J. Am. Chem. Soc. **1998,** *120,* 3257−3258 3257

Synthesis and Structure of the Stable Paramagnetic Cyclopentadienyl Polyhydride Complexes $[Cp^*MH_3(dppe)]^+$ (M = Mo, W): Stronger M−H Bonds upon Oxidation

Brett Pleune,[1a] Rinaldo Poli,*,[1b] and James C. Fettinger[1a]

Department of Chemistry and Biochemistry
University of Maryland
College Park, Maryland 20742
Laboratoire de Synthèse et d'Electrosynthèse
Organométallique, Faculté des Sciences "Gabriel"
Université de Bourgogne
6 Boulevard Gabriel, 21100 Dijon, France

Received August 22, 1997

Transition-metal polyhydride derivatives have been at the focus of much experimental[2] and theoretical[3] work, especially dealing with their high fluxionality[4] and their structure type (i.e. classical vs nonclassical).[5] There is scarce information on how these properties change upon oxidation to the 17-electron configuration because of the paucity of stable complexes. Only a few monohydride complexes have have been isolated,[6] as facile decomposition via deprotonation or disproportionation pathways usually occurs.[7] Isolable paramagnetic *poly*hydrides are even less common. We are only aware of $TaCl_2H_2L_4$ ($L = PMe_3$ or L_2 = dmpe)[6g] and $[WCl_2H_2(PMe_3)_4]^+BF_4^-$,[6h] as well characterized, unambiguous examples.[8] Chemical reactivity studies of such species are also rare.[9] When these compounds are obtained by one-electron oxidation of neutral precursors, H_2 reductive elimination is facilitated by the decreased metal p basicity[10] and adds to the array of decomposition pathways available.[11]

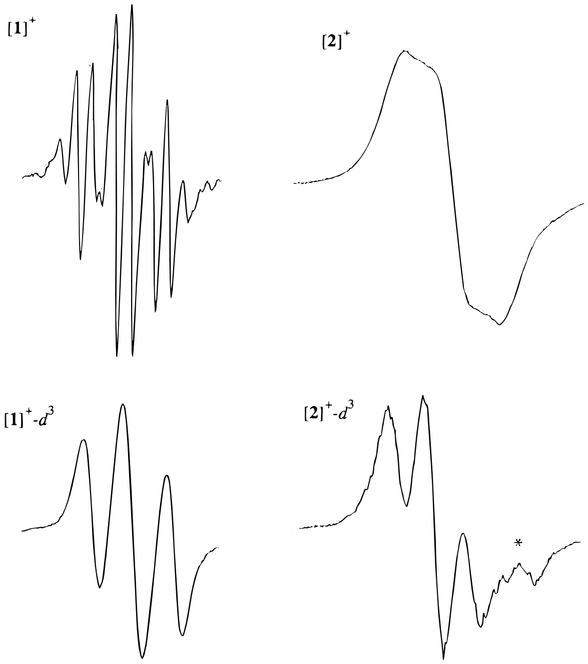


Figure 1. EPR spectra of complexes $[Cp^*MX_3(dppe)]^+$ (M = Mo, W; X = H, D). Solvent = THF. The starred peak in the spectrum of $[\mathbf{2}\text{-}d^3]^+$ is due to an impurity.

We wish to report here the new complexes $[Cp^*MH_3(dppe)][PF_6]$ (M = Mo, ([**1**]PF_6), W ([**2**]PF_6)), which are accessible by 1-electron oxidation of the parent complexes **1** and **2** with $FcPF_6$.[12] Cyclovoltammetric studies show a reversible oxidation for both **1** and **2** in THF (−0.75 and −0.88 V vs Fc/Fc^+, respectively). Complex $[\mathbf{1}]^+$ exhibits a triplet of quartets in the EPR spectrum ($g = 1.989$, $a_P = 28.9$ G, $a_H = 11.8$ G; see Figure 1) consistent with coupling to three equivalent H and two equivalent P ligands. Chemical oxidation of $Cp^*MoD_3(dppe)$ leads to the formation of $[\mathbf{1}]^+\text{-}d^3$, which is characterized by an EPR broad triplet ($g = 1.991$, $a_P = 28.9$ G; see Figure 1). IR investigations[13] show the expected isotope shift upon deuteration, and a 10−20 cm^{-1} *blue* shift upon oxidation. From simple theory, the vibrational frequency correlates directly with the bond energy.[14] Thus, the IR data indicate that the M−H/D bonds are stronger in the oxidized materials, consistent with expectations on the basis of a $M^{\delta+}-H^{\delta-}$ bond polarity. Previous IR studies on $Cp^*FeH(dppe)$

---

[1] (a) University of Maryland. (b) Université de Bourgogne.

[2] (a) Arliguie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989**, *8*, 1308−1314. (b) Parkin, G.; Bercaw, J. E. *J. Chem. Soc., Chem. Commun.* **1989**, 255−257. (c) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875−883. (d) Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161−171. (e) Klooster, W. T.; Koetzle, T. F.; G., J.; Fong, T. P.; Morris, R. H.; Albinati, A. *J. Am. Chem. Soc.* **1994**, *116*, 7677−7681.

[3] (a) Lin, Z.; Hall, M. B. *Organometallics* **1992**, *11*, 3801−3804. (b) Lin, Z.; Hall, M. B. *Organometallics* **1993**, *12*, 4046−4050. (c) Lin, Z. Y.; Hall, M. B. *Coord. Chem. Rev.* **1994**, *135*, 845−879. (d) Abugideiri, F.; Fettinger, J. C.; Pleune, B.; Poli, R.; Bayse, C. A.; Hall, M. B. *Organometallics* **1997**, *16*, 1179−1185.

[4] Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6775−6783.

[5] (a) Crabtree, R. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. II, pp 689−714. (b) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789−805. (c) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95−101.

[6] (a) Brintzinger, H. H. *J. Am. Chem. Soc.* **1967**, *89*, 6871−6876. (b) Kenworthy, J. G.; Myatt, J.; Symons, M. C. R. *J. Chem. Soc. A* **1971**, 1020−1024. (c) Sanders, J. R. *J. Chem. Soc., Dalton Trans.* **1973**, 748−749. (d) Sanders, J. R. *J. Chem. Soc., Dalton Trans.* **1975**, 2340−2342. (e) Gargano, M.; Giannoccaro, P.; Rossi, M.; Vasapollo, G.; Sacco, A. *J. Chem. Soc., Dalton Trans.* **1975**, 9−12. (f) Allison, J. D.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1983**, 401−403. (g) Luetkens, M. L., Jr.; Elcesser, W. L.; Huffman, J. C.; Sattelberger, A. P. *Inorg. Chem.* **1984**, *23*, 1718−1726. (h) Sharp, P. R.; Frank, K. G. *Inorg. Chem.* **1985**, *24*, 1808−1813. (i) Hamon, P.; Toupet, L.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1992**, *11*, 1429−1431. (j) Attanasio, D.; Mura, P.; Maldotti, A.; Sostero, S.; Traverso, O. *New J. Chem.* **1992**, *16*, 347−350.

[7] (a) Pilloni, G.; Schiavon, G.; Zotti, G.; Zecchin, S. *J. Organomet. Chem.* **1977**, *134*, 305−318. (b) Klinger, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 208−216. (c) Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2618−2626. (d) Smith, K.-T.; Rømming, C.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 8681−8689.

[8] (a) Herrmann, W. A.; Theiler, H. G.; Herdtweck, E.; Kiprof, P. *J. Organomet. Chem.* **1989**, *367*, 291−311. (b) Capitani, D.; Mura, P. *Inorg. Chim. Acta* **1997**, *258*, 169−181.

[9] (a) Elson, I. H.; Kochi, J. K.; Klabunde, U.; Manzer, L. E.; Parshall, G. W.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 7374−7375. (b) Elson, I. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 1262−1264.

[10] (a) Costello, M. T.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 2563−2564. (b) Westerberg, D. E.; Rhodes, L. F.; Edwin, J.; Geiger, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 1107−1112. (c) Zlota, A. A.; Tilset, M.; Caulton, K. G. *Inorg. Chem.* **1993**, *32*, 3816−3821.

[11] (a) Detty, M. R.; Jones, W. D. *J. Am. Chem. Soc.* **1987**, *109*, 5666−5673. (b) Pedersen, A.; Tilset, M. *Organometallics* **1994**, *13*, 4887−4894. (c) Smith, K.-T.; Tilset, M.; Kuhlman, R.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 9473−9480.

[12] To a solution of **2** (115 mg, 0.160 mmol) in 4 mL of CH_2Cl_2 was added $FcPF_6$ (53 mg, 0.160 mmol) at room temperature. The yellow-orange solution immediately turned red-orange. The solution was filtered and concentrated under reduced pressure to ca. 0.5 mL. Orange single crystals of $[\mathbf{2}]^+PF_6^-$ were obtained by diffusion of a layer of diethyl ether into this solution. Yield: 97 mg (70%). $[\mathbf{1}]^+$ can be obtained from **1** in an analogous manner in either THF or CH_2Cl_2. The oxidized complexes do not give rise to any observable NMR resonances.

[13] IR bands (THF, cm^{-1}, all broad): **1**, 1815 (m, sh), 1775 (m); $[\mathbf{1}]^+$, 1896 (w, sh), 1824 (m); **1**-d^3, 1307 (m); $[\mathbf{1}]^+\text{-}d^3$, 1318 (m); **2**, 1885 (w), 1815 (m); $[\mathbf{2}]^+$, 1897 (m), 1830 (w). W−D bands could not be located for compounds **2**-d^3 and $[\mathbf{2}]^+\text{-}d^3$ (no significant changes were observed upon oxidation). The spectra of $[\mathbf{1}]^+$ and $[\mathbf{1}]^+\text{-}d^3$ were recorded immediately after charging the cell with the cold solution. The follow-up decompositions (see text) generated a new weaker band at 1818 cm^{-1} from $[\mathbf{1}]^+$, assigned to **3**. A corresponding band for **3**-*d* could not be observed.

[14] Berry, R. S.; Rice, S. A.; Ross, J. *Physical Chemistry*; Wiley: New York, 1980; pp 266−268.

S0002-7863(97)02948-X CCC: $15.00

and $WH_2Cl(PMe_3)_4$ indicated either no change or a slight *red* shift upon oxidation,[6h,i,15] and a lowering of M−H BDE's was indicated for lower-valent carbonyl complexes by thermodynamic cycles involving acidity and electrochemical measurements.[16]

Despite the supposedly greater Mo−H bond energy relative to the neutral precursor, complex $[\mathbf{1}]^+$ decomposes rapidly ($t_{1/2}$ = 2 min at 25 °C in either THF or CH_2Cl_2) with gas evolution, to afford a new signal consisting of a doublet of triplets (g = 1.950, a_P = 16.5 G, a_H = 24.0 G; solvent independent), consistent with the formation of Cp*MoH(dppe)(PF_6), **3**. $[\mathbf{1}]^+$-d^3 correspondingly decomposes to yield a triplet of 1:1:1 triplets (a_D = 4.0 G). This indicates that $[\mathbf{1}]^+$ decomposes by reductive elimination of H_2. The similar decomposition rate in THF and CH_2Cl_2 suggests that H_2 elimination may occur without solvent precoordination. Solvent-independent R−R reductive eliminations from dialkyl complexes have previously been reported.[17] No solvent is coordinated to solid **3**,[18] which is therefore formulated as either the salt of a rather uncommon[19] 15-electron cation or a 17-electron complex with a coordinated FPF_5 ligand. Solvent coordination cannot be excluded in solution. Additional studies on this compound are in progress and will be reported later.

Compound $[\mathbf{2}]^+$ exhibits a broad triplet resonance in the EPR spectrum (g = 2.017; see Figure 1), which decays slowly at room temperature in THF ($t_{1/2}$ = 3 h). The nature of the decomposition products is under current investigation. Cooling to −80 °C does not affect the line shape of the signal. Oxidation of Cp^*WD_3(dppe) leads to $[\mathbf{2}]^+$-d^3, which better reveals the phosphorus coupling (g = 2.022, a_P = 27.6 G; see Figure 1). A single crystal of $[\mathbf{2}]PF_6$ could be investigated by X-ray diffraction,[20] which permitted the location and refinement of the three hydride ligands (see Figure 2).

The cation and anion are well separated, the closest contacts being between F atoms and Cp* and dppe C atoms (>3.0 Å). Neglecting the hydrogen positions, the geometry of $[\mathbf{2}]^+$ is very close to that of $[Cp^*WH_4(dppe)]^+$, previously determined as the BF_4^- salt.[21] The major difference consists of a small displacement (0.025(8) Å, as opposed to 0.002(9) Å in the tetrahydrido complex) of the W atom from the plane defined by CNT, P(1), and P(2) toward the side of the molecule occupied by H2 and H3 (see Figure 2). The W−P and W−Cp* bond distances are also very similar for $[\mathbf{2}]^+$ and $[Cp^*WH_4(dppe)]^+$,[21a] suggesting that the replacement of a W−H bond with a singly occupied W orbital does not greatly affect the effective metal charge (i.e. the W−H bond is highly covalent). Although the H positions are not determined with high precision, the relatively long H···H separations (H1−H2 2.81 Å; H2−H3 2.11 Å) suggest a classical formulation for $[\mathbf{2}]^+$. The geometry of $[\mathbf{2}]^+$ is intermediate between **I** (a pseudotrigonal prism) and **II** (a pseudooctahedron), i.e., the ideal geometries adopted by the isoelectronic d^2 complexes **1** and $[Cp^*MoH(dppe)(MeCN)_2]^{2+}$, respectively.[21a,22]

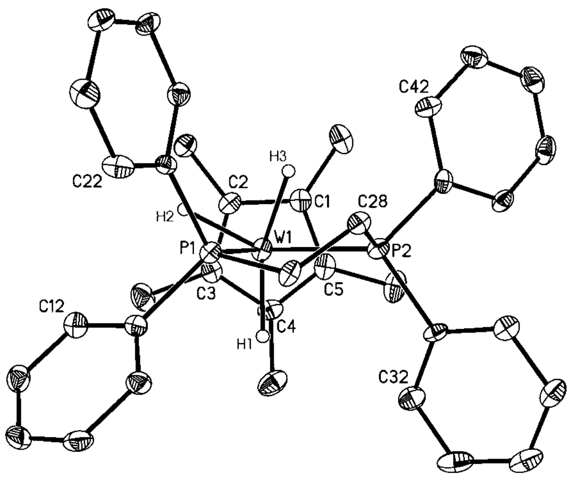
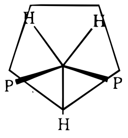
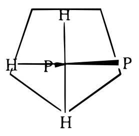


Figure 2. A view of the cation in compound $[\mathbf{2}]^+PF_6^-$. Selected bond distances (Å) and angles (deg):W1−P1, 2.474(2); W1−P2, 2.506(2); W1−CNT, 1.999(15); W1−H1, 1.71(2); W1−H2, 1.67(3); W1−H3, 1.69(3); CNT−W1−P1, 162.0(2); CNT−W1−P2, 119.1(2); CNT−W1−H1, 109(2); CNT−W1−H2; 103(2); CNT−W1−H3, 113(2); P1−W1−P2, 78.85(5).



I



II

The equivalence of the P and H hyperfine couplings in the EPR spectrum of $[\mathbf{1}]^+$ clearly indicates fluxionality. A scrambling mechanism involving a pseudo-Bailar twist between **I** and **II**, as previously proposed for the precursor complexes **1** and **2**, could also be adopted by $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$.[21a] Our future work will attempt to define the chemical reactivity of this new class of 17-electron polyhydride complexes and their decomposition products.

Acknowledgment. We are grateful to the DOE Office of Energy Research (Grant No. DEFG059ER14230) for support of this work and to a reviewer for useful suggestions.

Supporting Information Available: Tables of crystal and refinement parameters, fractional coordinates, bond distances and angles, and anisotropic displacement parameters (10 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA9729488

---

[15] Roger, C.; Hamon, P.; Toupet, L.; Rabaâ, H.; Saillard, J.-Y.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1991**, *10*, 1045−1054.

[16] (a) Tilset, M. *J. Am. Chem. Soc.* **1992**, *114*, 2740−2741. (b) Skagestad, V.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 5077−5083.

[17] (a) Pedersen, A.; Tilset, M. *Organometallics* **1993**, *12*, 56−64. (b) Fooladi, E.; Tilset, M. *Inorg. Chem.* **1997**, *36*, 6021−6027.

[18] Anal. for **3**. Calcd for $C_{36}H_{40}F_6MoP_3$: C, 55.8; H, 5.2. Found: C, 55.1; H, 5.3. IR (Nujol mull, cm^{-1}): 1820 [br, w, ν(M−H)], 840 [s, $\nu(PF_6)$]. The IR spectra of **3** crystallized from THF and from MeCN showed no difference attributable to coordinated solvent. μ_{eff} = 1.50 μ_B.

[19] Poli, R. *Chem. Rev.* **1996**, *96*, 2135−2204.

[20] Crystal data: Mr = 856.46, monoclinic, $P2_1/n$, a = 14.3763(8) Å, b = 16.684(2) Å, c = 15.0123(12) Å, β = 100.424(6)°, V = 3541.4(5) Å^3, Z = 4, D_x = 1.623 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, μ(Mo Kα) = 3.454 mm^{-1}, F(000) = 1724, T = 153(2) K, $R(F)$ = 7.13%, $R(wF^2)$ = 8.61% for all 6226 independent reflections [$R(F)$ = 4.12%, $wR(F^2)$ = 7.67% for 4577 data with $F_o > 4\sigma(F_o)$]. Structure solution by direct methods located the W and P atoms and several F atoms. All other non-hydrogen atoms were located by alternating least-squares refinement cycles and difference Fourier maps (SHELXTL) and refined anisotropically. All hydrogen atoms except the three hydrides were placed in calculated positions (AFIX). The three hydride atoms were located from the highest peaks near the W atom with W-peak distances ranging from 1.4 to 1.7 Å. Their refinement was assisted by restraining the W−H distances to be near 1.70 Å (ADFIX with esd of 0.03 Å). Thermal parameters were allowed to refine freely.

[21] (a) Pleune, B.; Poli, R.; Fettinger, J. C. *Organometallics* **1997**, *16*, 1581−1594. (b) Crystals of $[\mathbf{2}]^+PF_6^-$ are orange, while those of $[Cp^*WH_4(dppe)]^+BF_4^-$ are colorless. Colorless crystals of $[Cp^*WH_4(dppe)]^+PF_6^-$ have a significantly different unit cell from that of $[\mathbf{2}]^+PF_6^-$: a = 14.439(4) Å, b = 16.575(4) Å, c = 15.080(4) Å, β = 100.29(2)°, V = 3551.0(14) Å^3.

[22] Fettinger, J. C.; Pleune, B.; Poli, R. *J. Am. Chem. Soc.* **1996**, *118*, 4906−4907.