Cp*MoH$_5$(PMe$_3$): A Classical Polyhydride with a Pentagonal-Bipyramidal Structure and a Long T_1 Relaxation Time

Fatima Abugideiri, Malcolm A. Kelland, and Rinaldo Poli*[,1]

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

Received December 8, 1992

*Summary: Cp*MoH$_5$(PMe$_3$) has been prepared from Cp*MoCl$_2$(PMe$_3$) and LiAlH$_4$. The compound is analogous to the previously reported Cp*WH$_5$(PMe$_3$) and CpWH$_5$(PMe$_3$) (Green, M. L. H.; Parkin, G. J. Chem. Soc., Chem. Commun. 1984, 1467. Schrock, R. R.; et al. Organometallics 1986, 5, 1681) for which structural assignments were not made. A single sharp ^{1}H-NMR resonance is observed for the five hydrides down to 183 K, consistent with either a static symmetric structure or a highly fluxional structure, either classical or nonclassical. The measured minimum longitudinal relaxation time, T_1, is quite long (780 ms at 400 MHz and 230 K) and consistent with a classical structure based on the pentagonal bipyramid which gives rise to a substantially anisotropic moment of inertia.*

There has been an enormus revival of interest in recent years around the structure and properties of polyhydride complexes, mainly due to the discovery of dihydrogen complexes (nonclassical hydrides),[2] the somewhat controversial application of ^{1}H-NMR T_1 determinations to the elucidation of their structure,[3] and the discovery of interesting quantum-mechanical exchange H–H coupling phenomena in the ^{1}H-NMR spectra of these materials.[4] Polyhydride complexes containing one cyclopentadienyl ring and phosphine ligands are quite common.[5] In general, these materials display fluxional behavior at room temperature. For instance, the ^{1}H-NMR spectrum of (η^5-C$_5$H$_4$-*i*-Pr)MoH$_3$(PMe$_3$)$_2$ shows equivalence of the three hydride ligands at −90 °C,[5a] although no conceivable static structure, either classical or nonclassical, would predict such behavior. Cyclopentadienyl-substituted tungsten *pentahydride* complexes, CpWH$_5$(PMe$_3$)[6] and Cp*WH$_5$(PMe$_3$),[7] have been reported in the literature. In both cases, a single ^{1}H-NMR resonance was observed for the hydride ligands and this was attributed to the well-known property of hydride ligands to undergo low energy exchange processes. No mention was made of the possibility that the structure is in fact a static pseudopentagonal bipyramid (if considering the five membered ring as occupying a single coordination position) with five equivalent hydride ligands in a pentagonal arrangement. Pentagonal bipyramidal arrangements are quite common for hydride-containing 7-coordinate complexes,[8] and such an arrangement has also been reported both in the solid state and in the gas phase for Cp*ReH$_6$,[9] which is isoelectronic with the aforementioned tungsten species. Another point of interest is that most cyclopentadienyl-containing polyhydride complexes investigated so far have a classical structure.[10] However, a variety of cationic derivatives [Cp*RuH$_2$(PR$_3$)$_2$]$^+$ has recently been reported to exhibit a nonclassical structure.[11] Upon an increase of the metal formal oxidation state, one might expect the nonclassical structures to become more favored. We report herein the preparation of the (pentamethylcyclopentadienyl)molybdenum analogue of the above mentioned tungsten pentahydride complexes, Cp*MoH$_5$(PMe$_3$), and solution T_1 studies which demonstrate a static, classical pentahydride structure for which a pentagonal-bipyramidal geometry is proposed.

Experimental Section

General Information. All operations were carried out under an atmosphere of argon by using standard Schlenk-line techniques. The NMR spectra were recorded with a Bruker AM-400 spectrometer. The ^{1}H-NMR chemical shifts are reported downfield of TMS and were calculated on the basis of the residual proton resonances of the solvent. The ^{31}P-NMR chemical shifts are reported downfield of external 85% H$_3$PO$_4$. The Cp*MoCl$_2$-

---

(1) Presidential Young Investigator, 1990–95; Alfred P. Sloan Research Fellow, 1992–94.

(2) (a) Kubas, G. J.; Ryan, R. R.; Vergamini, P. J.; Wassermann, H. J. *J. Am. Chem. Soc.* **1984,** *106,* 451. (b) Wassermann, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986,** *108,* 2294. (c) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986,** *108,* 7000.

(3) (a) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988,** *28,* 299. (b) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988,** *110,* 4126. (c) Cotton, F. A.; Luck, R. L. *J. Am. Chem. Soc.* **1989,** *111,* 5757. (d) Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1990,** *29,* 2788. (e) Crabtree, R. H. *Acc. Chem. Res.* **1990,** *23,* 95. (f) Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chem.* **1991,** *30,* 3118. (g) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991,** *113,* 4173.

(4) (a) Jones, D. H.; Labinger, J. A.; Weitekamp, D. P. *J. Am. Chem. Soc.* **1989,** *111,* 3087. (b) Zilm, K. W.; Heinekey, D. M.; Millar, J. M.; Payne, N. G.; Demou, P. *J. Am. Chem. Soc.* **1989,** *111,* 3088. (c) Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990,** *112,* 909. (d) Zilm, K. W.; Heinekey, D. M.; Millar, J. M.; Payne, N. G.; Neshyba, S. P.; Duchamp, J. C.; Szczyrba, J. *J. Am. Chem. Soc.* **1990,** *112,* 920. (e) Heinekey, D. M.; Harper, T. G. P. *Organometallics* **1991,** *10,* 2891.

(5) (a) Grebenik, P. D.; Green, M. L. H.; Izquierdo, A.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1987,** 9. (b) Jones, W. D.; Maguire, J. A. *Organometallics* **1987,** *6,* 1301. (c) Heinekey, D. M.; Payne, N. G.; Schulte, G. K. *J. Am. Chem. Soc.* **1988,** *110,* 2303. (d) Arliguie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989,** *8,* 1308.

(6) Green, M. L. H.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1984,** 1467.

(7) Okuda, J.; Murray, R. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1986,** *5,* 1681.

(8) (a) Hart, D. W.; Bau, R.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977,** *99,* 7557. (b) Hanckel, J. M.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1983,** *105,* 6979. (c) Garlaschelli, L.; Kahn, S. L.; Bau, R.; Longoni, G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1985,** *107,* 7212. (d) Ankianiec, B. C.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1991,** *113,* 4710. (e) Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991,** *113,* 3027.

(9) Herrmann, W. A.; Theiler, H. G.; Kiprof, P.; Tremmel, J.; Blom, R. *J. Organomet. Chem.* **1990,** *395,* 69.

(10) Lin, Z.; Hall, M. B. *Organometallics* **1992,** *11,* 3801 and references therein.

(11) (a) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987,** *109,* 5865. (b) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989,** *8,* 1824. (c) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990,** *112,* 5166. (d) Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992,** *11,* 161.

0276-7333/93/2312-2388$04.00/0

Table I. Variation of the Longitudinal Relaxation Time for the Hydride Resonance of $Cp^*MoH_5(PMe_3)$ with Temperature (Instrument Frequency = 400 MHz)

T (K)	T_1 (s)	T (K)	T_1 (s)
200	0.98	260	1.14
220	0.84	270	1.54
230	0.78	297	2.46

$(PMe_3)_2$ starting material was prepared according to the reported literature method.[12]

Preparation of $Cp^*MoH_5(PMe_3)$. A solution of $Cp^*MoCl_2(PMe_3)_2$ (238 mg, 0.52 mmol) in Et_2O was added to a slurry of $LiAlH_4$ (80 mg, 2.1 mmol) in Et_2O (total volume ca. 30 mL) at 0 °C with stirring. The solution was warmed to room temperature over 30 min, during which time the color changed from red-brown to pale yellow. After filtration, the solution was cooled to −78 °C and MeOH was added dropwise with stirring. A vigorous effervescence took place, resulting in a color change to pale brown and the formation of a precipitate. When no more effervescence was noted (1.2 mL), addition of MeOH was stopped and the mixture was evaporated to dryness. The residue was extracted with pentane (40 mL) and the solution was filtered and evaporated to dryness. Yield: 101 mg (62%). Anal. Calc for $C_{13}H_{29}MoP$: C, 50.00; H, 9.36. Found: C, 49.7; H, 9.0. ^1H-NMR ($C_6D_5CD_3$, δ, room temperature and 183 K): 2.17 (s, 15H, Cp*), 1.15 (d, 9H, J_{PH} = 9.5 Hz, PMe_3), −3.17 (d, 5H, J_{PH} = 50.3 Hz, Mo–*H*). ^{31}P-NMR ($C_6D_5CD_3$, δ, room temperature): 12.08 (sextet of decets, J_{PH}(sextet) = 50.5 Hz, J_{PH}(decet) = 9.6 Hz, PMe_3). $^{31}P\{^1H\}$-NMR ($C_6D_5CD_3$, δ, 183 K): 12.08 (s). The compound is very soluble in pentane. Colorless single crystals were grown by cooling the pentane solution to −80 °C.

Results and Discussion

Treatment of $Cp^*MoCl_2(PMe_3)_2$ with excess $LiAlH_4$ in Et_2O followed by methanolysis yields colorless $Cp^*MoH_5(PMe_3)$ in moderate yields. The compound has NMR properties similar to those reported for its tungsten analogue.[7] The ^1H-NMR resonance for the hydride protons is found as a doublet (J_{PH} = 50.3 Hz) at δ −3.17, and no modification of the spectrum is observed upon cooling to 183 K in analogy to compound $CpWH_5(PMe_3)$.[6] The presence of five equivalent hydrides is further confirmed by proton-coupled ^{31}P-NMR, which shows a binomial sextet pattern.

The longitudinal relaxation time (T_1) for the resonance due to the five equivalent hydride ligands as a function of temperature, which was measured by the standard inversion-recovery-pulse technique, is summarized in Table I. The lowest value is 780 ms at 230 K (400 MHz). This value is very large compared to those usually found for other polyhydrides, even when they have a classical structure, and it suggests that the hydride ligands are arranged in a way that minimizes the number of short H···H contacts. A molecular arrangement that would fulfill this requirement is the pentagonal bipyramid, with five hydride ligands in the pentagonal plane and the Cp* and the PMe_3 ligands located in the two axial positions. A preliminary single crystal X-ray investigation has been carried out, but the quality of the data were insufficient to locate the hydride ligands. However, the Cp* and PMe_3 ligands indeed occupy opposite positions with respect to the metal center, in accord with the expected pentagonal-bipyramidal geometry.[13]

With the assumptions that the solid state structure is retained in solution and that the five hydride ligands are equally displaced from the metal center in an ideal pentagonal planar array with a Mo(VI)–H distance of 1.675 Å, as estimated by Halpern,[3g] the maximum average H···H(proximal) and H···H(distal) distances are calculated as 1.97 and 3.19 Å, respectively. By using the standard formula and under the assumption of only H–H dipolar contributions to the relaxation rate, an upper limit of 357 ms can be calculated for T_1. Inclusion of other contributions to the relaxation can only lower the calculated minimum T_1 value, as would an umbrella distortion of the pentagonal array of the five hydride ligands. Of course, an equilibrium with a nonclassical structure would also lower the expected minimum T_1 value. This discrepancy between observed and calculated T_1 values exactly parallels what was found for the pentagonal bipyramidal $IrH_5(P\text{-}i\text{-}Pr_3)_2$ [observed 599 ms, calculated 270 ms (H–H dipole only) at 500 MHz].[3g] In that case, the discrepancy was attributed to the anisotropy of the moment of inertia tensor, making it impossible to use a single correlation time for the calculation of T_1. Thus, the observed high T_1 for $Cp^*MoH_5(PMe_3)$ is consistent with a rigid, classical structure which is based on the pentagonal bipyramid.

Treatment of $Cp^*MoH_5(PMe_3)$ with excess PMe_3 did not result in the formation of the known[14] $Cp^*MoH_3(PMe_3)_2$ and $Cp^*MoH(PMe_3)_3$ complexes over several days at room temperature. Similarly, treatment of $Cp^*MoH_3(PMe_3)_2$ with H_2 did not produce significant amounts of $Cp^*MoH_5(PMe_3)$ over several days at room temperature. These experiments indicate that there is a substantial kinetic barrier to PMe_3 dissociation from $Cp^*MoH_3(PMe_3)_2$ and/or to H_2 reductive elimination from $Cp^*MoH_5(PMe_3)$.

Acknowledgment. We are grateful to DOE-OER (Grant No. 92ER14230) for support. Additional support from the Exxon Education Foundation is also gratefully acknowledged.

OM920780N

---

[12] (a) Baker, R. T.; Morton, J. R.; Preston, K. F.; Williams, A. J.; Le Page, Y. *Inorg. Chem.* **1991**, *20*, 113. (b) Baker, R. T.; Calabrese, J. C.; Harlow, R. L.; Williams, I. D. *Organometallics* **1993**, *12*, 830.

[13] Hope, H., personal communication.

[14] Abugideiri, F.; Kelland, M. A.; Poli, R.; Rheingold, A. L. *Organometallics* **1992**, *11*, 1304.