Synthesis and characterization of molybdenum species: dinuclear and mononuclear species of the molecular formulas $[Mo_2(O_2CCH_3)_2(LL)_2][BF_4]_2$ and $[Mo(O)(F)(LL)_2][BF_4]$ where LL = bis-phosphine. The use of $[Mo_2(NCCH_3)_{10}][BF_4]_4$ as a source for the $[Mo_2]^{4+}$ core

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Abstract

The complex $[Mo_2(NCCH_3)_{10}][BF_4]_4$ (**1**) acts as a source for the $[Mo_2]^{4+}$ core as shown by its reaction with $Mo_2(O_2CCH_3)_4$ and LL (LL = dppm, dppe, dppee) to yield complexes of the type $[Mo_2(O_2CCH_3)_2(LL)_2][BF_4]_2$. Mononuclear compounds of the type $[Mo(O)(F)(LL)_2][BF_4]$ (LL = dppe, dppee) have also been isolated from these same reactions. All of these compounds have been characterized by single crystal X-ray diffraction experiments and NMR, IR, and UV–Vis spectroscopy, where appropriate. Crystallographic data for $[Mo_2(O_2CCH_3)_2(dppm)_2][BF_4]_2 \cdot 3CH_3CN$ (**2**), $[Mo_2(O_2CCH_3)_2(dppe)_2][BF_4]_2$ (**3**), $[Mo_2(O_2CCH_3)_2(dppee)_2][BF_4]_2 \cdot 2CH_3CN$ (**5**) and $[Mo(O)(F)(dppee)_2][BF_4]$ (**6**) are as follows: **2**, space group, $P\bar{1}$, $a = 13.432(4)$, $b = 20.456(9)$, $c = 12.751(4)$ Å, $\alpha = 104.37(3)$, $\beta = 114.00(4)$, $\gamma = 83.57(3)°$, $V = 3097(4)$ Å^3, $Z = 2$; **3**, space group, $P2_1/c$, $a = 12.547(6)$, $b = 11.076(6)$, $c = 20.245(13)$ Å, $\beta = 102.24(4)°$, $V = 2750(5)$ Å^3, $Z = 2$; **5**, space group, $P\bar{1}$, $a = 11.942(9)$, $b = 13.451(9)$, $c = 11.693(12)$ Å, $\alpha = 95.76(9)$, $\beta = 114.62(8)$, $\gamma = 111.98(5)°$, $V = 1508(3)$ Å^3, $Z = 1$; **6**, space group, Cc, $a = 17.481(4)$, $b = 15.050(3)$, $c = 18.150(6)$ Å, $\beta = 95.23(2)°$, $V = 4755(2)$ Å^3, $Z = 4$.

Introduction[†]

The preparation and properties of $[M_2]^{n+}$ cores surrounded only by weakly coordinated, often neutral, ligands has been of continuing interest for some years [1] although the whole body of results is not large. Reasons for this interest are first that loosely coordinated $[M_2]^{n+}$ species may serve as versatile starting materials in the synthesis of other complexes of the M_2 unit, and second that they have potential catalytic activity for carbonylation and hydrogenation reactions [1]. Some examples of the previously reported compounds containing the $[Mo_2]^{4+}$ core surrounded partially or completely by weakly bound ligands are $[Mo_2(H_2O)_4(CF_3SO_3)_2](CF_3SO_3)_2$ [2], $[Mo_2(NCCH_3)_8](CF_3SO_3)_4$ [2], *cis*-$[Mo_2(O_2CCH_3)_2(NCCH_3)_6](X)_2$ ($X = BF_4^-$, $CF_3SO_3^-$) [3, 4], $[Mo_2(EtO_2CCH_3)_4](CF_3SO_3)_4$ [5], $Mo_2(CF_3SO_3)_4$ [5], $[Mo_2(en)_4](Cl)_4$ [6, 7], $Mo_2^{4+}(aq)$ [7], *trans*-$[Mo_2(O_2CCH_3)_2(dmpe)_2](BF_4)_2$ [8] and $[Mo_2(O_2CCH_3)_2(NCCH_3)_5](BF_3OH)_2$ [9]. Unfortunately, many of the reported synthetic procedures lead to impure products or uncertain formulations, and only in the cases of $[Mo_2(O_2CCH_3)_2(NCCH_3)_6](X)_2$ ($X = BF_4^-$, $CF_3SO_3^-$) [3, 4] were the actual structures determined crystallographically. For $[Rh_2]^{4+}$, the recently reported compounds $[Rh_2(NCCH_3)_{10}](BF_4)_4$ [10] and $[Rh_2(H_2O)_2(NCCH_3)_8](PF_6)_4 \cdot 2H_2O$ [11] are also of the type we are interested in here.

In 1988 [8], the synthesis and characterization of *trans*-$[Mo_2(O_2CCH_3)_2(dmpe)_2](BF_4)_2$ from the reaction of *cis*-$[Mo_2(O_2CCH_3)_2(NCCH_3)_6](BF_4)_2$ with dmpe was reported. It was speculated that the reaction proceeded by a *cis*-to-*trans* transformation of the acetate ligands because of the ligation of dmpe via attack on the metal center between the two *cis*-acetates. However, the bulkier dppe and other similar ligands were only able to form Mo_2:LL ratios of 1:1.

In this paper, we first report a new and more efficient synthesis of the $[Mo_2]^{4+}$ compound $[Mo_2(NCCH_3)_8(ax\text{-}NCCH_3)_2](BF_4)_4 \cdot 2CH_3CN$ (**1**). The previously described

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[†] Abbreviations: dppm = bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, dppee = *cis*-1,2-bis(diphenylphosphino)ethylene.

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method [12], while effective, is more cumbersome than the one now available. We shall then show how **1** may be used as a convenient source of the $[Mo_2]^{4+}$ core to synthesize *trans*-$[Mo_2(O_2CCH_3)_2(LL)_2](BF_4)_2$ compounds in a general way. A by-product containing the $Mo^{IV}{=}O$ unit will also be described.

Experimental

General procedures

All experiments and manipulations were performed under an atmosphere of dry oxygen-free argon by the use of standard vacuum-line, Schlenk and dry box techniques. All glassware was dried at 120 °C for >12 h prior to use. When appropriate, liquid reagents were handled with syringes that were pretreated with suitable solvents.

All solvents were predried over molecular sieves, refluxed over the appropriate drying agent for at least 24 h, then freshly distilled before use. Toluene, tetrahydrofuran, diethyl ether and hexanes were dried over a sodium–potassium alloy in the presence of benzophenone. Ethanol and methylene chloride were dried over magnesium turnings and phosphorus pentoxide, respectively. Acetonitrile (2 l) was passed through a column (3×40 cm) of alumina gel (dried at 120 °C for 48 h) and then distilled from calcium hydride; the first 20 ml of distillate were discarded.

Dimolybdenum(II) tetraacetate was prepared as reported [13]. The phosphines were purchased from Strem and used as received. Tetrafluoroboric acid was purchased from Aldrich and used as received.

Measurements of physical properties

NMR spectra were recorded at 22 °C on either a Varian XL-200 spectrometer at 200 MHz for ^1H, 81 MHz for ^{31}P, or a Varian XL-400 spectrometer at 376 MHz for ^{19}F and 162 MHz for ^{31}P. Reference standards were: ^1H, CH_3CN (1.95 ppm); ^{19}F, $CF_3C_6H_5$ (−63.75 ppm); ^{31}P, H_3PO_4 (0.00 ppm). UV–Vis spectra were recorded on a Cary 17-D spectrophotometer. IR spectra were recorded as Nujol or Fluorolube mulls on an IBM FTIR-44 spectrophotometer. Numerical data for pertinent physical properties appear in Table 1.

Synthesis of cationic molybdenum compounds

Improved preparation of $[Mo_2(NCCH_3)_{10}][BF_4]_4$ (1) [12]

Dimolybdenum(II) tetraacetate (1.20 g, 2.80 mmol) was dissolved in a solution of acetonitrile (20 ml) and methylene chloride (100 ml). To this vigorously stirring yellow solution was added $HBF_4 \cdot Et_2O$ (6.0 ml, 85% HBF_4 solution) with a color change to red. The solution was continuously stirred at room temperature and progressed from red to purple to blue–purple within 30 min. During this period, a large crop of bright blue–purple solid precipitated from the reaction solution. The reaction mixture was heated to reflux temperature and gently refluxed for 40 min. Since the

TABLE 1. Spectroscopic data for compounds **1**–**6**

Compound	UV–Vis (nm)	IR (cm^{-1})	NMR (ppm)
1	597	2325m, 2293s 2247vs, 1059s, br	^1H: 1.95(s)
2	512	2285s, 2249s 1583w, 1570w, 1055s, br	^{31}P: 19.39 (s, >90%) 19.76 (s, <10%)
3	503	1583w, 1569w, 1052s, br 780–650m	^1H: 7.8–6.8 (m, 40 H) 2.82 (s, 6 H), O_2CCH_3 2.29 (s, 8 H), P–CH_2CH_2–P
4	503	1052s, br 780–650m 944m	^{31}P: 40.03 (d, $^2J_{P,F}=40.6$ Hz) ^{19}F: −121.21 (qn, Mo–*F*, $^2J_{F,P}=40.2$ Hz) −152.87 (s, $^{10}BF_4$) −152.93 (s, $^{11}BF_4$)
5	512	1590w, 1575w 1055s, br 780–650m	^{31}P: 18.60(s)
6	500	1055s, br 945m	^{31}P: 51.85 (d, $^2J_{P,F}=41.1$ Hz) ^{19}F: −122.48 (qn, $^2J_{F,P}=41.2$ Hz) −152.91 (s, $^{10}BF_4$) −152.96 (s, $^{11}BF_4$)

blue–purple solid formed so quickly, the solution was refluxed for a short period of time in order to coagulate the precipitate and remove any impurities. The reaction solution was cooled to room temperature to give a weakly colored, light blue solution and a blue–purple solid. The supernatant liquid was decanted.

The solid was rinsed with methylene chloride (4 × 10 ml) until the wash solution was clear. The solid was further rinsed with diethyl ether to remove any residual $HBF_4 \cdot Et_2O$. After drying under vacuum at 35 °C for 8 h, 2.24 g (93% yield) of a bright blue solid **1** was isolated. The solid can be purified by dissolving the material in acetonitrile, and then allowing toluene, diethyl ether or methylene chloride to diffuse into the acetonitrile layer. In all following reactions, the molecular weight of compound **1** was that for the dried material, $[Mo_2(NCCH_3)_8(ax\text{-}NCCH_3)_{0.5}](BF_4)_4$ [12]. A description of this method of preparation will be published elsewhere [14].

Preparation of $[Mo_2(O_2CCH_3)_2(dppm)_2]$-$[BF_4]_2 \cdot 3CH_3CN$ (2)

Dimolybdenum(II) tetraacetate (0.100 g, 0.234 mmol) and dppm (0.370 g, 0.934 mmol) were placed in a 100 ml flask equipped with a stir bar; the solids were dissolved in THF (20 ml) to give a clear yellow solution. In a separate Schlenk tube, $[Mo_2(NCCH_3)_8(ax\text{-}NCCH_3)_{0.5}](BF_4)_4$ (**1**) (0.203 g, 0.234 mmol) was dissolved in acetonitrile (15 ml) to give a bright blue solution. The acetonitrile solution was poured into the THF solution. To the resulting THF/acetonitrile solution was added degassed glacial acetic acid (0.5 μl) to act as an acid catalyst; the reaction does not occur in the absence of acid. This solution was stirred for 4 days at 23 °C, during which time the solution became deep wine red colored. All volatiles were removed to give a red residue. A solution of ethanol:acetonitrile (4:1, 15 ml) was added to give a deep red solution, which was filtered through Celite and layered with a hexane:ether solution (8:6, 20 ml). After 3–4 weeks, red crystals were deposited on the sides of the Schlenk tube. The structure of one of these crystals has been determined to be **2**. The isolated yield was 314 mg (about 50%); the amount of acetonitrile in the final dried product was not determined. We have not seen any evidence for a mononuclear oxo species containing dppm from this reaction.

Preparation of $[Mo_2(O_2CCH_3)_2(dppe)_2][BF_4]_2$ (3) and $[Mo(O)(F)(dppe)_2][BF_4]$ (4)

Method A. Dimolybdenum(II) tetraacetate (0.100 g, 0.234 mmol) and dppe (0.372 g, 0.934 mmol) were placed in a 100 ml flask equipped with a stir bar; the solids were dissolved in THF (20 ml) to give a clear yellow solution. In a separate Schlenk tube, $[Mo_2(NCCH_3)_8(ax\text{-}NCCH_3)_{0.5}](BF_4)_4$ (**1**) (0.203 g, 0.234 mmol) was dissolved in acetonitrile (15 ml) to give a bright blue solution. The acetonitrile solution was poured into the THF solution. To the resulting THF/acetonitrile solution was added degassed glacial acetic acid (0.5 μl) to act as an acid catalyst; as before the reaction does not occur in the absence of acid. This solution was stirred for 4 days at 23 °C, during which time the color of the solution became red–orange. All volatiles were removed to give a red–brown oily solid. A solution of ethanol:acetonitrile (4:1, 15 ml) was added to give a deep red solution which turned orange after several minutes. The solution was filtered through Celite and layered with a hexane:ether solution (8:6, 20 ml). After 3–4 weeks, two differently shaped sets of orange crystals were deposited on the sides of the Schlenk tube. The structure of one of these crystals has been determined to be **3**. The crystals are stable in mineral oil long enough to separate the two sets of crystals by hand. The physical properties listed in Table 1 support the formulation of these two types of crystals as **3** and **4**.

Alternatively, the red–brown oily solid can be washed with a toluene:hexane (1:1, 3 × 10 ml) mixture and then dried. The solid can be redissolved in acetonitrile (20 ml), filtered, all volatiles removed, and the solid dried for 8 h to yield 423 mg of a red–brown solid. This solid has been identified to be a mixture of **3** and **4** (43:57) by $^{31}P\{^1H\}$ NMR.

Method B. Dimolybdenum(II) tetraacetate (0.100 g, 0.234 mmol) and dppe (0.186 g, 0.468 mmol) were placed in a 100 ml flask equipped with a stir bar; the solids were dissolved in THF (20 ml) to give a clear yellow solution. To this solution was added $HBF_4 \cdot Et_2O$ (1 ml, 85% HBF_4 in diethyl ether). The solution was stirred for 12 h during which time the color changed from yellow to orange; the solution also became very viscous. A portion of this solution (2.5 ml) was diluted with THF and examined by $^{31}P\{^1H\}$ NMR to reveal a mixture (52:48) of **3** and **4** as well as some minor peaks of unknown origin. These species were not isolated in this method.

Preparation of $[Mo_2(O_2CCH_3)_2(dppee)_2]$-$[BF_4]_2 \cdot 2CH_3CN$ (5) and $[Mo(O)(F)(dppee)_2]$-$[BF_4]$ (6)

The same proportions and conditions were used here as for the species **3** and **4** (method A). Crystals of **5** and **6** were red and orange, respectively and were obtained in the same way. It was obviously much easier to separate these two sets of crystals due to their different colors.

An alternative workup procedure may also be followed. After stirring the original solution for 4 days, the THF/acetonitrile solution was reduced to 5 ml to give a deep burgundy oily solution and a bright orange finely divided solid. Acetonitrile (5 ml) was added to give a burgundy solution and the bright orange solid. The addition of hexanes (10 ml) caused the formation of two liquid phases; THF (8 ml) was then added with gentle stirring until the two layers disappeared. The resulting burgundy solution was removed by filtration to leave behind a bright orange solid, **6** (47 mg, after washing with toluene and drying). The filtrate was set aside at room temperature. After 4 days, both orange and red crystals had precipitated from the solution. The supernatant solution was shown by $^{31}P\{^1H\}$ NMR to contain 90% of **5** and 10% of **6**.

General X-ray diffraction methods

All single crystals were grown as described above. In all cases, unless otherwise noted, the crystals were handled in degassed mineral oil (stored over sodium) which was mixed with a small amount of the solvent. Crystals were examined under polarized light, and, when necessary cut to the proper size. Two general methods were used to mount the crystals: (i) the crystal was coated with epoxy cement and mounted on the end of a glass fiber, or (ii) the crystal was sealed inside a capillary tube containing mineral oil and solvent from the reaction vessel.

Each crystal was placed on the X-ray diffractometer, optically centered, and 25 reflections were found from three regions of reciprocal space. Centering, indexing and a least-squares calculation on the 25 reflections gave a tentative identification of the crystal system, which was confirmed by axial photographs. The X-ray data were collected, reduced, and corrected as described elsewhere [15, 16]. The data were corrected for absorption by using azimuthal scans of 6 reflections with Eulerian angle of χ near 90°. No decay correction was used for those data sets that showed decay of $<5\%$.

Crystal data and data collection parameters for **2**, **3**, **5** and **6** are listed in Table 2. The positional parameters and the equivalent isotropic thermal parameters, and selected bond distances and angles for **2**, **3**, **5** and **6** are listed in Tables 3–10.

TABLE 2. Crystal data for $[Mo_2(O_2CCH_3)_2(dppm)_2][BF_4]_2 \cdot 3CH_3CN$ (**2**), $[Mo_2(O_2CCH_3)_2(dppe)_2][BF_4]_2$ (**3**), $[Mo_2(O_2CCH_3)_2(dppee)_2][BF_4]_2 \cdot 2CH_3CN$ (**5**) and $[Mo(O)(F)(dppee)_2][BF_4]$ (**6**)

	2	**3**	**5**	**6**
Formula	$Mo_2P_4F_8N_3O_4C_{60}B_2H_{59}$	$Mo_2P_4F_8O_4C_{56}B_2H_{54}$	$Mo_2P_4F_8N_2O_4C_{60}B_2H_{56}$	$Mo_1P_4F_5O_1C_{52}B_1H_{44}$
Formula weight	1378.44	1280.44	1358.51	1010.57
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	Cc
a (Å)	13.432(4)	12.547(6)	11.942(9)	17.481(4)
b (Å)	20.456(9)	11.076(6)	13.451(9)	15.050(3)
c (Å)	12.751(4)	20.245(13)	11.693(12)	18.150(6)
α (°)	104.37(3)		95.76(9)	
β (°)	114.00(4)	102.24(4)	114.62(8)	95.23(2)
γ (°)	83.57(3)		111.98(5)	
V (Å^3)	3097(4)	2750(5)	1508(3)	4755(2)
Z	2	2	1	4
D_{calc} (g/cm^3)	1.475	1.547	1.495	1.411
Crystal size (mm)	$0.41 \times 0.39 \times 0.38$	$0.52 \times 0.49 \times 0.36$	$0.36 \times 0.32 \times 0.20$	$0.49 \times 0.37 \times 0.29$
μ (Mo Kα) (cm^{-1})	11.212	6.298	5.794	4.564
Data collection instrument	Enraf-Nonius CAD-4	Nicolet P3	Rigaku AFC-5R	Nicolet P3
Radiation monochromated, Mo Kα	0.71073	0.71073	0.71073	0.71073
Orientation reflections (no.; range)	25; $21 < 2\theta < 33$	25; $20 < 2\theta < 30$	23; $23 < 2\theta < 30$	25; $22 < 2\theta < 30$
Temperature (°C)	23	23	22	23
Scan method	ω–2θ	ω–2θ	ω–2θ	ω–2θ
Data collection range, 2θ (°)	$4 < 2\theta < 47$	$4 < 2\theta < 50$	$4 < 2\theta < 45$	$4 < 2\theta < 55$
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	8669, 6829	4557, 4063	3711, 2751	4939, 4205
No. parameters refined	748	343	411	529
Transmission factors, max., min.	1.00, 0.94	1.00, 0.65	1.00, 0.96	1.00, 0.92
R^a	5.20	6.32	5.43	0.0521
R_w^b	7.59	8.27	6.89	0.0743
Quality of fit indicator^c	1.894	2.31	1.33	1.835
Largest shift/e.s.d., final cycle	0.10	0.07	0.02	0.10
Largest peak (e/Å^3)	1.31	1.163	0.84	0.728

$^aR = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

TABLE 3. Positional parameters and equivalent isotropic thermal parameters (Å^2) and their e.s.d.s for $[Mo_2(O_2CCH_3)_2(dppm)_2][BF_4]_2 \cdot 3CH_3CN$ (2)

Atom	x	y	z	B[a]
Mo(1)	0.17331(4)	0.71485(2)	0.49203(4)	2.49(1)
Mo(2)	0.20698(4)	0.76860(2)	0.38696(4)	2.47(1)
P(1)	0.0920(1)	0.60676(7)	0.3334(1)	2.53(3)
P(2)	0.2166(1)	0.80672(7)	0.6851(1)	2.63(3)
P(3)	0.1537(1)	0.67741(7)	0.1924(1)	2.63(3)
P(4)	0.2853(1)	0.87584(7)	0.5495(1)	2.63(3)
F(1)	0.3607(5)	0.4791(3)	0.2526(5)	11.1(2)
F(2)	0.5407(6)	0.4626(5)	0.3461(6)	16.3(3)
F(3)	0.4665(5)	0.4609(4)	0.1567(5)	11.9(2)
F(4)	0.4424(8)	0.3870(4)	0.2296(8)	17.3(4)
F(5)	0.1003(5)	1.0382(3)	0.7551(5)	10.3(2)
F(6)	0.1893(5)	1.1238(3)	0.9065(5)	10.0(2)
F(7)	0.1304(7)	1.0395(4)	0.9439(6)	14.8(3)
F(8)	0.2569(7)	1.0224(4)	0.8811(7)	15.7(3)
O(1)	0.3262(3)	0.6662(2)	0.5250(3)	4.0(1)
O(2)	0.0189(3)	0.7592(2)	0.4588(3)	2.90(9)
O(3)	0.0536(3)	0.8160(2)	0.3497(3)	3.7(1)
O(4)	0.3573(3)	0.7224(2)	0.4125(3)	2.91(9)
N(1)	0.2044(5)	0.6313(3)	0.6472(5)	5.3(2)
N(2)	0.2239(5)	0.8395(3)	0.2544(5)	6.2(2)
N(3)	0.6663(7)	0.7512(5)	0.4304(8)	12.1(3)
C(1)	0.3903(5)	0.6792(3)	0.4769(5)	3.4(1)
C(2)	0.4978(6)	0.6452(4)	0.4972(6)	5.5(2)
C(3)	−0.0129(4)	0.8002(3)	0.3901(5)	3.2(1)
C(4)	−0.1275(6)	0.8274(4)	0.3546(7)	5.5(2)
C(5)	0.2337(5)	0.5903(3)	0.6975(6)	4.7(2)
C(6)	0.2714(7)	0.5342(4)	0.7611(7)	6.4(2)
C(7)	0.198(1)	0.8799(5)	0.2012(7)	8.5(3)
C(8)	0.203(1)	0.9356(7)	0.144(1)	16.7(5)
C(9)	0.5864(8)	0.7758(6)	0.3631(9)	10.5(3)
C(10)	0.495(1)	0.8036(8)	0.291(1)	13.0(5)
C(11)	0.1605(4)	0.5962(3)	0.2313(4)	2.9(1)
C(12)	0.1212(4)	0.5268(3)	0.3799(4)	2.7(1)
C(13)	−0.0534(4)	0.6030(3)	0.2430(5)	2.7(1)
C(21)	0.2103(4)	0.8876(3)	0.6444(4)	2.6(1)
C(22)	0.1121(5)	0.8150(3)	0.7458(5)	3.2(1)
C(23)	0.3455(4)	0.8094(3)	0.8130(5)	3.2(1)
C(32)	0.2525(5)	0.6675(3)	0.1238(5)	3.4(1)
C(33)	0.0227(4)	0.6762(3)	0.0669(4)	2.8(1)
C(42)	0.4288(4)	0.8815(3)	0.6484(5)	3.2(1)
C(43)	0.2595(5)	0.9539(3)	0.4964(5)	3.2(1)
C121	0.0405(5)	0.4904(3)	0.3769(5)	4.0(2)
C122	0.0647(5)	0.4296(3)	0.4126(6)	5.0(2)
C123	0.1693(6)	0.4059(3)	0.4522(6)	4.8(2)
C124	0.2535(5)	0.4440(4)	0.4609(6)	4.6(2)
C125	0.2282(5)	0.5037(3)	0.4249(5)	3.9(2)
C131	−0.1258(5)	0.6384(3)	0.2917(6)	4.0(2)
C132	−0.2390(5)	0.6353(4)	0.2217(7)	5.3(2)
C133	−0.2769(6)	0.5985(4)	0.1091(6)	5.2(2)
C134	−0.2056(5)	0.5613(4)	0.0599(6)	4.8(2)
C135	−0.0932(5)	0.5633(3)	0.1290(5)	3.7(2)
C221	0.0626(5)	0.7575(4)	0.7386(6)	4.9(2)
C222	−0.0116(6)	0.7622(4)	0.7891(7)	6.1(2)
C223	−0.0411(6)	0.8248(4)	0.8450(6)	5.5(2)
C224	0.0062(6)	0.8815(4)	0.8458(6)	4.9(2)
C225	0.0808(5)	0.8777(3)	0.7973(5)	4.1(2)
C231	0.3666(5)	0.8620(3)	0.9109(6)	4.4(2)
C232	0.4684(7)	0.8659(4)	1.0070(6)	5.7(2)
C233	0.5450(6)	0.8167(4)	1.0031(6)	5.7(2)
C234	0.5241(5)	0.7617(4)	0.9047(6)	5.1(2)
C235	0.4224(5)	0.7590(3)	0.8099(5)	3.7(2)
C321	0.3402(5)	0.6232(3)	0.1498(5)	4.1(2)
C322	0.4133(6)	0.6187(4)	0.0993(6)	5.6(2)
C323	0.3987(5)	0.6592(4)	0.0181(6)	5.2(2)
C324	0.3127(6)	0.7035(4)	−0.0060(6)	5.1(2)
C325	0.2362(5)	0.7086(3)	0.0436(5)	4.0(2)
C331	0.0027(5)	0.6246(3)	−0.0321(5)	3.8(2)
C332	−0.1008(6)	0.6204(3)	−0.1256(5)	4.4(2)
C333	−0.1787(6)	0.6686(4)	−0.1190(6)	4.8(2)
C334	−0.1575(5)	0.7214(4)	−0.0200(6)	4.9(2)
C335	−0.0560(5)	0.7249(3)	0.0730(5)	3.8(2)
C421	0.5033(5)	0.8373(3)	0.6178(5)	3.9(2)
C422	0.6140(5)	0.8416(4)	0.6956(6)	4.9(2)
C423	0.6472(5)	0.8879(4)	0.8024(6)	5.2(2)
C424	0.5728(6)	0.9329(4)	0.8322(6)	5.5(2)
C425	0.4620(5)	0.9299(4)	0.7547(6)	4.4(2)
C431	0.3455(6)	0.9863(4)	0.5010(6)	5.2(2)
C432	0.3230(7)	1.0459(4)	0.4544(7)	6.5(2)
C433	0.2191(7)	1.0696(4)	0.4084(6)	5.8(2)
C434	0.1350(6)	1.0354(4)	0.4054(7)	5.7(2)
C435	0.1563(5)	0.9780(3)	0.4492(6)	4.6(2)
B(1)	0.4545(7)	0.4536(5)	0.2510(7)	5.2(2)
B(2)	0.1664(9)	1.0580(5)	0.8667(9)	6.7(3)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$.

Single crystal X-ray diffraction experiments

$[Mo_2(O_2CCH_3)_2(dppm)_2][BF_4]_2 \cdot 3CH_3CN$ (2)

The crystals were examined and handled in a mineral oil/solvent mixture, and one was mounted on a glass fiber with epoxy. Normal procedures were followed for data collection and reduction. No decay was observed but a correction for absorption was applied. Refinement was started in $P\bar{1}$ and this space group was determined to be correct by successful refinement. Direct methods revealed all atoms except those of the uncoordinated solvent. The BF_4^- counterions were not disordered. Final residuals and figures of merit are reported in Table 2. Positional and equivalent isotropic thermal parameters are listed in Table 3. Selected bond distances and bond angles are listed in Table 7.

$[Mo_2(O_2CCH_3)_2(dppe)_2][BF_4]_2$ (3)

Crystals grown by method A as described in 'Experimental' were handled in mineral oil, and one was mounted on a glass fiber with epoxy cement. Normal procedures were followed for data collection and reduction. No decay correction was applied; a correction for absorption was applied. The space group was uniquely defined as $P2_1/c$. A three dimensional Pat-

TABLE 4. Positional parameters and equivalent isotropic thermal parameters (Å^2) and their e.s.d.s for $[Mo_2(O_2CCH_3)_2(dppe)_2][BF_4]_2$ (**3**)

Atom	x	y	z	B^a
Mo(1)	0.42936(3)	0.02155(4)	0.01722(2)	2.736(8)
P(1)	0.2936(1)	−0.1418(1)	−0.03576(7)	3.31(3)
P(2)	0.5190(1)	−0.2155(2)	−0.09278(7)	3.67(3)
F(1)	0.6951(4)	0.5573(5)	0.0888(3)	7.4(1)
F(2)	0.8194(4)	0.6977(4)	0.1246(3)	8.0(1)
F(3)	0.8736(5)	0.5142(5)	0.1000(3)	8.5(1)
F(4)	0.8017(5)	0.5434(6)	0.1921(3)	9.7(2)
B(1)	0.7991(7)	0.5788(9)	0.1266(5)	5.5(2)
O(1)	0.4632(3)	−0.1000(4)	0.0967(2)	3.71(8)
O(2)	0.6147(3)	−0.1484(4)	0.0613(2)	4.36(9)
C(27)	0.5512(5)	−0.1619(6)	0.1044(3)	3.7(1)
C(28)	0.5835(6)	−0.2421(8)	0.1664(3)	6.2(2)
C(1)	0.3535(5)	−0.2943(6)	−0.0260(4)	4.8(1)
C(2)	0.4583(5)	−0.3254(6)	−0.0499(3)	4.6(1)
C(3)	0.2076(5)	−0.1312(6)	−0.1203(3)	3.9(1)
C(4)	0.1864(6)	−0.0168(8)	−0.1475(4)	6.3(2)
C(5)	0.1141(8)	−0.001(1)	−0.2124(5)	8.6(3)
C(6)	0.0666(6)	−0.106(1)	−0.2445(4)	8.7(3)
C(7)	0.0912(8)	−0.221(1)	−0.2166(4)	9.3(3)
C(8)	0.1600(7)	−0.2310(9)	−0.1543(4)	7.3(2)
C(9)	0.1907(4)	−0.1515(6)	0.0158(3)	3.7(1)
C(10)	0.1302(5)	−0.2557(7)	0.0168(4)	5.3(2)
C(11)	0.0494(6)	−0.2579(8)	0.0556(4)	5.8(2)
C(12)	0.0312(5)	−0.1591(8)	0.0914(4)	5.7(2)
C(13)	0.0900(6)	−0.0545(9)	0.0904(4)	6.9(2)
C(14)	0.1716(6)	−0.0495(7)	0.0519(4)	5.6(2)
C(15)	0.6494(5)	−0.2663(6)	−0.1038(3)	4.0(1)
C(16)	0.7077(5)	−0.3512(8)	−0.0615(4)	5.7(2)
C(17)	0.8117(6)	−0.388(1)	−0.0704(5)	7.3(2)
C(18)	0.8561(6)	−0.3373(9)	−0.1210(4)	6.7(2)
C(19)	0.7974(6)	−0.2504(9)	−0.1632(4)	6.3(2)
C(20)	0.6940(5)	−0.2146(8)	−0.1555(3)	5.4(2)
C(21)	0.4382(5)	−0.2000(8)	−0.1788(3)	5.4(2)
C(22)	0.4250(7)	−0.0925(9)	−0.2131(4)	8.0(2)
C(23)	0.3587(8)	−0.088(1)	−0.4788(4)	11.3(3)
C(24)	0.3112(7)	−0.197(2)	−0.3065(4)	12.6(4)
C(25)	0.3298(8)	−0.308(1)	−0.2734(4)	11.3(3)
C(26)	0.3933(7)	−0.310(1)	−0.2084(4)	8.5(2)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\ \gamma)\beta_{12}+ac(\cos\ \beta)\beta_{13}+bc(\cos\ \alpha)\beta_{23}]$.

TABLE 5. Positional parameters and equivalent isotropic thermal parameters (Å^2) and their e.s.d.s for $[Mo_2(O_2CCH_3)_2(dppee)_2][BF_4]_2\cdot 2CH_3CN$ (**5**)

Atom	x	y	z	B^a
Mo(1)	0.47748(7)	0.46352(6)	0.7004(7)	2.52(3)
P(1)	0.5121(2)	0.2833(2)	0.0425(2)	2.89(8)
P(2)	0.4267(2)	0.6050(2)	0.1855(2)	2.99(9)
B(1)	0.1312(7)	0.8264(6)	0.1378(7)	5.4(6)
F(1)	0.183(2)	0.877(2)	0.070(2)	19(2)
F(2)	0.085(2)	0.720(1)	0.094(2)	11(1)
F(3)	0.030(2)	0.845(2)	0.128(3)	18(3)
F(4)	0.225(2)	0.863(2)	0.260(1)	11.5(9)
F(5)	0.182(3)	0.772(3)	0.215(3)	15(3)
F(6)	0.172(2)	0.831(2)	0.049(2)	10(2)
F(7)	0.176(3)	0.929(1)	0.208(4)	20(3)
F(8)	−0.005(1)	0.774(2)	0.078(2)	9(1)
O(1)	0.6864(5)	0.5306(4)	0.2133(5)	3.1(2)
O(2)	0.2599(6)	0.3903(5)	−0.0682(6)	4.7(3)
N(1)	0.370(1)	0.3430(8)	0.197(1)	5.8(5)
C(1)	0.7792(8)	0.5893(7)	0.1838(8)	3.0(3)
C(2)	0.9296(9)	0.634(1)	0.284(1)	6.0(4)
C(3)	0.6568(8)	0.2990(7)	0.0135(9)	3.6(3)
C(4)	0.3173(8)	0.6568(7)	0.0732(8)	3.2(3)
C(5)	0.3682(8)	0.1479(7)	−0.0772(8)	2.9(3)
C(6)	0.2346(9)	0.1302(7)	−0.1101(9)	3.8(3)
C(7)	0.123(1)	0.0252(8)	−0.190(1)	5.0(4)
C(8)	0.147(1)	−0.0608(8)	−0.234(1)	5.1(4)
C(9)	0.281(1)	−0.0418(8)	−0.203(1)	5.0(4)
C(10)	0.3926(9)	0.0629(7)	−0.1222(9)	3.9(4)
C(11)	0.5674(9)	0.2466(7)	0.1967(8)	3.4(3)
C(12)	0.481(1)	0.1485(9)	0.208(1)	4.4(4)
C(13)	0.523(1)	0.120(1)	0.326(1)	5.6(5)
C(14)	0.648(2)	0.192(1)	0.433(1)	6.2(6)
C(15)	0.737(1)	0.292(1)	0.423(1)	6.4(5)
C(16)	0.698(1)	0.3199(8)	0.3039(9)	4.6(4)
C(17)	0.3206(9)	0.5395(7)	0.2593(9)	3.3(3)
C(18)	0.179(1)	0.4721(8)	0.180(1)	4.5(4)
C(19)	0.095(1)	0.413(1)	0.230(1)	6.0(5)
C(20)	0.160(1)	0.425(1)	0.367(1)	6.5(6)
C(21)	0.302(1)	0.4929(9)	0.447(1)	5.5(5)
C(22)	0.382(1)	0.5511(8)	0.393(1)	4.5(4)
C(23)	0.5661(9)	0.7357(7)	0.3177(9)	3.6(3)
C(24)	0.703(1)	0.7614(9)	0.356(1)	4.9(4)
C(25)	0.809(1)	0.868(1)	0.454(1)	6.1(5)
C(26)	0.775(1)	0.9416(9)	0.503(1)	5.5(5)
C(27)	0.639(1)	0.9142(8)	0.463(1)	5.6(5)
C(28)	0.532(1)	0.8134(8)	0.367(1)	4.7(4)
C(29)	0.290(1)	0.271(1)	0.206(1)	6.0(6)
C(30)	0.178(1)	0.169(1)	0.209(2)	8.3(7)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\ \gamma)\beta_{12}+ac(\cos\ \beta)\beta_{13}+bc(\cos\ \alpha)\beta_{23}]$.

terson function and a subsequent difference Fourier map revealed all the atoms. The BF_4^- counterions were not disordered. Final residuals and figures of merit are reported in Table 2. Positional and equivalent isotropic thermal parameters are listed in Table 4. Selected bond distances and bond angles are listed in Table 8.

$[Mo_2(O_2CCH_3)_2(dppee)_2][BF_4]_2\cdot 2CH_3CN$ (5)

The crystals were handled in a mineral oil/solvent mixture, and one was mounted on a glass fiber with epoxy cement. A normal beam rotation photograph showed some initial solvent loss; another crystal was mounted in a capillary tube in the mineral oil/solvent mixture. Normal procedures were followed for data collection and reduction. No decay correction was applied; a correction for absorption was applied. Refinement was started in $P\bar{1}$ and this space group was determined to be correct by successful refinement. A three dimensional Patterson synthesis and a subsequent

TABLE 6. Positional parameters and equivalent isotropic thermal parameters ($Å^2$) and their e.s.d.s for $[Mo(O)(F)(dppee)_2][BF_4]$ (**6**)

Atom	x	y	z	B^a
Mo(1)	0.7179(6)	0.0057(6)	0.2559(5)	2.00(8)
Mo(2)	0.7244(9)	−0.008(1)	0.2662(6)	2.00(8)
P(1)	0.6059(2)	0.0444(3)	0.3270(2)	2.35(7)
P(2)	0.7655(2)	0.1493(2)	0.3118(2)	1.94(6)
P(3)	0.8364(2)	−0.0448(3)	0.1924(2)	2.26(7)
P(4)	0.6763(2)	−0.1474(2)	0.2083(2)	2.46(7)
F(1)	0.7616(6)	−0.0382(8)	0.3516(4)	2.2(1)*
F(2)	0.680	0.035(2)	0.172	2.5(2)*
F(11)	0.7085(6)	0.3949(7)	0.5765(5)	11.4(1)*
F(12)	0.7878(6)	0.3281(6)	0.5072(6)	11.4(1)*
F(13)	0.6873(6)	0.3970(7)	0.4519(5)	11.4(1)*
F(14)	0.7810(8)	0.4758(6)	0.5100(6)	11.4(1)*
O(1)	0.6866(8)	0.051(1)	0.1723(6)	2.5(2)*
O(2)	0.767(1)	−0.055(1)	0.3453(6)	2.2(1)*
C(1)	0.6373(8)	0.1337(9)	0.3900(7)	2.3(2)
C(2)	0.7062(8)	0.182(1)	0.3833(8)	4.5(3)
C(3)	0.8034(8)	−0.1392(9)	0.1322(7)	3.1(3)
C(4)	0.7404(6)	−0.1757(6)	0.1361(5)	1.6(2)
C(5)	0.5188(8)	0.091(1)	0.2790(9)	2.6(3)
C(6)	0.463(1)	0.127(2)	0.3115(9)	5.1(4)
C(7)	0.3965(9)	0.165(1)	0.2800(9)	4.8(4)
C(8)	0.382(1)	0.140(2)	0.199(1)	6.3(6)
C(9)	0.429(1)	0.098(2)	0.164(1)	6.6(6)
C(10)	0.504(1)	0.066(1)	0.2002(8)	4.1(3)
C(11)	0.5695(7)	−0.0413(8)	0.3940(6)	1.5(2)
C(12)	0.503(1)	−0.071(1)	0.3868(7)	3.6(3)
C(13)	0.478(1)	−0.130(1)	0.438(1)	5.2(4)
C(14)	0.531(2)	−0.157(2)	0.501(1)	7.3(7)
C(15)	0.599(1)	−0.120(1)	0.5046(7)	4.1(3)
C(16)	0.631(1)	−0.058(1)	0.4565(9)	3.8(3)
C(17)	0.8635(8)	0.148(1)	0.3641(8)	1.9(2)
C(18)	0.920(1)	0.173(1)	0.321(1)	4.2(3)
C(19)	0.9963(8)	0.157(1)	0.367(1)	4.0(4)
C(20)	1.0031(7)	0.125(1)	0.4328(7)	3.5(3)
C(21)	0.9423(8)	0.104(1)	0.4684(6)	3.2(3)
C(22)	0.8704(8)	0.113(1)	0.4289(8)	2.8(3)
C(23)	0.7669(9)	0.245(1)	0.2578(9)	3.3(3)
C(24)	0.790(1)	0.337(1)	0.290(1)	3.3(3)
C(25)	0.775(1)	0.4040(9)	0.249(1)	5.1(4)
C(26)	0.746(1)	0.401(1)	0.167(1)	4.8(4)
C(27)	0.733(1)	0.326(2)	0.144(1)	4.3(5)
C(28)	0.7419(9)	0.239(1)	0.1773(8)	4.7(4)
C(29)	0.9252(9)	−0.084(1)	0.2418(9)	3.0(3)
C(30)	0.9415(8)	−0.073(1)	0.3141(9)	3.1(3)
C(31)	1.0089(9)	−0.097(1)	0.3523(7)	3.7(3)
C(32)	1.0640(7)	−0.142(1)	0.3112(9)	3.8(3)
C(33)	1.048(1)	−0.155(1)	0.237(1)	6.4(5)
C(34)	0.9750(7)	−0.137(1)	0.1972(8)	3.7(3)
C(35)	0.865(1)	0.027(1)	0.129(1)	3.5(3)
C(36)	0.8239(9)	0.061(1)	0.0694(9)	3.2(3)
C(37)	0.837(1)	0.118(2)	0.012(1)	5.5(5)
C(38)	0.918(1)	0.154(1)	0.0242(8)	4.3(3)
C(39)	0.970(2)	0.132(2)	0.084(1)	6.6(5)
C(40)	0.9472(9)	0.071(1)	0.137(1)	4.9(4)
C(41)	0.6810(8)	−0.253(1)	0.2640(7)	2.1(2)
C(42)	0.704(1)	−0.249(1)	0.337(1)	3.5(3)
C(43)	0.703(1)	−0.327(2)	0.385(1)	5.4(4)
C(44)	0.680(1)	−0.408(1)	0.339(1)	4.6(4)
C(45)	0.660(1)	−0.416(1)	0.273(1)	4.8(4)
C(46)	0.665(1)	−0.3250(9)	0.230(1)	3.2(2)
C(47)	0.5856(9)	−0.1430(9)	0.1621(8)	2.6(3)
C(48)	0.5141(7)	−0.1694(9)	0.1913(7)	2.3(2)
C(49)	0.443(1)	−0.161(1)	0.163(1)	4.0(3)
C(50)	0.429(1)	−0.123(1)	0.087(1)	4.7(4)
C(51)	0.498(1)	−0.093(1)	0.053(1)	4.8(4)
C(52)	0.5755(9)	−0.108(1)	0.0849(8)	3.9(3)
B(1)	0.7404(4)	0.3986(5)	0.5109(4)	5.6(3)*

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$. Starred atoms were refined isotropically.

difference Fourier map revealed all atoms except the BF_4^- counterion. After several cycles of full matrix refinement and difference Fourier maps, the BF_4^- counterions were located and found to be disordered. The model was then refined in SHELX-76 with the B–F distances of each set of fluorine atoms fixed and a common thermal parameter given to each set. Final residuals and figures of merit are reported in Table 2. Positional and equivalent isotropic thermal parameters are listed in Table 5. Selected bond distances and bond angles are listed in Table 9.

[Mo(O)(F)(dppee)$_2$][BF$_4$] (6)

The crystals were handled in a mineral oil/solvent mixture, inspected, and one was mounted on a glass fiber with epoxy. Normal procedures were followed for data collection and reduction. No decay correction was applied; a correction for absorption was applied. The systematic absences indicated two possible space groups, *Cc* or *C2/c*. The ambiguity of space groups was resolved by the successful refinement in the space group *Cc*. The entire structure was determined from a three dimensional Patterson function and a subsequent difference Fourier map. The BF_4^- counterion was not disordered. The model refined to $R=5.78\%$ and $R_w=7.98\%$ with all atoms anisotropic. There was a disorder problem which warrants a more thorough description.

The chemical and spectroscopic evidence (see Table 1 and later discussion) support a formulation as $[Mo(O)(F)(dppee)_2][BF_4]$ (**6**). However, in the initial model, the Mo–O and Mo–F distances refined to values of 1.810 and 1.804 Å, respectively. The oxygen and fluorine atoms were switched, but refinement resulted in the same values. There was thus a clear indication that the O and F atoms are disordered, since one short (Mo=O) and one longer (Mo–F) bond would be expected. The thermal parameters appeared to be normal

TABLE 7. Selected bond distances (Å) and angles (°) for $[Mo_2(O_2CCH_3)_2(dppm)_2][BF_4]_2\cdot 3CH_3CN$ (2)[a]

Distances			
Mo(1)–Mo(2)	2.1321(8)	P(2)–C(21)	1.836(6)
Mo(1)–P(1)	2.587(1)	P(2)–C(22)	1.835(7)
Mo(1)–P(2)	2.590(1)	P(2)–C(23)	1.826(5)
Mo(1)–O(1)	2.105(4)	P(3)–C(11)	1.832(6)
Mo(1)–O(2)	2.087(4)	P(3)–C(32)	1.835(7)
Mo(2)–P(3)	2.588(1)	P(3)–C(33)	1.830(5)
Mo(2)–P(4)	2.587(1)	P(4)–C(21)	1.825(7)
Mo(2)–O(3)	2.096(4)	P(4)–C(42)	1.819(5)
Mo(2)–O(4)	2.065(4)	P(4)–C(43)	1.830(6)
Mo(1)–N(1)	2.802(7)	N(1)–C(5)	1.12(1)
Mo(2)–N(2)	2.573(8)	N(2)–C(7)	1.13(1)
P(1)–C(11)	1.839(7)	C(5)–C(6)	1.49(1)
P(1)–C(12)	1.825(6)	C(7)–C(8)	1.52(2)
P(1)–C(13)	1.817(5)		
Angles			
Mo(2)–Mo(1)–P(1)	99.06(4)	C(11)–P(1)–C(13)	106.2(3)
Mo(2)–Mo(1)–P(2)	100.28(4)	C(12)–P(1)–C(13)	103.4(3)
Mo(2)–Mo(1)–O(1)	89.1(1)	Mo(1)–P(2)–C(21)	106.0(2)
Mo(2)–Mo(1)–O(2)	92.9(1)	Mo(1)–P(2)–C(22)	113.4(2)
P(1)–Mo(1)–P(2)	159.40(6)	Mo(1)–P(2)–C(23)	122.9(2)
P(1)–Mo(1)–O(1)	86.5(1)	C(21)–P(2)–C(22)	104.3(3)
P(1)–Mo(1)–O(2)	91.71(9)	C(21)–P(2)–C(23)	104.1(3)
P(2)–Mo(1)–O(1)	100.9(1)	C(22)–P(2)–C(23)	104.3(3)
P(2)–Mo(1)–O(2)	80.32(9)	Mo(2)–P(3)–C(11)	106.7(2)
O(1)–Mo(1)–O(2)	177.5(2)	Mo(2)–P(3)–C(32)	113.5(2)
Mo(1)–Mo(2)–P(3)	99.29(4)	Mo(2)–P(3)–C(33)	123.9(2)
Mo(1)–Mo(2)–P(4)	97.37(4)	C(11)–P(3)–C(32)	103.7(3)
Mo(1)–Mo(2)–O(3)	89.7(1)	C(11)–P(3)–C(33)	104.3(3)
Mo(1)–Mo(2)–O(4)	93.6(1)	C(32)–P(3)–C(33)	102.8(3)
P(3)–Mo(2)–P(4)	162.92(6)	Mo(2)–P(4)–C(21)	106.0(2)
P(3)–Mo(2)–O(3)	96.9(1)	Mo(2)–P(4)–C(42)	121.6(2)
P(3)–Mo(2)–O(4)	80.59(9)	Mo(2)–P(4)–C(43)	114.5(2)
P(4)–Mo(2)–O(3)	86.9(1)	C(21)–P(4)–C(42)	105.6(3)
P(4)–Mo(2)–O(4)	94.62(9)	C(21)–P(4)–C(43)	104.3(3)
O(3)–Mo(2)–O(4)	176.1(2)	C(42)–P(4)–C(43)	103.3(3)
Mo(1)–P(1)–C(11)	105.4(2)	N(1)–C(5)–C(6)	178.4(7)
Mo(1)–P(1)–C(12)	117.6(1)	N(2)–C(7)–C(8)	161(1)
Mo(1)–P(1)–C(13)	119.7(2)	P(1)–C(11)–P(3)	107.7(3)
C(11)–P(1)–C(12)	102.8(3)	P(2)–C(21)–P(4)	106.9(3)

[a] Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 8. Selected bond distances (Å) and angles (°) for $[Mo_2(O_2CCH_3)_2(dppe)_2][BF_4]_2$ (3)[a]

Distances			
Mo(1)–Mo(1)′	2.0928(7)	P(1)–C(3)	1.824(5)
Mo(1)–P(1)	2.560(2)	P(1)–C(9)	1.827(6)
Mo(1)–P(2)	2.547(2)	P(2)–C(2)	1.838(7)
Mo(1)–O(1)	2.071(4)	P(2)–C(15)	1.827(6)
Mo(1)–O(2)	2.105(4)	P(2)–C(21)	1.820(6)
P(1)–C(1)	1.842(7)		
Angles			
Mo(1)′–Mo(1)–P(1)	103.58(4)	Mo(1)–P(1)–C(3)	123.8(2)
Mo(1)′–Mo(1)–P(2)	104.87(4)	Mo(1)–P(1)–C(9)	106.9(2)
Mo(1)′–Mo(1)–O(1)	93.5(1)	C(1)–P(1)–C(3)	107.8(3)
Mo(1)′–Mo(1)–O(2)	90.4(1)	C(1)–P(1)–C(9)	101.9(3)
P(1)–Mo(1)–P(2)	151.51(5)	C(3)–P(1)–C(9)	101.0(3)
P(1)–Mo(1)–O(1)	82.8(1)	Mo(1)–P(2)–C(2)	111.9(2)
P(1)–Mo(1)–O(2)	96.4(1)	Mo(1)–P(2)–C(15)	104.3(2)
P(2)–Mo(1)–O(1)	94.0(1)	Mo(1)–P(2)–C(21)	124.5(3)
P(2)–Mo(1)–O(2)	85.0(1)	C(2)–P(2)–C(15)	105.2(3)
O(1)–Mo(1)–O(2)	176.1(2)	C(2)–P(2)–C(21)	105.9(3)
Mo(1)–P(1)–C(1)	112.5(2)	C(15)–P(2)–C(21)	103.1(3)

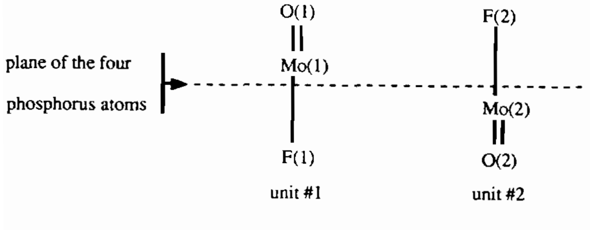
[a] Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 9. Selected bond distances (Å) and angles (°) for $[Mo_2(O_2CCH_3)_2(dppee)_2][BF_4]_2\cdot 2CH_3CN$ (5)[a]

Distances			
Mo(1)′–Mo(1)	2.144(1)	P(1)–C(11)	1.83(1)
Mo(1)–P(1)	2.617(3)	P(2)–C(4)	1.83(1)
Mo(1)–P(2)	2.615(3)	P(2)–C(17)	1.83(1)
Mo(1)–O(1)	2.092(5)	P(2)–C(23)	1.836(7)
Mo(1)–O(2)	2.145(6)	N(1)–C(29)	1.13(2)
Mo(1)–N(1)	2.64(1)	C(3)–C(4)′	1.31(2)
P(1)–C(3)	1.84(1)	C(29)–C(30)	1.53(2)
P(1)–C(5)	1.835(6)		
Angles			
Mo(1)′–Mo(1)–P(1)	103.42(8)	Mo(1)–P(1)–C(5)	121.2(3)
Mo(1)′–Mo(1)–P(2)	104.12(7)	Mo(1)–P(1)–C(11)	111.5(4)
Mo(1)′–Mo(1)–O(1)	93.9(2)	C(3)–P(1)–C(5)	104.3(4)
Mo(1)′–Mo(1)–O(2)	89.7(2)	C(3)–P(1)–C(11)	99.7(5)
Mo(1)′–Mo(1)–N(1)	167.6(2)	C(5)–P(1)–C(11)	101.8(4)
P(1)–Mo(1)–P(2)	152.37(9)	Mo(1)–P(2)–C(4)	114.6(3)
P(1)–Mo(1)–O(1)	80.4(2)	Mo(1)–P(2)–C(17)	112.7(3)
P(1)–Mo(1)–O(2)	98.9(2)	Mo(1)–P(2)–C(23)	122.2(4)
P(1)–Mo(1)–N(1)	74.1(3)	C(4)–P(2)–C(17)	100.1(5)
P(2)–Mo(1)–O(1)	95.5(2)	C(4)–P(2)–C(23)	101.6(4)
P(2)–Mo(1)–O(2)	83.4(2)	C(17)–P(2)–C(23)	102.7(5)
P(2)–Mo(1)–N(1)	79.5(3)	Mo(1)–N(1)–C(29)	155.6(9)
O(1)–Mo(1)–O(2)	176.4(3)	P(1)–C(3)–C(4)′	125.7(8)
O(1)–Mo(1)–N(1)	97.6(3)	P(2)′–C(4)′–C(3)	123.3(9)
O(2)–Mo(1)–N(1)	78.8(3)	N(1)–C(29)–C(30)	176(2)
Mo(1)–P(1)–C(3)	115.4(3)		

[a] Numbers in parentheses are e.s.d.s in the least significant digits.

for the fluorine and oxygen atoms, but the thermal parameter for the molybdenum atom was elongated along the F–Mo–O axis. Since it is common for the metal atom to be displaced out of the P_4 plane toward the atom with shorter metal to ligand distance (Mo=O), as seen for example in the case of $[W(O)Br(Me_2PCH_2CH_2PMe_2)_2]Br\cdot 5H_2O$ [17], the model consisted of two superimposed units:



Common thermal parameters were assigned to O(1) and F(2), as well as to F(1) and O(2). The multiplicities of the two units were allowed to refine freely. The

TABLE 10. Selected bond distances (Å) and angles (°) for $[Mo(O)(F)(dppee)_2][BF_4]$ (**6**)[a]

Distances			
Mo(1)–P(1)	2.51(1)	P(1)–C(1)	1.82(1)
Mo(1)–P(2)	2.498(9)	P(1)–C(5)	1.82(2)
Mo(1)–P(3)	2.58(1)	P(1)–C(11)	1.92(1)
Mo(1)–P(4)	2.54(1)	P(2)–C(2)	1.80(2)
Mo(1)–F(1)	1.95(1)	P(2)–C(17)	1.88(1)
Mo(1)–O(1)	1.71(2)	P(2)–C(23)	1.74(2)
Mo(2)–P(1)	2.56(2)	P(3)–C(3)	1.85(1)
Mo(2)–P(2)	2.59(1)	P(3)–C(29)	1.82(2)
Mo(2)–P(3)	2.53(2)	P(3)–C(35)	1.69(2)
Mo(2)–P(4)	2.46(1)	P(4)–C(4)	1.85(1)
Mo(2)–F(2)	1.93(1)	P(4)–C(41)	1.88(1)
Mo(2)–O(2)	1.71(2)	P(4)–C(47)	1.73(1)
Angles			
P(1)–Mo(1)–P(2)	80.6(3)	P(1)–Mo(2)–P(2)	78.0(4)
P(1)–Mo(1)–P(3)	174.7(4)	P(1)–Mo(2)–P(3)	172.3(6)
P(1)–Mo(1)–P(4)	99.9(4)	P(1)–Mo(2)–P(4)	100.9(5)
P(1)–Mo(1)–F(1)	83.2(5)	P(1)–Mo(2)–F(2)	90.1(6)
P(1)–Mo(1)–O(1)	99.3(7)	P(1)–Mo(2)–O(2)	94.1(8)
P(2)–Mo(1)–P(3)	100.6(4)	P(2)–Mo(2)–P(3)	99.4(5)
P(2)–Mo(1)–P(4)	174.9(4)	P(2)–Mo(2)–P(4)	172.3(6)
P(2)–Mo(1)–F(1)	80.9(5)	P(2)–Mo(2)–F(2)	93.2(9)
P(2)–Mo(1)–O(1)	94.6(7)	P(2)–Mo(2)–O(2)	91.2(8)
P(3)–Mo(1)–P(4)	78.3(3)	P(3)–Mo(2)–P(4)	80.7(4)
P(3)–Mo(1)–F(1)	91.9(5)	P(3)–Mo(2)–F(2)	82.8(5)
P(3)–Mo(1)–O(1)	85.8(6)	P(3)–Mo(2)–O(2)	93.3(9)
P(4)–Mo(1)–F(1)	94.1(5)	P(4)–Mo(2)–F(2)	79.2(8)
P(4)–Mo(1)–O(1)	90.3(7)	P(4)–Mo(2)–O(2)	96.5(9)
F(1)–Mo(1)–O(1)	174.5(9)	F(2)–Mo(2)–O(2)	175(1)
Mo(1)–P(1)–C(1)	106.8(5)	C(3)–P(3)–C(29)	104.5(7)
Mo(1)–P(1)–C(5)	120.1(6)	C(3)–P(3)–C(35)	100.9(8)
Mo(1)–P(1)–C(11)	119.2(5)	C(29)–P(3)–C(35)	104.4(8)
C(1)–P(1)–C(5)	102.0(7)	Mo(1)–P(4)–C(4)	106.0(4)
C(1)–P(1)–C(11)	101.3(6)	Mo(1)–P(4)–C(41)	125.8(5)
C(5)–P(1)–C(11)	104.5(7)	Mo(1)–P(4)–C(47)	110.6(5)
Mo(1)–P(2)–C(2)	109.6(6)	C(4)–P(4)–C(41)	100.8(5)
Mo(1)–P(2)–C(17)	116.7(5)	C(4)–P(4)–C(47)	104.7(6)
Mo(1)–P(2)–C(23)	120.4(6)	C(41)–P(4)–C(47)	106.7(7)
C(2)–P(2)–C(17)	101.4(6)		
C(2)–P(2)–C(23)	102.7(8)		
C(17)–P(2)–C(23)	103.6(7)		
Mo(1)–P(3)–C(3)	105.6(5)		
Mo(1)–P(3)–C(29)	124.1(6)		
Mo(1)–P(3)–C(35)	114.5(7)		

[a] Numbers in parentheses are e.s.d.s in the least significant digits.

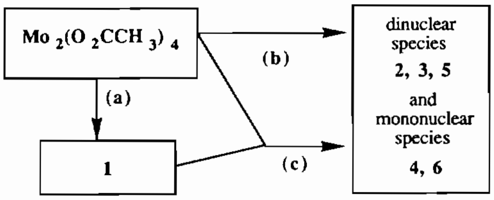
Mo–O distances were fixed to 1.693 (0.021) Å [18]. The Mo–F distances were set by taking the sum of the refined distances before accounting for disorder (1.810 + 1.804 Å) and subtracting the Mo–O distance (1.693 Å) to arrive at a fixed value of 1.921 (0.021) Å. All of these distances were then allowed to refine. Final residuals and figures of merit are reported in Table 2. Positional and equivalent isotropic thermal parameters are listed in Table 6. Selected bond distances and bond angles are listed in Table 10.

Results and discussion

Synthesis and spectroscopic characterization – cationic species

The general synthetic routes to compounds **1**–**6** are shown in Scheme 1. The characterization of **1** has been described elsewhere [12]. However, we will note that this synthesis has three distinct advantages over our earlier preparative route. The reaction is faster; the product is purer and is free from all acetate impurities; the reaction proceeds in greater yields.

We will now turn our discussion to compounds **2**–**6**. In Scheme 1, the appear to be two routes for obtaining compounds **2**–**6**. However, we will quickly dispose of route (b) by the following discussion. This particular route was investigated only for LL = dppe, compounds



Scheme 1. (a) $HBF_4 \cdot Et_2O + CH_3CN$ (**1**); (b) $HBF_4 \cdot Et_2O$ + LL (LL = dppe (**3**) and (**4**)); (c) HO_2CCH_3, 0.5 μl + LL (LL = dppm (**2**), dppe (**3**) and (**4**), dppee (**5**) and (**6**)). See text for the formulations of **1**–**6**.

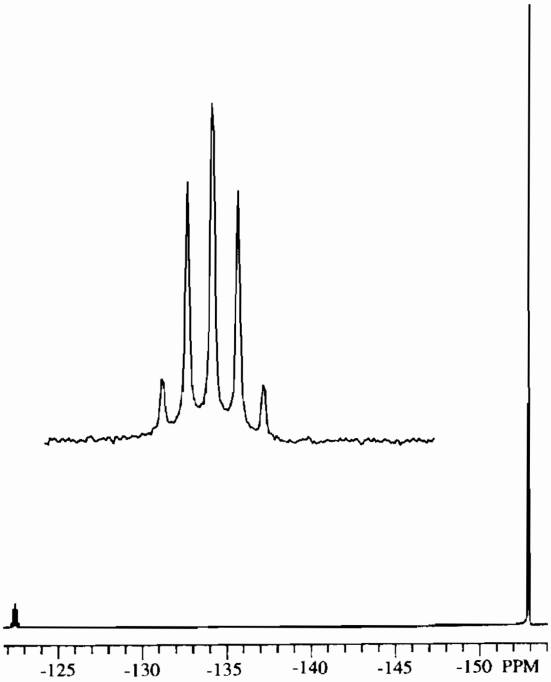


Fig. 1. The ^{19}F NMR spectrum of $[Mo(O)(F)(dppee)_2][BF_4]$ (**6**).

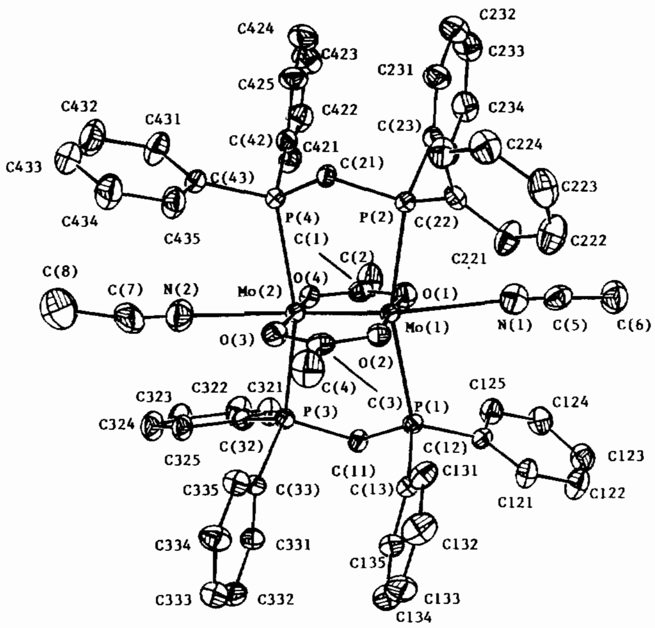


Fig. 2. ORTEP drawing of the $[Mo_2(O_2CCH_3)_2(dppm)_2]^{2+}$ cation in **2**.

3 and **4**, but we believe that the results should be applicable to the other bis-phosphines in our study. As mentioned in 'Experimental' under method B for the synthesis **3** and **4**, the final solution became very viscous after stirring for 12 h. The viscosity of the solution seems to indicate that a polymeric substance (poly-THF?) is present. The $^{31}P\{^1H\}$ NMR spectrum of a diluted sample of the reaction solution indicated a mixture (52:48) of **3** and **4**, as well as other contaminants. We were attempting to synthesize the pure dinuclear species **3** but to our dismay we obtained again a mixture of both **3** and **4**. However, this reaction does provide some insight as to how the fluoride transfer from the BF_4^- counterion to the molybdenum core to form **4** may occur.

We have attempted to prepare pure **4** or **6** by reacting acetonitrile solutions of **1** with an excess of bisphosphine and a small amount of either water or oxygen. In all cases, the solutions turned green and then brown. The brown material had very different properties from those of **4** and **6** and was not investigated further. The oxygen atoms of **4** and **6** probably originate from either water in the glacial acetic acid or the acetic acid itself. The fluorine of **4** and **6** no doubt results from abstraction of F^- from the BF_4^- counterion. There is precedent [19] in the literature for such a reaction.

The spectroscopic evidence for the formulation of compounds **2**–**6** as shown in Table 1 is by itself convincing. The single crystal X-ray diffraction experiments

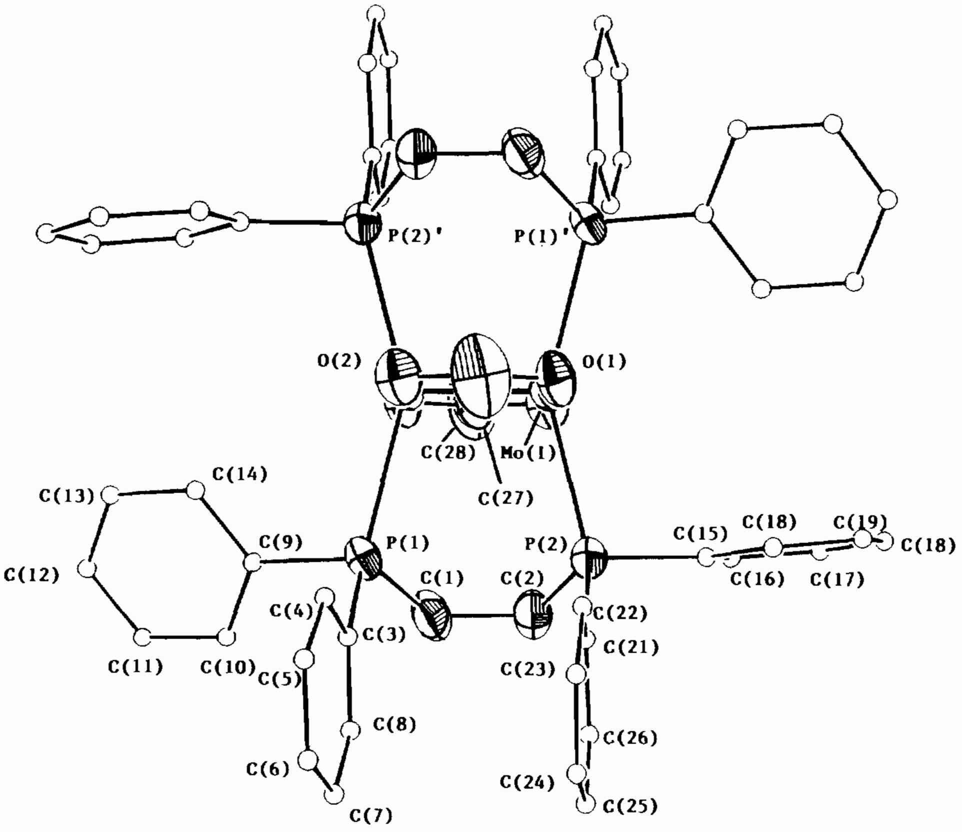


Fig. 3. ORTEP drawing of the $[Mo_2(O_2CCH_3)_2(dppe)_2]^{2+}$ cation in **3**.

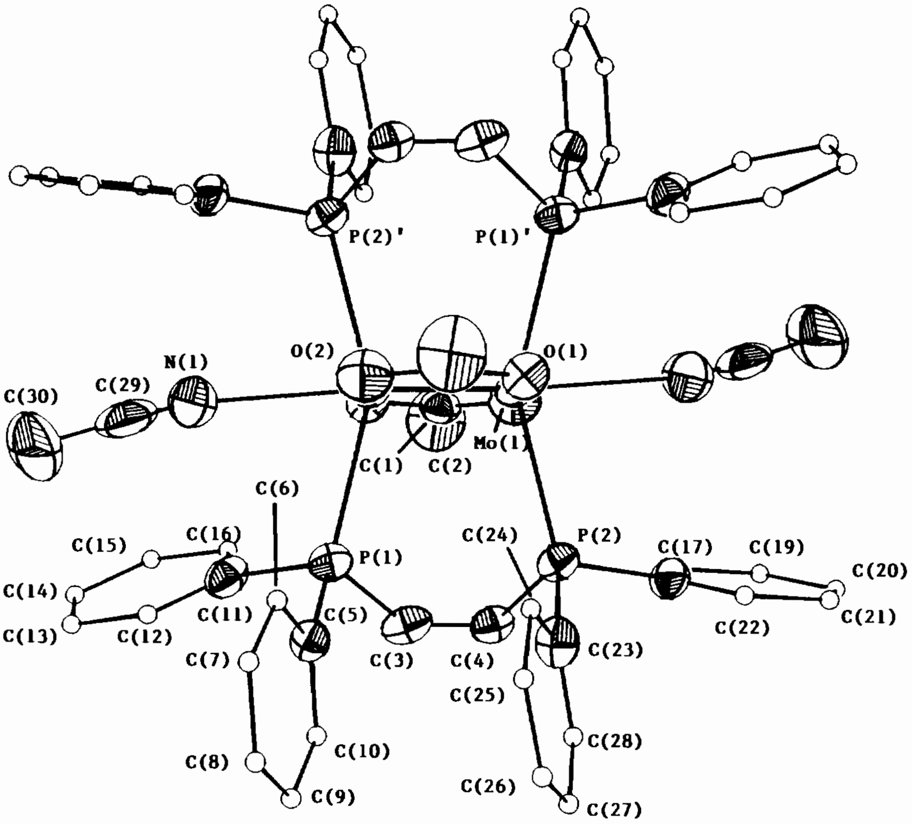


Fig. 4. ORTEP drawing of the $[Mo_2(O_2CCH_3)_2(dppee)_2]^{2+}$ cation in **5**.

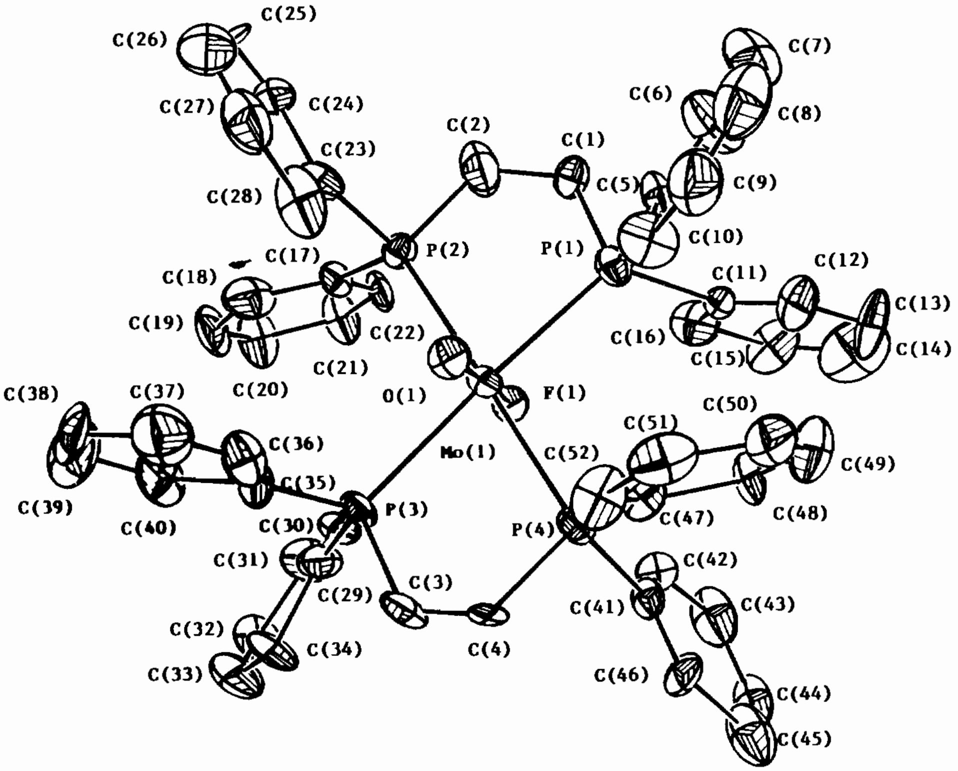


Fig. 5. ORTEP drawing of the $[Mo(O)(F)(dppee)_2]^{1+}$ cation in **6**.

provide full confirmation. For **4** and **6**, the IR shows the Mo=O stretch at 944 and 945 cm^{-1}, respectively, and the ^{19}F NMR spectrum for **6** shown in Fig. 1 is as expected. The fluorine atom couples with the four phosphorus atoms to give the quintet shown, and conversely the $^{31}P\{^1H\}$ NMR spectrum for **6** shows a doublet at 51.85 ppm. The coupling constants shown in Table 1 are consistent with this interpretation. In the ^{19}F NMR, there is also a peak for the BF_4^- counterion which is split slightly in accord with the relative abundances of ^{10}B versus ^{11}B. All of these observations agree well with previously reported [20] data for a compound formulated as **4**, except that we would describe the color as orange and not pink.

The dinuclear species **2**, **3** and **5** have similar $^{31}P\{^1H\}$ NMR and IR spectra. In the $^{31}P\{^1H\}$ NMR, resonances appear at 19.39 (>90% of the signal), 23.58 and 18.60 ppm for **2**, **3** and **5**, respectively. For **2**, there is another resonance present at 19.76 ppm which may be due to a species with an axial acetic acid, as will be discussed more thoroughly under 'Structural results'. The IR spectra are all very similar. Bridging acetate stretches are present at 1569–1590 cm^{-1}; the bridging acetate deformations (generally [21] around 675 cm^{-1}) are in the same region (650–780 cm^{-1}) as those for the bisphosphine ligand vibrations. In several samples of **2**, a weak band at 1649 cm^{-1} indicated the presence of a small impurity containing a unidentate acetate [21]. The ^1H NMR chemical shifts of **3** were assigned on the basis of comparison to $[Mo_2(O_2CCH_3)_2(NCCH_3)_6][BF_4]_2$ [3, 4] and $[Mo_2(O_2CCH_3)_2(dmpe)_2][BF_4]_2$ [8]; the peaks at 1.95 and 7.8–6.8 ppm are assigned to the free acetonitrile and phenyl group resonances, respectively. The apparent equivalence of the protons on the $P(-(CH_2)_2-P$ backbone indicates that the dppe ligands is fluxional in solution at 23 °C, perhaps by interconverting between the boat and twisted boat conformations, which would result in the observed proton equivalence.

Structural results

2, 3 and 5

These three compounds have similar structures, as shown in Figs. 2–4. Compounds **2** and **5** both have axial acetonitrile ligands, whereas **3** has only a weak axial contact with the hydrogen atom of C(14) at a distance of 2.939(3) Å. These structures are analogous to that reported for $[Mo_2(O_2CCH_3)_2(dmpe)_2][BF_4]_2$ [8]. For **3**, it appears that a small acetic acid impurity (<10%) may be present in the crystal, as the IR spectrum shows a band at 1649 cm^{-1} which is indicative of a unidentate HO_2CCH_3 ligand [21]. An attempt was made to model this by the inclusion of 10% of acetic acid in the structural refinement, but this was unsuccessful. We simply note here that the angle for N(2)–C(7)–C(8) is 161(1)°. There are several features that require further comment.

For **3** and **5**, the [Mo–Mo–P–C–C–P–] rings have adopted a boat conformation with the phosphines in the 3, 6 positions. Two phenyl rings are in the equatorial and two are in the axial positions and oriented face to face, an orientation that has precedents, for example in the structure of $Mo_2I_4(dppe)_2$ [22]. Since the bridging acetate ligands force the P–Mo–Mo–P to be nearly planar and make the ring rigid, two different ^1H NMR resonances were expected for the protons of the ethylene backbone in **3**. However, there is only one resonance which indicates that the protons exchange on the NMR time scale at 23 °C. Since the P–Mo–Mo–P chain must be nearly planar at all times, the exchange must occur by a boat–twist–boat conversion. Examination of a model shows that this is not unreasonable.

[Mo(O)(F)(dppee)$_2$][BF$_4$] (6)

This structure does not warrant a detailed discussion because the disorder in the O–Mo–F units causes some disorder in the dppee ligands which cannot be resolved. This is evident in the thermal parameters, which are generally 2–3 times larger in this complex than in compounds **2**, **3** and **5**. Suffice it to say that the reported distances make sense and are in much better agreement with literature values [18] than are some distances in other reported X–Mo–O disordered structures. The ORTEP drawing of the cation is shown in Fig. 5.

Supplementary material

Tables of structure factors, anisotropic thermal ellipsoids and complete bond lengths and angles for all four compounds are available from author F.A.C.

Acknowledgement

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