2] The latter contributes to raise the energy of the HOMO and to stabilize the 16-electron product of oxidation. These two synergic bonding interactions express themselves on both the molecule's HOMO and SHOMO (see Figure 3a). It is important to realize that although the Mo–Cl π interaction *raises* the energy of HOMO and SHOMO, it is an overall stabilizing interaction because only three metal electrons populate the two orbitals with the Mo–Cl π^* component as opposed to four electrons ending up in the corresponding bonding combinations. The replacement of the two chlorine atoms with methyl groups introduces two important changes (Figure 3b). Since a methyl group is less electronegative than chlorine, the metal orbital's energy is raised favoring a better interaction with the empty phosphine orbitals. This idea is consistent with the EPR spectra, which show higher coupling of the unpaired electron with the phosphorus nuclei and lower coupling to the molybdenum nucleus on going from the dichloride complex (Figure 1a) to the dimethyl complex (Figure 1b). Also, methyl groups are void of lone pairs and thus cannot establish a stabilizing π interaction. The observed reactivity of the dimethyl complex (reduction to an 18-electron Mo(II) complex) suggests that its half-occupied HOMO is low in energy, a situation that can occur only if substantial Mo–P π back-bonding is present.

The formation of the ortho-metalated material could take place through the same initial steps shown in Scheme I. However, perhaps because of the increased steric bulk of the phosphine, a hypothetical CpMoMe(PMe$_2$Ph)$_3$ compound would not be stable. In support of this idea, the corresponding chloride compound, CpMoCl(PMe$_2$Ph)$_3$, is not a stable compound and Na/Hg reduction of CpMoCl$_2$(PMe$_2$Ph)$_2$, either in the presence or in the absence of excess PMe$_2$Ph, generates the stable coordinatively unsaturated, paramagnetic CpMoCl(PMe$_2$Ph)$_2$.[25] A possible reaction pathway for the ortho-metalation reaction would thus involve formation, either substitution followed

---

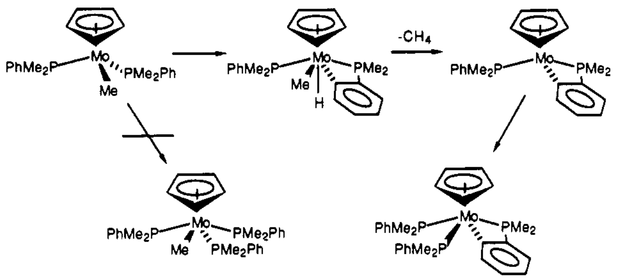
[22] Kubacek, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180.

[23] Poli, R.; Abugideiri, F.; Kelland, M. A.; Rheingold, A. L. Manuscript in preparation.

[24] Screttas, C. G.; Eastham, J. F. *J. Am. Chem. Soc.* **1966**, *88*, 5668.

[25] Poli, R.; Kelland, M. A. To be submitted for publication.

Scheme II



by reduction or vice versa, of the 16-electron CpMoMe(PMe$_2$Ph)$_2$ complex. This molecule could undergo oxidative addition of one of the ortho C–H bonds, followed by reductive elimination of methane, to produce another 16-electron intermediate, CpMo(o-C$_6$H$_4$PMe$_2$)(PMe$_2$Ph) (Scheme II). This molecule is less sterically congested than CpMoMe(PMe$_2$Ph)$_2$ and can thus accept a third phosphine molecule in the coordination sphere to form the observed product.

Conclusions

The different stability and reactivity of 17-electron compounds of the CpMoX$_2$L$_2$ class (X = electronegative π-donor ligand (halide) or less electronegative π-neutral ligand (methyl)) has been given a simple molecular orbital interpretation based on the π-acidic properties of the phosphine ligands and the synergic stabilization due to the contemporary presence of π acids and π bases. The structural distortions observed for the ortho-metalated phosphine molecule CpMo(o-C$_6$H$_4$PMe$_2$)(PMe$_2$Ph)$_2$ are in agreement with the π-acidic nature of the phosphine in this molecule.

Further synthetic and mechanistic studies of the alkylation reaction of 17-electron CpMoX$_2$L$_2$ (X = halogen, L = phosphine) compounds are in progress.

Acknowledgment. R.P. is grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Further support from the Camille and Henry Dreyfus Foundation (New Faculty Award) and the National Science Foundation (Presidential Young Investigator Award, CHE-9058375) are also gratefully acknowledged.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and calculated hydrogen atom coordinates for CpMo(o-C$_6$H$_4$PMe$_2$)(PMe$_2$Ph)$_2$ (5 pages); listings of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Relative Consecutive–Competitive Rate Constants in the Synthesis of Organoalkoxysilanes Using Molten Sodium

John L. Speier* and Don L. Kleyer

Central Research Department, Dow Corning Corporation, Midland, Michigan 48640

Received December 7, 1990

Relative specific rate constants for replacing successive alkoxy groups with phenyl groups on R$_x$*Si*(OR′)$_{4-x}$ (R = Me, Ph; R′ = Me, Et; x = 0–2) to make industrially important phenylalkoxysilanes were determined by addition of chlorobenzene to a dispersion of molten sodium in the alkoxysilanes. For (MeO)$_4$Si, the relative values of $k_4/k_3/k_2/k_1$ are 1/23/72/65. For MeSi(OMe)$_3$, the values $k_4/k_3/k_2$ are 1/5.9/9.8. For Me$_2$Si(OEt)$_2$, the values of k_4/k_3 are 1/3.6. Syntheses are much easier to carry out if a mixture of chlorobenzene containing 1 equiv of a chlorosilane is added to the molten sodium. The chlorosilane did not change the relative rate constants, and quantitative yields of phenylalkoxysilanes were obtained not only with PhCl but also with PhBr and PhI. The same procedure formed organo-functional alkoxysilanes in excellent yields when CH═CH$_2$CH$_2$Cl, F$_3$CCH$_2$CH$_2$Br, p-Me$_2$NC$_6$H$_4$Br, p-(Me$_3$Si)$_2$NC$_6$H$_4$Cl, 2-chlorothiophene, PhCH$_2$Cl, or EtOCH$_2$Cl mixed with 1 eqiv of a chlorosilane was added to molten sodium dispersed in alkoxysilanes.

Introduction

We recently used a procedure patented 45 years ago[1] to prepare phenylalkoxysilanes and then used improvements in that procedure patented by Tiganik 40 and 30 years ago.[2a–c] The procedure proved to be superb, but no references could be found to its use in the last 30 years.

Addition of an organic halide to molten sodium dispersed in an alkoxysilane leads to vigorously exothermic reactions that quantitatively produce organoalkoxysilanes. Use of an organic halide mixed with 1 equiv of a chlorosilane[2] forms the same quantitative yield of organoalkoxysilane in a mixture that is much easier to stir and filter.

Organic halides react with molten sodium extremely rapidly.

$$\mathrm{RX} + 2\mathrm{Na} \rightarrow \mathrm{RNa} + \mathrm{NaX}\downarrow$$

RNa reacts with the surrounding medium of alkoxysilanes.

$$\equiv\mathrm{SiOR}' + \mathrm{RNa} \rightarrow \equiv\mathrm{SiOR}'\mathrm{R}^{-}\mathrm{Na}^{+}$$

A chlorosilane then reacts to re-form an alkoxysilane.

$$\equiv\mathrm{SiOR}'\mathrm{R}^{-}\mathrm{Na}^{+} + \equiv\mathrm{SiCl} \rightarrow \equiv\mathrm{SiR} + \equiv\mathrm{SiOR}' + \mathrm{NaCl}\downarrow$$

The number of equivalents of alkoxysilyl groups remains constant in this system.

A slurry of finely divided NaX and NaCl is formed that remains easily stirrable and from which the solids are easily filtered. The distribution of organoalkoxysilanes that are

---

[1] Bondy, C.; Reiser, K. Brit. Patent 573, 906, Dec 12, 1945.

[2] (a) Tiganik, L. U.S. Patent 2,521,267, Sept 5, 1950. (b) Tiganik, L. Brit. Patent 668,532, March 18, 1952. (c) Tiganik, L. Can. Patent 598,441, May 24, 1960.