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First Structure of a Cyclopentadienyl Trihydride d^2 System: A Pseudotrigonal Prism Rather Than the Expected Pseudooctahedron and Its Mechanism of Hydrogen Scrambling

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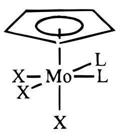
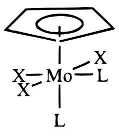
Half-sandwich cyclopentadienyl polyhydride derivatives of the transition metals have recently been the subject of intensive experimental[1−8] and theoretical[9−11] investigations, especially with regard to their high fluxionality and the choice between classical and nonclassical formulations and the consequent effects on physical properties and reactivity. The particular (ring)MH$_3$L$_2$ class of derivatives (ring = Cp or substituted derivative; M = Mo or W; L = 2-electron neutral donor, e.g. a tertiary phosphine ligand) has been known since 1979, when Green reported the first synthesis of CpMoH$_3$(dppe).[12] Single-crystal diffraction studies have never been reported, but corresponding trihalides adopt a pseudooctahedral structure (when considering the Cp ring as accupying a single coordination position) which, depending on the nature of the L ligands, can either be *fac* (**I**), e.g. CpMoCl$_3$[P(OCH$_2$)$_3$CEt]$_2$,[13] *cis-mer* (**II**), e.g. CpMoCl$_3$(L−L) (L−L = dppe[14] or dmpe[15]), or *trans-mer* (**III**), e.g. CpMoCl$_3$(PMe$_2$Ph)$_2$.[16] ^{1}H-NMR studies have not been helpful to elucidate the structure of these hydride compounds: a single triplet resonance (due to ^{31}P coupling) for the three hydride protons is observed for (C$_5$H$_4$Pr^i)MoH$_3$(PMe$_3$)$_2$ down to −90 °C.[17] For neither of the geometries **I**−**III** where X = H nor any other conceivable geometry, would a single hydride resonance be expected in the slow-exchange limit. Since increasing the steric bulk has the effect of slowing down fluxional processes (e.g. see the low-temperature ^{1}H-NMR properties of Cp*MoH(PMe$_3$)$_3$[18]), we explored previously unreported Cp*Mo trihydride derivatives. We now report that, in the solid state, the Cp*MoH$_3$(dppe) compound adopts a novel structure for the (ring)MH$_3$L$_2$ stoichiometry which is based on the trigonal prism rather than the octahedron and the structure of a protonation product, which suggests a likely path for the fluxional process.



I



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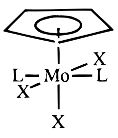

III

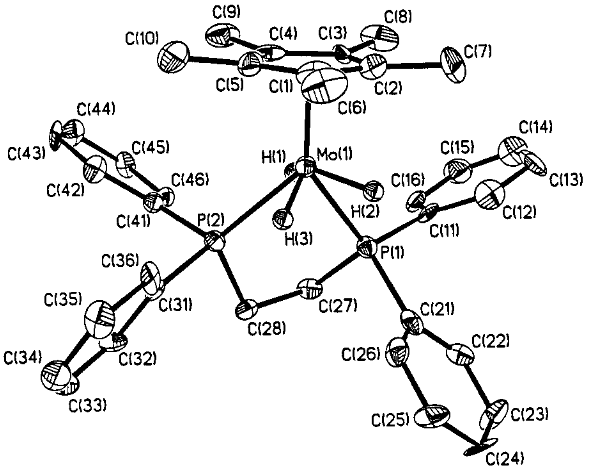

Figure 1. A view of the Cp*MoH$_3$(dppe) molecule. Carbon-bonded hydrogen atoms are omitted for clarity. Selected bonding parameters (CNT = Cp* center of gravity): Mo−CNT, 2.006(5) Å; Mo−P (av), 2.368(12) Å; Mo−H1, 1.65(5) Å; Mo−H2, 1.57(5) Å; Mo−H3, 1.55(5) Å; CNT−Mo−H1, 107(2)°; CNT−Mo−H2, 102(2)°; CNT−Mo−H3, 114(2)°; CNT−Mo−P1, 140.3(1)°; CNT−Mo−P2, 132.6(1)°.

Compound Cp*MoH$_3$(dppe), **1**, can be synthesized in 63% yields from Cp*MoCl$_4$ and LiAlH$_4$ in THF in the presence of dppe.[19] Compound **1** has NMR properties similar to the other previously reported trihydride derivatives, showing a single hydride resonance (triplet, $J_{PH} = 42$ Hz) at δ −5.27 and a single ^{31}P{^{1}H} resonance at δ 91.8, which do not decoalesce upon cooling to −80 °C. Thus, hydride-scrambling processes are still too rapid for this compound to afford structural information by ^{1}H-NMR spectroscopy.

The single-crystal X-ray structure of **1**[20] is shown in Figure 1. The position of the three hydrides was directly located from the difference Fourier synthesis and refined without contraints. The geometry cannot be based on the pseudooctahedron (cf. **I**−**III**). Rather, it can be idealized to a pseudotrigonal prism with the center of the Cp* ligand and two hydride ligands defining one triangular face and the dppe and the third hydride ligand defining the opposite triangular face, as illustrated schematically in **IV**. For a regular trigonal prism, identical CNT−Mo−P angles should be observed. Such angles are quite close at 132.6(1)° and 140.3(1)° indicating a small twist toward

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[1] Arliguie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989**, *8*, 1308−1314.

[2] Parkin, G.; Bercaw, J. E. *J. Chem. Soc., Chem. Commun.* **1989**, 255−257.

[3] Herrmann, W. A.; Theiler, H. G.; Kiprof, P.; Tremmel, J.; Blom, R. *J. Organometal. Chem.* **1990**, *395*, 69−84.

[4] Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875−883.

[5] Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161−171.

[6] Klooster, W. T.; Koetzle, T. F.; G., J.; Fong, T. P.; Morris, R. H.; Albinati, A. *J. Am. Chem. Soc.* **1994**, *116*, 7677−7681.

[7] Gross, C. L.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1994**, *116*, 10294−10295.

[8] Le Husebo, T.; Jensen, C. M. *Organometallics* **1995**, *14*, 1087−1088.

[9] Lin, Z.; Hall, M. B. *Organometallics* **1992**, *11*, 3801−3804.

[10] Lin, Z.; Hall, M. B. *Organometallics* **1993**, *12*, 4046−4050.

[11] Lin, Z. Y.; Hall, M. B. *Coord. Chem. Rev.* **1994**, *135*, 845−879.

[12] Aviles, T.; Green, M. L. H.; R., D. A.; Romao, C. *J. Chem. Soc., Dalton Trans.* **1979**, 1367−1371.

[13] Poli, R.; Kelland, M. A. *J. Organometal. Chem.* **1991**, *419*, 127−136.

[14] Stärker, K.; Curtis, M. D. *Inorg. Chem.* **1985**, *24*, 3006−3010.

[15] Owens, B. E.; Poli, R. *Inorg. Chim. Acta* **1991**, *179*, 229−237.

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

[17] Grebenik, P. D.; Green, M. L. H.; Izquierdo, A.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1987**, 9−19.

[18] Abugideiri, F.; Kelland, M. A.; Poli, R.; Rheingold, A. L. *Organometallics* **1992**, *11*, 1303−1311.

[19] Cp*MoCl$_4$ (734 mg, 1.97 mmol) and dppe (783 mg, 1.97 mmol) in THF (60 mL) were stirred with LiAlH$_4$ (820 mg, 19.7 mmol) at room temperature for 12 h. After addition of MeOH (ca. 5 mL), evaporation to dryness, and extraction with heptane, 782 mg of crude product (63% yield) was recovered as a yellow−orange powder, which was recrystallized by dissolving in heptane and cooling to −80 °C. Single crystals were obtained from a saturated warm heptane solution upon cooling to room temperature. Anal. calcd for C$_{36}$H$_{42}$MoP$_2$: C, 68.35; H, 6.69. Found: C, 67.6; H, 7.0. ^{1}H-NMR (C$_6$D$_6$, δ): 7.8−7.0 (m, 20H, Ph), 1.85 (m, 4H, CH$_2$), 1.83 (s, 15H, Cp*), −5.27 (t, $J_{PH} = 42$ Hz, 3H, MoH).

[20] Crystal data for **1**: monoclinic, space group $P2_1/c$, $a = 10.5920(6)$ Å, $b = 29.010(2)$ Å, $c = 11.3044(9)$ Å, $\beta = 114.402(5)°$, $V = 3163.3(4)$ Å^3, $Z = 4$, $D_x = 1.328$ g cm^{-3}, λ(Mo Kα) = 0.71073 Å, μ(Mo Kα) = 0.539 mm^{-1}, $F(000) = 1320$, $T = 153$ K, $R(F) = 0.0545$, $wR(F^2) = 0.1006$ for 369 parameters and 4405 data with $F_o > 4\sigma(F_o)$. The structure solution by direct methods and refinement by full-matrix least-squares and different Fourier syntheses were carried out with programs contained in the SHELXTL package. At convergence for the Cp*Mo(dppe) model with all non-hydrogen atoms anisotropic, a difference Fourier map showed the position of the three Mo-bonded hydrogen atoms. These atoms were allowed to refine freely (*xyzU*), converging to chemically reasonable positions. A final difference Fourier map was featureless with $|\Delta\rho| < 0.42$ e Å^{-3}.

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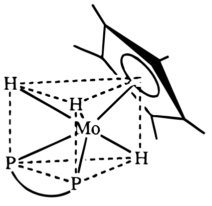


IV

an octahedral geometry, whereas the angles should be very different from each other in a structure of type **II**, or much smaller in a structure of type **I**. In addition, the Mo atom is displaced significantly from the plane defined by CNT and the two P atoms (by 0.283 Å), one hydride ligand being located on one side of such plane and the other two hydride ligands being located on the other side.

The average Mo−P distance of 2.368(12) Å is far shorter than those in the isoelectronic CpMoCl$_3$(dppe),[14] which is of type **II** (axial, 2.521(2) Å; equatorial, 2.688(4) Å). If these distances are regulated mostly by steric interactions, the replacement of three Cl with three H is more important than the replacement of the Cp with Cp*. The less electronegative H ligands could also have the effect of expanding the metal orbitals and favoring stronger Mo−P covalent interactions. The Mo−H distances average 1.59(5) Å, which compares with 1.52(4) Å for (C$_5$Me$_4$Et)MoH$_5$(PMe$_3$).[21] The distance between H2 and H3 of 1.71 Å is much longer than the longest separation reported for a "dihydrogen" ligand, e.g. 1.357(7) Å for ReH$_7$[P(p-tolyl)$_3$]$_2$,[22] thus **1** can be considered as a classical trihydride complex.

There are no previous examples of (ring)ML$_5$ compounds with a geometry based on the trigonal prism. For d^2 systems, the octahedral geometry should be electronically favored because the six σ bonds formed by the s, p, and d (e$_g$ set) orbitals are augmented by the two Mo−Cp π bonds that use the d$_{xz}$ and d$_{yz}$ set, while the two metal electrons would reside in the d$_{xy}$ orbitals which can engage in Mo−Cp δ back bonding. It is then likely that the pseudotrigonal prismatic structure for **1** is enforced by steric requirements.

Protonation of **1** with HBF$_4$·OEt$_2$ in MeCN, followed by diffusion of ether, produces single crystals of [Cp*MoH(MeCN)$_2$(dppe)][BF$_4$]$_2$ (**2**). The NMR properties of this complex[23] indicate a pseudooctahedral structure, which is confirmed by an X-ray structural determination (see Figure 2).[24] In particular, the structure is of type **II**, with the seric interaction between the Cp* and equatorial PPh$_2$ groups causing a severe distortion which compresses the P1 donor against the hydride ligand (P1−Mo−H1 = 59(2)°). The CNT−Mo−P angles are in this case quite different from each other [104.8(2)° and 159.5(2)°], and the Mo atoms lie essentially in the plane defined by the two P atoms and CNT (deviation 0.033 Å).

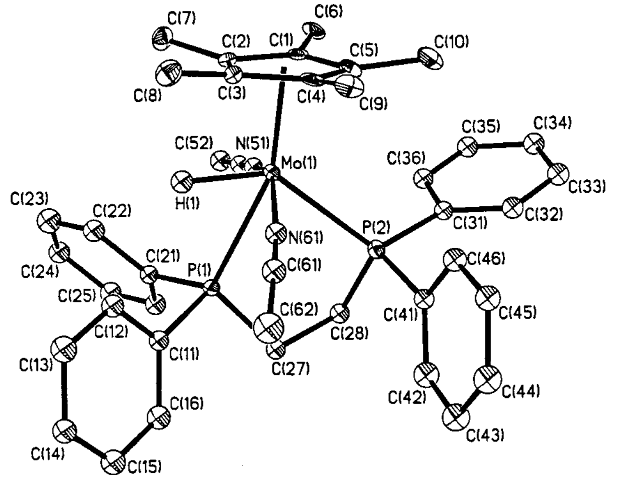
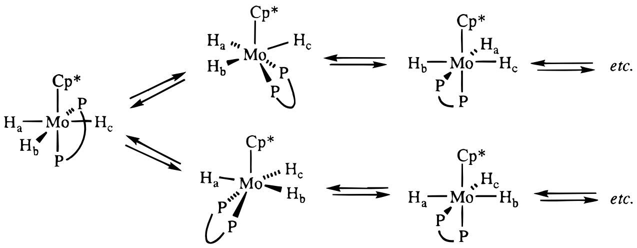


Figure 2. A view of the [Cp*MoH(MeCN)$_2$(dppe)]$^+$ cation for compound **2**. Carbon-bonded hydrogen atoms are omitted for clarity. Selected bonding parameters (CNT = Cp* center of gravity): Mo−CNT, 1.998(7) Å; Mo−P1, 2.541(2) Å; Mo−P2, 2.554(2) Å; Mo−H1, 1.69(6) Å; Mo−N51, 2.137(6) Å; Mo−N61, 2.122(6) Å; CNT−Mo−H1, 100(2)°; CNT−Mo−N51, 103.1(2)°; CNT−Mo−N61, 104.8(2)°; CNT−Mo−P1, 159.5(2)°; CNT−Mo−P2, 121.6(2)°.

Scheme 1



On the basis of these two structures, it is possible to propose a mechanism of scrambling of the hydride positions in (ring)MoH$_3$L$_2$ complexes as illustrated in the Scheme 1, which can be viewed as a special case of a Bailar twist. We shall next seek solid state structural information of less sterically hindered (ring)MoH$_3$L$_2$ compounds, to determine whether the pseudooctahedral or the pseudotrigonal prismatic structure is more favored in general.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond distances and angles, and anisotropic thermal parameters (27 pages). Ordering information is given on any current masthead page.

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[21] Shin, J. H.; Parkin, G. *Polyhedron* **1994**, *13*, 1489−1493.

[22] Brammer, L.; Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L.; Stringer, A. M. *J. Chem. Soc., Chem. Commun.* **1991**, 241−243.

[23] ^{1}H-NMR (δ, CD$_3$CN): 7.9−7.1 (m, 20H, Ph), 3.2−2.4 (m, 4H, CH$_2$), 1.82 (s, 15H, Cp*), −4.05 (dd, J'_{HP} = 10 Hz; J''_{HP} = 84 Hz, 1H, M−H). ^{31}P{^{1}H}-NMR (δ, CD$_3$CN): 76.2 and 50.9 (both d, J_{PP} = 24 Hz).

[24] Crystal data for **2**: orthorhombic, space group $Pna2_1$, a = 22.245(2) Å, b = 10.6805(9) Å, c = 16.9237(11) Å, V = 4020.9(6) Å^3, Z = 4, D_x = 1.464 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, μ(Mo Kα) = 0.475 mm^{-1}, F(000) = 1816, T = 153 K, $R(F)$ = 0.0338, $wR(F^2)$ = 0.0735 for 347 parameters and 2369 data with $F_o > 4\sigma(F_o)$. Calculations were carried out as for compound **1**. The hydrogen atom bonded to molybdenum was located directly from a difference Fourier map and refined freely. A final difference Fourier map was featureless with $|\Delta\rho| < 0.42$ e Å^{-3}.