Bidodecahedral Coordination Geometry in a Dimolybdenum Tetrahydride Containing Three Fluoride Bridges: Crystal and Molecular Structure of $[((PMePh_2)_3H_2Mo)_2(\mu\text{-}F)_3]BF_4$

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Abstract: The reaction of MoH_4L_4 (L = $PMePh_2$) and HBF_4 in THF gives $[(H_2L_3Mo)_2(\mu\text{-}F)_3]BF_4$ (**2**). Single-crystal X-ray diffraction studies of the crystalline product [0.33 CH_2Cl_2 solvate, monoclinic unit cell; a = 21.989 (3) Å, b = 13.272 (3) Å, c = 25.976 (3) Å, β = 91.76 (2)°, V = 7577.1 (3) Å^3, space group $P2_1/c$, R = 6.3%, and Z = 4] show a dinuclear cation with the two metal atoms (Mo–Mo, 3.256 (2) Å) symmetrically bridged by three fluorine atoms. The presence of two hydrogen ligands per Mo was shown by IR and ^1H and ^{31}P NMR spectroscopy. The complex is the first example of face-sharing bidodecahedral geometry, of an $M_2(\mu\text{-}F)_3$ molecular arrangement, and of a hydridofluoride complex. The ligands are disposed in a dodecahedron about each metal; the two polyhedra share an equilateral triangular face. The various ways two dodecahedra might share a face are compared, and the noneclipsed geometry found for **2** is suggested to be the most favorable. The bridging fluorides in **2** were shown to arise from rapid abstraction of one F^- from the BF_4^- counterion. It is proposed that M–F–M bridges can be bent in an 18-electron system but will tend to be linear in systems with less than 18 electrons.

We report the structure of an unusual fluoro-bridged molybdenum hydride, which we prepared during an attempt to generate ligand-deficient species for our alkane activation studies.[1] We have previously found that solvento complexes of the type $[IrH_2S_2(PPh_3)_2]BF_4$ (S = Me_2CO or H_2O) are particularly useful for alkane activation. These can be formed by protonolysis of IrH_5L_2 in the solvent S. We wondered whether similar solvento complexes might be formed in the protonolysis of other polyhydrides. We are reporting elsewhere our results on polyhydrides of W, Re, and Os, which all give solvento complexes with acetonitrile. We also studied $[MoH_4(PMePh_2)_4]$ (**1**), but during the course of this work, Caulton et al.[2] reported that protonolysis of this complex with HBF_4 in MeCN gives $[MoH_2(MeCN)_3(PMePh_2)_3][BF_4]_2$, as we also found. MeCN is a strongly bound solvent ligand and fails to give alkane activation in the iridium case. We therefore attempted the protonolysis in THF, a much more weakly binding ligand. An orange crystalline complex was isolated, for which the usual spectroscopic methods failed to suggest a structure. An X-ray investigation, combined with spectroscopic results, led to the formulation $[(L_3H_2Mo)_2(\mu\text{-}F)_3]BF_4$ (**2**). This result differs from the formulation previously proposed for a product obtained from **1** and HBF_4 under very similar conditions.[3]

Since the source of the fluoride in **2** was the BF_4^- ion, these results strengthen doubts about its use as a noncoordinating anion, especially for ligand-deficient species. There is little precedent for **2**. It is the first example of face-sharing bidodecahedral geometry, of a hydrido fluoride complex, and is the first crystallographically confirmed case of a transition-metal compound containing an $M_2(\mu\text{-}F)_3$ group. The results also cast light on the general problem of the structures of polynuclear complexes of high coordination number and on the formation of linear and bent M–F–M bridges.

Results and Discussion

MoH_4L_4 (**1**, L = $PMePh_2$) in THF was treated with an excess (10 mol equiv) of aqueous or ethanolic HBF_4. At −80 °C, simple protonation seems to occur,[4] but on warming, H_2 is evolved. The solution turns successively blue, green, and then orange over 30 min. Orange crystals of **2** were obtained in 55% yield from the solution.

Table I. Crystal Data for $[(Ph_2MeP)_6H_4Mo_2(\mu\text{-}F)_3]BF_4\cdot 0.33CH_2Cl_2$

formula	$C_{78.33}H_{82.66}BCl_{0.66}F_7Mo_2P_6$
M_r	1569.31
a, Å	21.989 (3)
b, Å	13.272 (3)
c, Å	25.976 (3)
β, deg	91.76 (2)
V, Å^3	7577.1 (3)
$F(000)$	3218
λ(Mo Kα), Å	0.71069
μ(Mo Kα)	5.74
space group	$P2_1/c$
D_{calcd}, g cm^{-3}	1.375
Z	4
obsd reflctns	5180
R	6.3%
crystal size, mm	0.1 × 0.15 × 0.2

Crystallographic and Spectral Studies. The proposed formulation is supported by the combined single-crystal X-ray, spectroscopic, and analytical data. We therefore consider these together.

An X-ray crystallographic study of **2** gave the results shown in Tables I–III and 1–5 (supplementary data). Figure 1 shows a general projection of the cation. The BF_4^- group is not shown, but it was detected crystallographically and the formulation of the complex as a 1:1 salt was confirmed conductometrically (see Experimental Section). The 0.33 mol of dichloromethane of solvation is also omitted from the Figure for greater clarity. The dichloromethane was disordered in the solid state, but its presence was confirmed by microanalysis and by a ^1H NMR spectral study in acetone-d_6 on the X-ray sample itself. The binuclear cation (Figure 1 and 2) consists of two MoL_3 units. The Mo···Mo distance of 3.256 (2) Å does not suggest, but does not exclude, the presence of a metal–metal bond. Three fluoride ions bridge

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(4) Cf. $WH_5L_4^+$, the stable product of protonation of the tungsten analogue.[3]

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Table II. Positional and Anisotropic Thermal Parameters for Atoms in the Immediate Coordination Sphere of $[(Ph_2MeP)_6H_4Mo_2(\mu\text{-}F)_3]BF_4\cdot 0.33CH_2Cl_2$

atom	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo1	0.17245 (6)	0.14584 (9)	0.14299 (6)	316 (11)	291 (8)	431 (14)	−12 (6)	−28 (7)	14 (6)
Mo2	0.31737 (7)	0.12982 (9)	0.17144 (6)	322 (12)	357 (8)	447 (15)	−15 (6)	−52 (8)	20 (7)
P1	0.1215 (2)	0.2879 (3)	0.1810 (2)	401 (35)	303 (30)	602 (48)	12 (18)	−5 (26)	−21 (22)
P2	0.1154 (2)	0.0132 (3)	0.1870 (2)	346 (35)	333 (20)	580 (47)	−54 (18)	−25 (26)	42 (22)
P3	0.1542 (2)	0.2095 (3)	0.0559 (2)	432 (37)	435 (23)	516 (48)	6 (20)	−60 (27)	108 (24)
P4	0.3826 (2)	0.1218 (3)	0.0968 (2)	394 (36)	545 (26)	532 (48)	14 (22)	28 (27)	27 (26)
P5	0.3472 (2)	−0.0314 (3)	0.2088 (2)	391 (35)	388 (21)	521 (47)	11 (19)	−12 (26)	46 (22)
P6	0.3513 (2)	0.2294 (3)	0.2460 (2)	415 (36)	344 (20)	546 (48)	−40 (10)	−72 (27)	2 (22)
F11	0.2521 (4)	0.0513 (6)	0.1252 (4)	384 (65)	442 (47)	451 (82)	19 (40)	0 (49)	7 (45)
F22	0.2319 (4)	0.1249 (6)	0.2096 (3)	312 (61)	446 (46)	454 (79)	8 (39)	−77 (46)	−1 (45)
F33	0.2527 (4)	0.2374 (6)	0.1381 (4)	326 (63)	392 (44)	527 (86)	−38 (38)	−95 (50)	4 (43)
H1	0.111 (6)	0.153 (10)	0.117 (5)	*a*					
H2	0.389 (8)	0.125 (15)	0.194 (7)	*a*					

[a] The isotropic thermal parameters of these atoms were held constant during refinement.

Table III. Selected Distances (Å) and Bond Angles for $[(Ph_2MeP)_6H_4Mo_2(\mu\text{-}F)_3]BF_4\cdot 0.33CH_2Cl_2$

Mo1-Mo2	3.256 (2) Å	Mo1-F11-Mo2	97.4 (3)°
Mo1-H1	1.50 (13)	Mo1-F22-Mo2	98.2 (4)
Mo2-H2	1.67 (18)	Mo1-F33-Mo2	97.6 (3)
Mo1-F11	2.216 (9)	F11-Mo1-F22	68.3 (3)
Mo1-F22	2.154 (9)	F22-Mo1-F33	69.0 (3)
Mo1-F33	2.150 (8)	F11-Mo1-F33	69.7 (3)
Mo2-F11	2.118 (9)	F11-Mo2-F22	70.2 (3)
Mo2-F22	2.153 (8)	F22-Mo2-F33	68.5 (3)
Mo2-F33	2.176 (8)	F11-Mo2-F33	71.0 (3)
Mo1-P1	2.419 (5)	P1-Mo1-P2	96.8 (2)
Mo1-P2	2.463 (5)	P1-Mo1-P3	92.5 (2)
Mo1-P3	2.437 (6)	P2-Mo1-P3	127.3 (2)
Mo2-P4	2.450 (6)	P4-Mo2-P5	96.9 (2)
Mo2-P5	2.431 (4)	P4-Mo2-P6	118.7 (2)
Mo2-P6	2.442 (5)	P5-Mo2-P6	95.0 (2)
		P1-Mo1-F11	154.9 (2)
		P5-Mo2-F33	154.3 (2)
		H1-Mo1-P1	73 (5)
		H1-Mo1-F11	130 (5)
		H2-Mo2-P5	65 (7)
		H2-Mo2-F33	140 (7)

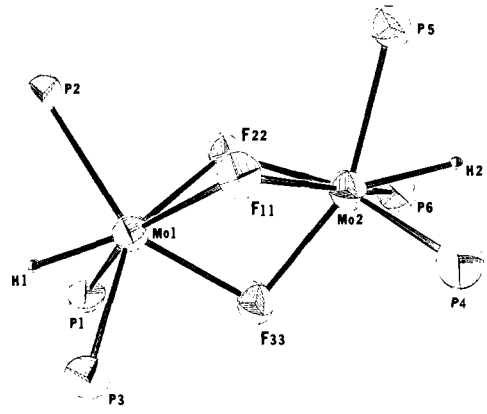

Figure 1. Side-on view of the experimentally determined structure of $[(Ph_2MeP)_6H_4Mo_2(\mu\text{-}F)_3]BF_4\cdot 0.33CH_2Cl_2$ (**2**). Only the atoms in the immediate coordination sphere of the metals are shown. Two of the hydrogen ligands were not detected in the X-ray diffraction experiment; these are not shown.

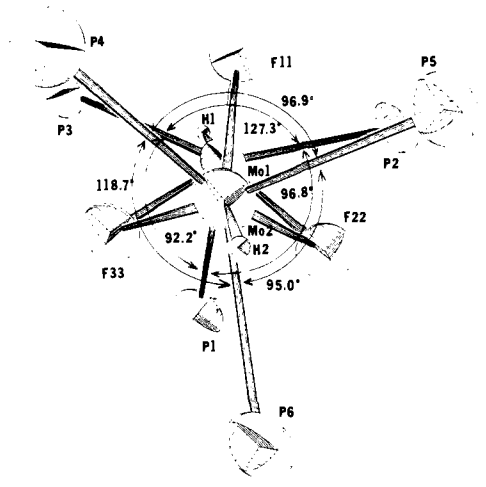

Figure 2. View of the title complex as in Figure 1, but end-on.

the two metals symmetrically. The angles at fluorine[5a] [Mo–F–Mo2: at F11, 97.4 (3); F22, 98.2 (4); and F33, 97.6 (3)°] are only 10° – 12° different from the sp^3 angle. These angles are probably decided by the opposing forces of F···F nonbonding repulsion, tending to close them, and Mo···Mo repulsion, tending to open them up. The 18-electron rule does not require the existence of a metal–metal bond. The elemental identification of the three bridging atoms as F and not O is supported by the structural work and proved by the analytical and spectral data to be discussed below. H1 and H2 were assigned to the two strongest peaks (0.6 e/Å^3) in the difference Fourier map. Their positions were stable to refinement, lending credence to the identification.[5b] Further evidence as to the number and positions of the H ligands is discussed below.

The Geometry of the Complex. The coordination geometry about each molybdenum is dodecahedral (Dod). In this geometry (Figure 3) two trapezoids BAAB, each coplanar with the metal, lie at right angles to one other. The presence of these orthogonal trapezoids constitutes a simple test for Dod. Table IV shows how complex **2** meets this criterion. Figure 4 shows the idealized bidoodecahedral geometry adopted; comparison with Figures 1 and 2 shows the close resemblance to the experimental structure.

The first conclusion we can make is that the second hydrogen ligand on each Mo, not located in the X-ray crystallographic study but detected spectroscopically, must lie in the otherwise vacant A sites of planes II and III. These are identified as H3 and H4 in Figure 4, which shows the molecule represented as two dodecahedra sharing a face. Indeed, such is the crowding of ligands around each metal, that H1–H4 can only be placed in the vicinity of the positions shown in Figure 4.[5b]

(5) (a) Smaller angles at bridging atoms, and shorter Mo···Mo distances have been observed without a Mo–Mo bond being present, e.g., Mo···Mo, 3.143 Å, and Mo–O–Mo, 93.8° (average), in a Mo(VI) complex containing a $Mo(\mu\text{-}O)_3Mo$ arrangement: Hedmann, B. *Acta Crystallogr., Sect. B* **1977**, *B33*, 3077. (b) Our conclusions do not rely on the direct crystallographic detection of the H ligands. The six heavy atoms around each metal make the coordination sphere so crowded that there are only two places around each metal where further ligands can reasonably be placed without prohibitive inter-ligand repulsions. When placed in these open positions, H1–H4 complete Dod coordination geometries around each metal. The appearance of this common geometry, together with the spectroscopic evidence that the H:Mo ratio is 2:1 confirms our assignment. We therefore only rely on crystallography for the heavy atoms and treat the distances and angles involving the crystallographically detected hydrogens with caution.

Table IV. Shape Characteristics of 2

plane	metal	ligands B	ligands A	ligands A	ligands B	std dev, Å	interplanar angles, deg	θ_A, deg	θ_B, deg
I	Mo1	P2	F22	F33	P3	0.06	89.37	34.5	63.65
II	Mo1	F11	[H(3)]	H1	P1	0.05			77.45
III	Mo2	P5	H2	[H(4)]	F33	0.02	89.47		77.15
IV	Mo2	P6	F22	F11	P4	0.08		35.1	59.35

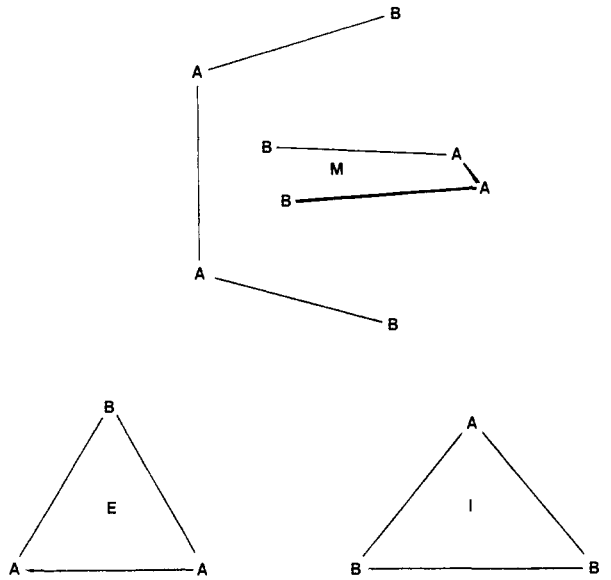

Figure 3. The two mutually orthogonal BAAB trapezoids that constitute the dodecahedral coordination geometry, and the two types of polyhedral face, equilateral (E) and isosceles (I) (see text).

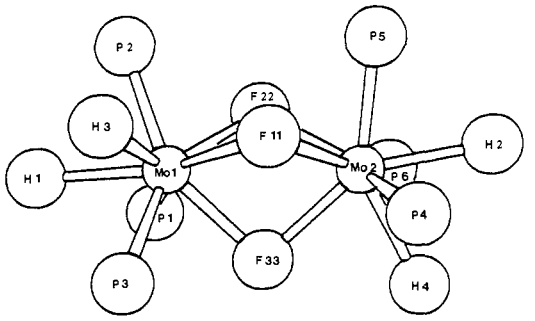

Figure 4. Idealized coordination geometry of the title complex. This view can most usefully be compared with Figure 1. All the ligands are shown and all M–L distances are set equal.

Since the A sites are more hindered then the B sites,[6a] it is not surprising that the bulky PR_3 groups occupy only the less hindered B sites, the less bulky F groups occupy the remainder of the B sites and also some A sites, and the least bulky H ligands occupy only the A sites.

In Table IV are also listed the values of θ_A and θ_B, which we have taken to be half the A–M–A and B–M–B angles, respectively. These help characterize the exact shape adopted. θ_A generally ranges[6a] from 30 to 40°, so our values (34.5 and 35.1°) are unexceptional. θ_B generally ranges[6a] from 65 to 85°. Planes II and III give normal θ_B values (77.45 and 77.15°), but planes I and IV give the smallest values of which we are aware (63.65 and 59.35°). Examination of Figure 4 shows why this is so. In each case, the abnormal values are the result of unusually small P–M–P angles. The presence of the ligands around the second metal tend to cause a decrease in this angle, only resisted by the two hydrogen ligands. For example, the ligands around Mo2 tend to decrease the angle P2–Mo1–P3, resisted only by the presence of H1 and H3. These effects lead to a deformation of nearly 15° in each M–P vector involved.

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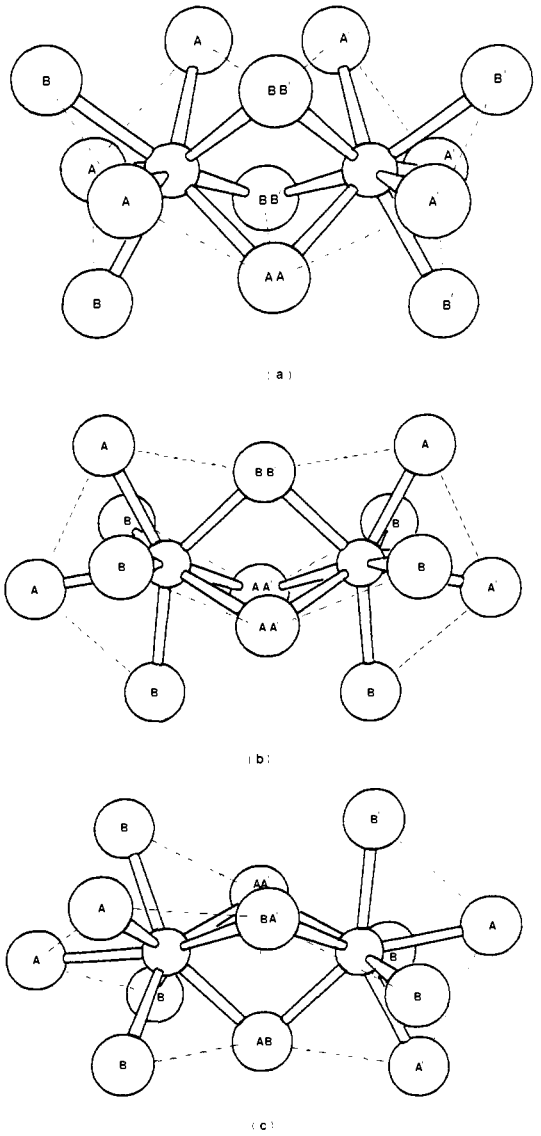

Figure 5. Possible ways that two dodecahedra can share faces: (a) I–I (note the unfavorable AA′ interaction in the uppermost part of the Figure; (b) eclipsed E–E (C_{2v}); (c) nonelcipsed E–E (C_2). The BAAB trapezoids are shown as dotted lines.

Geometrical Possibilities for Face Sharing by Dodecahedra. A consideration of the way the two dodecahedral units share a face in complex **2** led us to a more general enquiry into the problem. The hard-sphere model idealized dodecahedron of Hoard and Silverton[6b] has all M–L distances the same. The nonbonding L–L distances, however, are not all the same: B–B distances are 1.5, and the A–A and A–B distances are 1.2, relative to unit M–A or M–B distances. This means that there are two types of triangular face. One type, bounded by two A sites and a B site, is equilateral (E). The other, bounded by two B sites and an A, is isosceles (I), having a B–B distance of 1.5 and two A–B distance of 1.2 (Figure 3).

If two dodecahedra are to share a face, then they must share congruent faces, either I with I or E with E. In the first case,

I with I, the longer B–B side of one face must coincide with the longer B′–B′ face of the other. Examination of models shows that the I with I combination leads to an unacceptably short nonbonded interaction between the two polyhedra. In Figure 5a the short AA′ interaction is shown. The calculated AA′ distance is 0.92 (M–A = 1.0).[7]

If the dodecahedra share E faces, then two different orientations are possible. In one, of overall symmetry C_{2v}, the A, A, and B sites of one E face share with the A′, A′, and B′ sites of the other E face. In this orientation (Figure 5b) all the substituents on each metal are eclipsed, but there are no prohibitively close contacts (three of BB′ type, 1.62, 2.07, and 2.07, and one of AA′ type, 2.36). In the second unsymmetrical (C_2) orientation (Figure 5c), no pairs of M–L bonds are exactly eclipsed, and the resulting contacts are fewer and much less close (three BB′, 1.88, 2.60, and 2.64). The noneclipsed C_2 orientation is the one adopted by complex **2**. We conclude that dodecahedral polynuclear complexes will usually share only E faces and that the C_2 orientation is probably favored with respect to the C_{2v} for steric reasons.

Since fluoride occupies both A and B sites in the structure, we can compare M–A and M–B bond distances. The M–A distances vary from 2.118 (9) to 2.154 (9) Å and the M–B from 2.176 (8) to 2.216 (9) Å, giving an average (M–A)/(M–B) ratio of 0.976 (3), close to the range[5] usually observed (1.00–1.15).

Other Structural Features. The complex contains a $M_2(\mu\text{-}F)_3$ group, which has never previously been demonstrated among molecular fluorides, although it does occur in various ionic structures, particularly of the perovskite class (e.g., $RbNiF_3$[8a] and $CsMnF_3$[8b]). In $[Ru_2F_3L_6]^+$,[8c] and in one series of unstable carbonyl complexes, e.g. $[Mo_2F_3(CO)_6]^{3-}$,[8d] the presence of $M_2(\mu\text{-}F)_3$ groups was assumed but not proved spectroscopically or crystallographically.

Fluoride shows an almost exclusive tendency to form linear bridges[9] (e.g. $[MoF_4(\mu\text{-}F)]_4$). It has been proposed[9c] that this is a result of ligand to metal π–bonding in the bridge and the excessive crowding that would result in an $M_2(\mu\text{-}F)_2$ or $M_2(\mu\text{-}F)_3$ structure. Our results for **2** show that even an $M_2(\mu\text{-}F)_3$ arrangement does not lead to unusually short M··M (3.256 (2) Å) or F··F (average 2.46 (1) Å) distances. This suggests that the π-bonding in a linear $M_2(\mu\text{-}F)$ bridge may indeed be important, but would be expected to be most pronounced for an electron-deficient metal, e.g., in $(MoF_5)_4$. In **2**, in contrast, an 18-electron system, the metals cannot accept further electrons and so π-bonding loses its importance. We may therefore anticipate that linear bridges will occur in high-valent systems with less than 18 electrons and bent bridges will be common in 18-electron organometallic systems (e.g., ref 9d).

The fluoride must have arisen from the HBF_4 originally used in the synthesis. Deliberate addition of F^- ions to the solution (HF or KF) led to a great acceleration of the reaction. HPF_6, in contrast, did not give **2**, but rather a very air-sensitive material we have not yet characterized. The PF_6^- ion is probably more resistant to F^- abstraction, as PF_5 is a better Lewis acid. We made sure we did not have F^- contamination of our HBF_4 by synthesizing it from pure crystalline $[Et_3O]BF_4$ in situ.

Beck et al.[10] have given IR evidence that BF_4^- binds to an empty site in a variety of organometallic cations of Mo and W, but F^- abstraction[11a] was not seen. Other examples of F^- abstraction by the early transition metals are known, but some other cases of apparent F^- abstraction from BF_4^- may well be due to BF_4^- hydrolysis.[12]

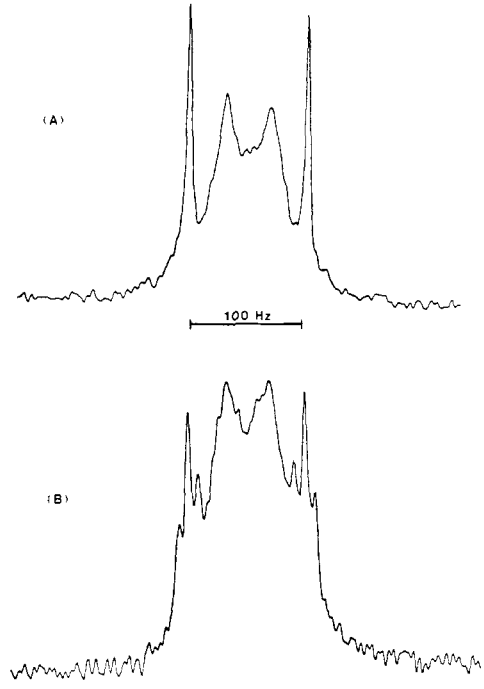

Figure 6. ^{31}P NMR spectra of the title complex **2**, (A) with broad-band ^1H decoupling; (B) with selective ^1H decoupling.

Further Spectral Studies. Only one hydrogen atom per molybdenum was detected crystallographically. We now describe in more detail the spectral data for complex **2**, which shows the presence of two hydrogens per Mo.

Apart from the protons of the ligands L, the ^1H NMR also shows a quartet due to MoH at δ −2.01. Coupling to L has been confirmed by ^{31}P decoupling ($^2J_{PH}$ = 57 Hz). It is notable that the hydrogens and $PMePh_2$ groups are each equivalent down to −80 °C, implying fluxionality. This is not unexpected in an 8-coordinate system. This fluxionality does not involve exchange of hydrogens between Mo1 and Mo2, in which case a septet would have been seen due to coupling to six PR_3 groups. This shows that H has no tendency to replace F in the bridge. In view of the known propensity[12] of H to bridge transition metals in all $M_2(\mu\text{-}H)_x$ (x = 1, 2, 3, and 4) arrangements, this is surprising. It suggests that the preference for F to bridge in this compound is substantial. The undecoupled ^{31}P NMR shows a broad feature at +50.8 ppm (relative to external 85% H_3PO_4). Broad-band ^1H decoupling leads to the appearance of a distorted quartet ($^2J_{PF}$ = 35 Hz) due to coupling to the fluorine bridge atoms. The outer lines are sharp, the inner are broad, and the appearance of the spectrum does not seem to vary markedly down to −80 °C. The molecule is therefore probably not fluxional at an intermediate rate of exchange, but rather is at the high-temperature limit; rearrangement barriers tend to be low in 8-coordination.[6a]

We next hoped to use selective ^1H decoupling to measure the number of hydrogen ligand present. Irradiation at the phenyl frequency removes coupling to these protons and, by off-resonance effects, diminishes the coupling to the PMe groups so greatly that they do not interfere. Only the coupling to the MoH_2 protons remains. Although the resulting spectrum is rather complex (Figure 6), triplets can be seen at the positions previously occupied by the sharp $\alpha\alpha\alpha$ and $\beta\beta\beta$ resonances. This suggests that two

(7) (a) The only situation in which the I–I face bridge might be adopted would be if a diatomic ligand, eg. O_2^{2-}, also bridged the A and A′ positions. (b) The calculations were performed on a TI-57 calculator and the calculated positions (see supplementary data) used to generate the ORTEP plots of Figure 5a–c.

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hydrogens are present per molybdenum.

As seems often to be the case, simple integration of the MoH vs. the L resonances does not reflect the true ratio of protons present, no doubt due to the differing relaxation times of the two sorts of proton. We have therefore performed the integration using an internal standard: a complex, $[ReH_5(PMe_2Ph)_3]$, having a known number of MH protons. The experimental H:Mo ratio so obtained, 1.8:1, is very close to the expected ratio based on the ^{31}P NMR results (2:1).

Finally, the IR spectrum also suggests the presence of an MoH_2 group. The appropriate vibrations are observed at 1956 (w) and 1860 (w) cm^{1} ($CDCl_3$ solution) and were confirmed by deuteriation (ν(Mo–D) = 1332 (w) and 1315 (w) cm^{-1}). We interpret this in terms of the strongly coupled symmetric and antisymmetric stretching modes of each MoH_2 group.

The ^1H decoupling experiment in the ^{31}P NMR spectrum described above also provides further evidence for the identification of the bridging atoms as F groups since O would have no spin. Confirmatory evidence arises from the microanalysis of **2** and of the corresponding PF_6 and BPh_4 salts for C, H, P, and, especially, F. In each case the data are consistent only with the presence of three F's in the bridge and the presence of one anion per binuclear cation.

The ^{19}F NMR showed a peak at δ −147 (relative to $CFCl_3$) due to free BF_4^- and a second, very much broader, peak, at δ −228 due to the bridging fluorides; coupling was not resolved.

It is striking that neither OH^- nor O^{2-} replaces F^- in the bridge under the conditions of preparation, when H_2O is present from the aqueous HBF_4 used, or on reflux of **2** with H_2O/THF or KOH/THF.

Hydrido halide complexes are common for the softer Cl, Br, and I but have never been seen for F. Compound **2** constitutes the first example. Fluoride normally binds only to metals at a strongly electrophilic site, not to the electron-rich sites that bind H. Further examples may be anticipated among the earlier transition metals.

Complex **2** may be related to a salt formulated as $[MoH_3L_3]BF_4$ (**3**), previously reported[3] as having been formed by the action of methanolic HBF_4 on **1** in THF. The complexes are spectroscopically identical, but **3** is reported to be more air sensitive than **2**. If the complexes do prove to be identical, then the reasons for the misassignment of the structure become clear. The quartet seen in the $\{^1H\}$ ^{31}P spectrum of **3** was assigned to phosphorus coupling to three hydrogens. If the complex is in fact **2**, the observed coupling is due to three fluorides. The calculated analysis for C and H in the two cases is remarkably close; only analysis for F would have served to distinguish **2** from **3**. Perhaps the strongest point against **3** is its 14-electron configuration; **2** in contrast is 18-electron.

It is possible that the blue solution initially formed from **1** and HBF_4 is the $[MoH_2(THF)_3L_3]^{+2}$ cation we originally sought, because MeCN addition at this stage gives the isolable complex **4**, $[MoH_2(MeCN)_3L_3](BF_4)_2$.[2] If so, it may be that this solvento complex is responsible for the F^- abstraction from BF_4^-. The acetonitrile complex **4** had almost the same ^1H NMR spectrum as **2**, but their ^{31}P NMR spectra are distinctive.

When 2 mol equiv of HBF_4 is allowed to react with 1 mol equiv of $MoH_4(PMePh_2)_4$ and the reactions are quenched with MeCN after varying lengths of time, the products can be detected by ^{31}P NMR. The complex **2**, once formed, does not react with MeCN, but all the intermediates react with MeCN to form the acetonitrile complex **4**. We found that the initial reaction did not go to completion under these conditions. Only as much **2** was formed as was consistent with the abstraction of 1 F^- ion per BF_4^- present. This abstraction was complete after 10 min at room temperature.

No products analogous to **2** could be obtained with $[WH_4(PMePh_2)_4]$ or $[WH_6(PMe_2Ph)_3]$.

Conclusion

We find that protonation of MoH_4L_4 in THF with HBF_4 gives the crystallographically characterized complex $[Mo_2(\mu\text{-}F)_3H_4L_6]^{2+}$. Each metal is dodecahedral with a shared face. This face is an equilateral E-face of the dodecahedra, and a noneclipsed geometry is adopted, probably for steric reasons. We have proposed that bent M–F–M groups will tend to occur in 18-electron systems, and linear groups in systems with less than 18 electrons. We have described the first crystallographically characterized $M_2(\mu\text{-}F)_3$ arrangement for a molecular fluoride, as well as the first hydrido fluoride. We have also determined that the fluoride arises by abstraction of a single F^- from a BF_4^- over a few minutes at room temperature.

Experimental Section

All reactions were run under an atmosphere of prepurified (concentrated H_2SO_4, then 3-Å molecular sieves) Ar with standard Schlenk-tube techniques. Solvents were distilled under N_2 and stored over molecular sieves under Ar:THF (sodium benzophenone ketyl), MeOH ($NaBH_4$/NaOMe), $CH_3NO_2(P_2O_5)$, CH_3CN (CaH_2). ^1H NMR spectra were recorded on JEOL FX-90Q and Brucker HX-270 spectrometers, ^{31}P NMR spectra on an Varian CFT-20 spectrometer, IR spectra on an Nicolet series 7000 FT-IR, and conductivity measurements on a Dike bridge (Leeds and Northup) at 25 °C $MoH_4(PMePh_2)_4$ and $MoD_4(PMePh_2)_4$ were prepared by our own reported procedure.[14] Methanolic HBF_4 was prepared from $HBF_4{\cdot}OR_2$ (R = Me or Et) (Aldrich) or Me_3OBF_4 (Alfa-Ventron) immediately before use. Methanolic DBF_4 was prepared from Me_3OBF_4 and MeOD.

Trifluorotetrahydridohexakis(methyldiphenylphosphine)dimolybdenum(IV) Tetrafluoroborate. The method used is similar to a reported procedure.[3] $MoH_4(PMePh_2)_4$ (0.90 g, 1.0 mmol) was dissolved in 40 mL of THF. Excess methanolic HBF_4 was added and the yellow solution evolved gas and turned successively blue-green, dark green, and, finally, within 5 min, clear red. After stirring for 4 h at room temperature, the solvent was removed in vacuo and 20 mL of CH_3OH added to the deep red oil. After stirring for 20 min, an orange-red precipitate was filtered off, washed with CH_3OH and Et_2O, and dried in vacuo. Recrystallization from CH_2Cl_2/CH_3OH gave 0.44 g (57%) of orange-red product. Anal. Found (Calcd) for $C_{78}H_{82}F_7P_6Mo_2B{\cdot}0.33CH_2Cl_2$: C, 59.90 (59.95); H, 5.58 (5.30); P, 11.93 (11.84); F, 8.50 (8.47). ^1H NMR (CD_2Cl_2): δ −2.01 (quartet, $^2J_{PH}$ = 57, 20 Hz), 1.32 (apparent singlet), 7.09 (multiplet). $^{31}P\{^1H\}$ NMR ($CDCl_3$): +50.8 ppm (downfield from external H_3PO_4) (distorted quartet, $^2J_{PF}$ = 35 Hz). IR ($CDCl_3$): ν_{MoH}, 1956 (w), 1860 (w) cm^{-1}. Conductivity: Λ_M (10^{-3} M solution), 83 (CH_3NO_2), 123 ohm^{-1} cm^2 mol^{-1} (CH_3CN). The d_4 complex was similarly prepared from DBF_4 and $MoD_4(PMePh_2)$[14] IR($CDCl_3$): ν_{MoD} 1332 (w), 1315 (w) cm^{-1}.

The PF_6^- and BPh_4^- salts were prepared metathetically by twice treating the BF_4^- salt with a 10-fold excess of $NaPF_6$ or $NaBPh_4$ in acetone. Anal. Found (Calcd) PF_6^- salt for $C_{78}H_{82}F_9P_7Mo$: C, 58.29 (58.58); H, 5.28 (5.17); P, 13.67 (13.56); F, 10.31 (10.69) BPh_4^- salt for $C_{120}H_{120}F_3Mo_2B$: C, 68.83 (69.08); H, 5.74 (5.80); P, 10.50 (10.48).

Collection and Treatment of Crystallographic Data A single crystal of **2**, of ca. 0.1 × 0.15 × 0.2 mm size ($C_{78.33}H_{82.66}BCl_{0.66}F_7Mo_2P_6$, m_r 1569.34, formulated as $[\{(PMePh_2)_3H_2Mo\}_2(\mu\text{-}F_3)]BF_4{\cdot}0.33CH_2Cl_2$, a = 21.989 (3)°, b = 13.272 (3) Å, c = 25.976 (3) Å, β = 91.76 (2)°, V = 7577.1 (3) Å^3, monoclinic space group $P2_1/c$, Z = 4, D_{calcd} 1.375 g cm^{-3}, 5180 observed reflections, MoKα μ 5.74 cm^{-1}), was mounted on a Syntex P3 diffractometer. Data were collected at room temperature MoKα, λ = 0.71069 Å, θ–2θ scan mode), and after correction for Lorentz and polarization effects used for solution and refinement of the structure. An absorption correction was not made in view of the low value of μ (5.74) and the shape of the crystal. Refinement of the scale factor, positional parameters, and anisotropic thermal parameters for all nonhydrogen atoms gave a final R factor of 6.3% (unit weights were used throughout). H1 and H2 were assigned to the two strongest peaks in the difference Fourier map; the positions were stable to refinement.[5b] No other hydrogens were found, and no other peaks exceeded 0.3 e/Å^3. The crystallographic data appear in Tables I–III and 1–5 (supplementary data).

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Supplementary Material Available: Listing of observed and calculated structure factors, complete positional parameters, anisotropic thermal parameters, complete bond angles and distances, and calculated positions of vertices in the ideal bidodecahedra (49 pages). Ordering information is given on any current masthead page.

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