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Hydrogen Bonding to Transition Metal Fluoride Ligands: The Synthesis and Structure of the Bifluoride Complex $Mo(PMe_3)_4H_2F(FHF)$

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The bifluoride anion $[HF_2]^-$, first identified during the early part of this century, has been the subject of numerous studies designed to probe the nature of the hydrogen-bonding interaction.[1−3] However, despite such intense study, molecular complexes in which the bifluoride moiety is covalently bound to a metal center are not well-characterized. In this paper, we describe the synthesis and structural characterization of the bifluoride complex $Mo(PMe_3)_4H_2F(FHF)$.

The dihydride $Mo(PMe_3)_5H_2$[4] is a useful precursor to a series of hydrido-fluoro derivatives *via* reaction with $HF_{(aq)}$ (Scheme 1). Thus, $Mo(PMe_3)_5H_2$ reacts immediately with $HF_{(aq)}$ to give $Mo(PMe_3)_4H_2F_2$.[5,6] However, in the presence of additional $HF_{(aq)}$, further reaction occurs to give the mono- and bis(hydrogen fluoride) adducts $[Mo(PMe_3)_4H_2F_2{\cdot}(HF)]$ and $[Mo(PMe_3)_4H_2F_2{\cdot}(HF)_2]$, respectively. While the latter complex is readily isolated from the reaction of $Mo(PMe_3)_5H_2$ with excess $HF_{(aq)}$, the mono(hydrogen fluoride) adduct $[Mo(PMe_3)_4H_2F_2{\cdot}(HF)]$ and $Mo(PMe_3)_4H_2F_2$ are best obtained *via* $[Mo(PMe_3)_4H_2F_2{\cdot}(HF)_2]$, rather than by the direct reaction of $Mo(PMe_3)_5H_2$ with $HF_{(aq)}$. Hence, $[Mo(PMe_3)_4H_2F_2{\cdot}(HF)]$ is conveniently synthesized by treatment of the bis(hydrogen fluoride) adduct $[Mo(PMe_3)_4H_2F_2{\cdot}(HF)_2]$ with $Mo(PMe_3)_5(N_2)$, which selectively abstracts one of the HF moieties.[7,8] Likewise, treatment of $[Mo(PMe_3)_4H_2F_2{\cdot}(HF)]$ with a mixture of Et_3N and KH removes the remaining HF moiety, thereby allowing isolation of $Mo(PMe_3)_4H_2F_2$.

The nature of the interaction between the HF and $Mo(PMe_3)_4H_2F_2$ moieties in $[Mo(PMe_3)_4H_2F_2{\cdot}(HF)_2]$ and $[Mo(PMe_3)_4H_2F_2{\cdot}(HF)]$ is most clearly illustrated by an X-ray diffraction study on the latter complex (Figure 1).[9] Thus, it is evident that the HF is involved in a hydrogen-bonding interaction with one of the Mo−F ligands, such that the complex is most appropriately described as a bifluoride derivative, $Mo(PMe_3)_4H_2F(FHF)$. As illustrated in Figure 1, the bifluoride ligand is not coordinated linearly to the molybdenum center, but rather exhibits a Mo−F···F angle of *ca.* 134°.[10] Furthermore, as would be expected, the Mo−FHF bond length [2.124(3) Å] is slightly longer than the unperturbed Mo−F bond length [2.077(4) Å]. By analogy, it is likely that in the solid state $[Mo(PMe_3)_4H_2F_2{\cdot}(HF)_2]$ may be best described as a bis(bifluoride) complex. However, such a proposal must be regarded as tentative since its structure has not been determined by X-ray diffraction.

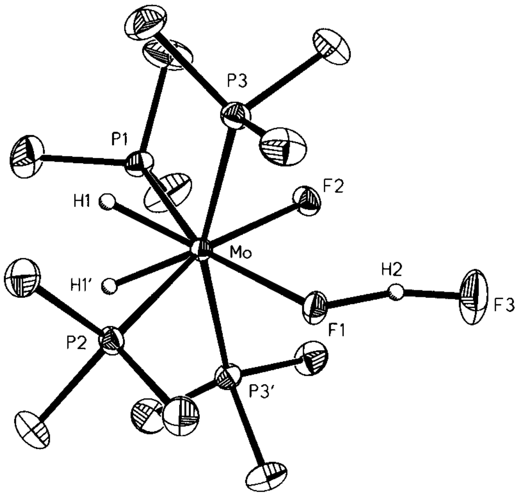
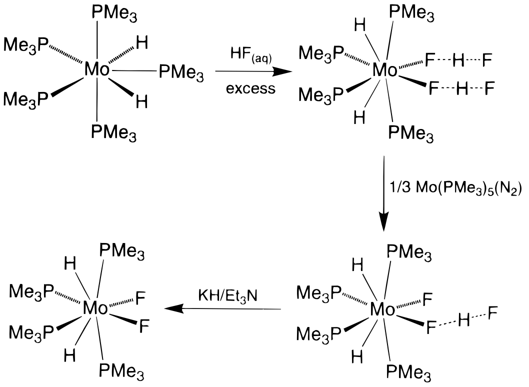


Figure 1. Molecular structure of $Mo(PMe_3)_4H_2F(FHF)$.

Scheme 1



Although hydrogen-bonding interactions of metal fluorides with HCl[11] and with −OH, −NH, and −CH groups[12] have been documented, such interactions with HF are surprisingly uncommon.[13] Hydrogen-bonded interactions of the type [AHB] generally belong to one of three categories, namely, "weak" (*ca.* 2−12 kcal mol^{-1}), "strong" (*ca.* 12−24 kcal mol^{-1}), and "very strong" (>24 kcal mol^{-1}),[2c] with the bifluoride anion containing one of the strongest known hydrogen bonds.[14] With

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[3] (a) Chandler, W. D.; Johnson, K. E.; Campbell, J. L. E. *Inorg. Chem.* **1995**, *34*, 4943−4949. (b) Heidrich, D.; van Eikema Hommes, N. J. R.; Schleyer, P. v. R. *J. Comput. Chem.* **1993**, *14*, 1149−1163. (c) Gronert, S. *J. Am. Chem. Soc.* **1993**, *115*, 10258−10266. (d) Clark, J. H.; Emsley, J.; Jones, D. J.; Overill, R. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1219−1222. (e) Karpfen, A.; Yanovitskii, O. *J. Mol. Struct. (THEOCHEM)* **1994**, *307*, 81−97.

[4] Lyons, D.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 695−700.

[5] For a review of transition metal−fluoro complexes, see: Doherty, N. M.; Hoffman, N. W. *Chem. Rev.* **1991**, *91*, 553−573.

[6] The tungsten analogue $W(PMe_3)_4H_2F_2$ has been structurally characterized. See: Murphy, V. J.; Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1995**, *117*, 9762−9763.

[7] Only 1/3 equiv of $Mo(PMe_3)_5(N_2)$ is required to effect this transformation, since $Mo(PMe_3)_5(N_2)$ itself reacts with 3 equiv of HF to give $Mo(PMe_3)_4H_2F(FHF)$.

[8] Selected spectroscopic data for $Mo(PMe_3)_4H_2F(FHF)$. ^1H NMR (C_6D_6): δ 1.16 [m, 2 PMe_3], 1.13 [m, 2 PMe_3], −4.86 [ddt, $^2J_{P-H} = 39$, $^2J_{P-H} = 43$, $^2J_{P-H} = 67$], 12.5 [d, $^1J_{H-F} = 410$ Hz, dissociated HF]. IR (cm^{-1}, KBr pellet): 2682 (br, m, ν_{H-F}), 1847 (br, w, ν_{Mo-H}).

[9] $Mo(PMe_3)_4H_2F(FHF)$ is orthorhombic, $Cmc2_1$ (no. 36), $a = 14.264(3)$ Å, $b = 12.880(3)$ Å, $c = 12.363(2)$ Å, $V = 2271(1)$ Å^3, $Z = 4$.

[10] The hydrogen atoms of both the [Mo−H] and $[HF_2]$ moieties were located and refined isotropically; however, in view of the relative uncertainty of the positions of hydrogen atoms as determined by X-ray diffraction, we prefer to restrict the discussion of the hydrogen-bonding interaction to the more reliable F···F separation. Nevertheless, for reference, the derived metrical parameters of the bifluoride ligand are: $d(H2-F1) = 1.27(11)$ Å, $d(H2-F3) = 1.13(12)$ Å; $\angle(F1-H2-F3) = 157(8)°$.

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[13] A ruthenium bifluoride complex, *trans*-$Ru(dmpe)_2(H)(FHF)$, has, however, been cited in a footnote of a recent communication: Whittlesey, M. K.; Perutz, R. N.; Moore, M. H. *J. Chem. Soc., Chem. Commun.* **1996**, 787−788.

respect to the strength of the hydrogen bonding interaction in $Mo(PMe_3)_4H_2F(FHF)$, the F···F separation of 2.351(8) Å[10] is considerably less than twice the van der Waals radius of fluorine (1.4 Å),[15] so that the interaction is appropriately described as comprising a strong hydrogen bond.[16] However, the F···F separation in $Mo(PMe_3)_4H_2F(FHF)$ is greater than the F···F separations in bifluoride salts (2.24−2.28 Å),[17] and is therefore indicative of a weakened hydrogen bond relative to that in $[HF_2]^-$. Such weakening with respect to the $[HF_2]^-$ anion is undoubtedly a consequence of the fact that one of the fluorines of the $[HF_2]$ moiety interacts strongly with the molybdenum center. Further evidence that the hydrogen-bonded interaction in $Mo(PMe_3)_4H_2F(FHF)$ is weaker than that in the bifluoride anion is provided by IR spectroscopy. Thus, the infrared spectrum of $Mo(PMe_3)_4H_2F(FHF)$ displays a broad absorption at a significantly higher frequency (2682 cm^{-1})[18] than that reported for the bifluoride ion in its various salts (1284−1749 cm^{-1}),[2c,19] and is therefore in accord with a weakened hydrogen-bonding interaction.[20]

Additional evidence to support the notion that $Mo(PMe_3)_4H_2F(FHF)$ contains a weakened hydrogen bond relative to that of the bifluoride anion is provided by solution NMR spectroscopy studies. Specifically, whereas the ^1H NMR spectrum of the bifluoride ion is a 1:2:1 triplet with a $^1J_{H-F}$ coupling constant of *ca.* 120 Hz,[21] the ^1H NMR spectrum of $Mo(PMe_3)_4H_2F(FHF)$ in C_6D_6 exhibits a *doublet* at 12.5 ppm with a $^1J_{H-F}$ coupling constant of 410 Hz, comparable to that of HF.[22] Correspondingly, the ^{19}F NMR spectrum of $Mo(PMe_3)_4H_2F(FHF)$ exhibits a doublet at −180 ppm.[23] The observation of doublet resonances in both the ^1H and ^{19}F NMR spectra, with coupling constants comparable to that of HF, strongly supports the notion that the Mo−F···H−F interaction is considerably weakened in solution compared to that in the solid state, to the extent that the HF may be regarded to be essentially dissociated.

Finally, the characterization of $Mo(PMe_3)_4H_2F(FHF)$ as a bifluoride complex prompts re-evaluation of the reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with $HF_{(aq)}$, which was originally believed to yield the hydrogen-bonded aqua derivative $[W(PMe_3)_4H_2F(OH_2)][F]$.[24] However, since the tungsten complex is isomorphous with $Mo(PMe_3)_4H_2F(FHF)$, and neither C and H elemental analyses nor X-ray diffraction is capable of distinguishing between OH and F, it is now apparent that "$[W(PMe_3)_4H_2F(OH_2)][F]$" should be reformulated as the bifluoride derivative $W(PMe_3)_4H_2F(FHF)$.[25]

In summary, structural and spectroscopic data suggest that the hydrogen-bonding interaction in the bifluoride complex $Mo(PMe_3)_4H_2F(FHF)$ may be regarded as "strong"; however, as would be expected on simple electrostatic grounds, the interaction between the covalently bound Mo−F moiety and H−F is weaker than that between F^- and H−F.

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Supporting Information Available: Synthetic details and analytical and spectroscopic data for $[Mo(PMe_3)_4H_2F_2\cdot(HF)_2]$, $Mo(PMe_3)_4H_2F(FHF)$, and $Mo(PMe_3)_4H_2F_2$ and crystallographic data for $Mo(PMe_3)_4H_2F(FHF)$ (12 pages). See any current masthead page for ordering and Internet access instructions.

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(14) See refs 2 and 3. Also see: (a) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1983**, *105*, 2944−2950. (b) Larson, J. W.; McMahon, T. B. *Inorg. Chem.* **1984**, *23*, 2029−2033.

(15) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

(16) Strong hydrogen bonds are typically characterized by A···B separations that are ≥0.25 Å less than the sum of the van der Waals radii. See ref 2c.

(17) (a) McDonald, T. R. R. *Acta Crystallogr.* **1960**, *13*, 113−124. (b) Frevel, L. K.; Rinn, H. W. *Acta Crystallogr.* **1962**, *15*, 286. (c) McGaw, B. L.; Ibers, J. A. *J. Chem. Phys.* **1963**, *39*, 2677−2684. (d) Ibers, J. *J. Chem. Phys.* **1964**, *40*, 402−404. (e) Williams, J. M.; Schneemeyer, L. F. *J. Am. Chem. Soc.* **1973**, *95*, 5780−5781. (f) Farnham, W. B.; Dixon, D. A.; Middleton, W. J.; Calabrese, J. C.; Harlow, R. L.; Whitney, J. F.; Jones, G. A.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1987**, *109*, 476−483.

(18) Likewise, $[Mo(PMe_3)_4H_2F_2\cdot(HF)_2]$ exhibits ν_{HF} stretches at 2565 cm^{-1} and 2802 cm^{-1}.

(19) Ault, B. S. *Acc. Chem. Res.* **1982**, *15*, 103−109.

(20) In general terms, as the strength of a hydrogen-bonded interaction increases, ν_{HX} is reduced considerably from that in free HX. Thus, the asymmetric stretch of $[HF_2]^-$ is reduced considerably from the value for ν_{HF} in the gas phase (3960 cm^{-1}). See ref 2.

(21) For example, $^1J_{H-F}$ have been reported for $[R_4N][HF_2]$ (R = Et, Bu^n)[21a,b] and $[Cp_2Co][HF_2]$.[21c] (a) Fujiwara, F. Y.; Martin, J. S. *J. Am. Chem. Soc.* **1974**, *96*, 7625−7631. (b) Martin, J. S.; Fujiwara, F. Y. *Can. J. Chem.* **1971**, *49*, 3071−3073. (c) Bennett, B. K.; Harrison, R. G.; Richmond, T. G. *J. Am. Chem. Soc.* **1994**, *16*, 11165−11166.

(22) For reference, $^1J_{H-F}$ for HF is solvent dependent (e.g., 479 Hz in MeCN and 410 Hz in DMSO).[22a] Furthermore, $^1J_{H-F}$ for HF is 529 and 521 Hz in the gas and liquid phases, respectively.[22b,c] (a) Martin, J. S.; Fujiwara, F. Y. *J. Am. Chem. Soc.* **1974**, *96*, 7632-7637. (b) Muenter, J. S.; Klemperer, W. *J. Chem. Phys.* **1970**, *52*, 6033−6041. (c) Mackor, E. L.; Maclean, C.; Hilbers, C. W. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 655−672.

(23) In addition to the signal attributed to HF, the $[MoF_2]$ group is characterized by a resonance at −230 ppm.

(24) (a) Green, M. L. H.; Parkin, G.; Chen, M.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1986**, 2227−2236. (b) Minqin, C.; Prout, K. *J. Struct. Chem.* **1986**, *5*, 23−27.

(25) Indeed, elemental fluorine analysis of $W(PMe_3)_4H_2F(FHF)$ is in accord with such a formulation (calcd 10.4%, found 10.5%). Also see footnote 24 from ref 6 for a discussion concerning the identity of the tungsten complex.