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# Crystal Structure of $[Mo(diphos)_2(O)(OH)][BF_4]$

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The species $[Mo(diphos)_2(O)(OH)^+][BF_4^-]$, obtained as the unexpected product of the reaction of $H_4Mo(diphos)_2$ and $[Ph_3C^+][BF_4^-]$, has been studied by the technique of single-crystal x-ray structural analysis. The species crystallizes in the noncentrosymmetric monoclinic space group *Cc* ($C_s^4$, No. 9) with $a = 9.973$ (3) Å, $b = 22.589$ (8) Å, $c = 21.256$ (6) Å, $\beta = 92.85$ (2)°, $V = 4783$ (4) Å$^3$, and $Z = 4$. Observed and calculated densities are 1.404 (5) and 1.406 g cm$^{-3}$ for mol wt 1012.61. Diffraction data were collected on a Picker FACS-1 four-circle automated diffractometer, and the structure was determined using a combination of Patterson, Fourier, and least-squares refinement techniques. All nonhydrogen atoms were located accurately. Using anisotropic thermal parameters for the heavier (>C) atoms and isotropic thermal parameters for carbon and boron atoms, with phenyl hydrogen atoms in calculated positions, refinement converged with $R_F = 5.83\%$ and $R_{wF} = 6.09\%$ for all 4247 independent reflections with $2\theta < 50°$ (Mo K$\alpha$ radiation). The central molybdenum(IV) ion is octahedrally surrounded by two diphos ligands (which occupy the four equatorial positions), an oxide ion (Mo═O = 1.833 (5) Å), and a hydroxide ion (Mo—OH = 1.952 (5) Å). The absolute configurations of the two diphos ligands are opposite to one another; the cation is thus the $\delta\lambda$-$Mo(diphos)_2(O)(OH)^+$ isomer.

## Introduction

The material under study was isolated by Osborn and his co-workers[1] from the reaction of $H_4Mo(diphos)_2$ and $[Ph_3C^+][BF_4^-]$ in solution at 70 °C. NMR studies showed no remaining hydride resonances ($^1H$) and indicated two environments for phosphorus atoms ($^{31}P$). Elemental analysis was in reasonable agreement with the approximate composition $[Mo(diphos)_2][BF_4]$. A single-crystal x-ray structural analysis was undertaken to ascertain the precise nature of this product, since it was thought to be an unusual coordinatively unsaturated species. However, as shown below, the material is found to be $[Mo(diphos)_2(O)(OH)^+][BF_4^-]$, formed (possibly) by reaction of $HMo(diphos)_2^+$ with adventitious $O_2$.

## Experimental Section

Violet crystals were provided by Professor J. A. Osborn. The crystal chosen for the x-ray diffraction study was an irregular plate of thickness 0.185 mm between {010} faces; distances of faces from the origin defined by the point of intersection of $(01\bar{1})$, $(0\bar{1}\bar{1})$, and $(\bar{3}12)$ were 0.088 mm for $(0\bar{1}0)$, 0.097 mm for (010), 0.671 mm for (100), 0.450 mm for $(1\bar{1}5)$, and 0.334 mm for $(0\bar{1}7)$. This crystal was bound to the inside wall of a 0.5-mm diameter Lindemann glass capillary using Dow-Corning high-vacuum silicone grease; the capillary was flushed with $N_2$, flame-sealed, fixed in a brass pin using beeswax, and set in a eucentric goniometer head.

Preliminary precession (*hk*0, *hk*1, *h*0*l*, *h*1*l* levels) and cone-axis photographs (about the *b* and *c* axes) provided approximate unit-cell dimensions and indicated $C_{2h}$ (2/*m*) Laue symmetry. The systematic absences *hkl* for $h + k = 2n + 1$ and *h*0*l* for $l = 2n + 1$ are consistent with the centrosymmetric monoclinic space group *C*2/*c* ($C_{2h}^6$, No. 15) or with the noncentrosymmetric monoclinic space group *Cc* ($C_s^4$, No. 9). The latter was confirmed from the successful solution and refinement of the crystal structure.

The crystal was transferred to, and accurately centered on, a Picker FACS-1 automated four-circle diffractometer, and data to $2\theta = 50°$ (Mo K$\alpha$ radiation) were collected. The general procedure has been described previously;[2] details for this structure are given in Table I.

Following completion of data collection, the $a^*$ axis was reset to be coincident with the instrumental $\phi$ axis, and the effects of absorption were investigated by measuring ($\theta$–$2\theta$ scans) the intensity of the 600 reflection at $\chi = 90°$ and at 10° intervals of $\phi$ from 0 to 350°. The observed variation (defined as $100(I_{max} - I_{min})/I_{av}$) was 15.5%, indicating that an absorption correction was desirable. All data were then corrected for absorption.

**Table I.** Experimental Data for the X-Ray Diffraction Study of $[Mo(diphos)_2(O)(OH)]$ $[BF_4]$

(A) Crystal Parameters at 22.0 ± 2 °C[a]

| | |
|---|---|
| $a = 9.973$ (3) Å | Space group *Cc* ($C_s^4$, No. 9) |
| $b = 22.589$ (8) Å | $Z = 4$ |
| $c = 21.256$ (6) Å | Mol wt 1012.61 |
| $\cos\beta = -0.0498$ (4) | $\rho$(calcd) = 1.406 g cm$^{-3}$ |
| $\beta = 92.85$ (2)° | $\rho$(obsd)[b] = 1.404 (5) g cm$^{-3}$ |
| $V = 4783$ (4) Å$^3$ | |

(B) Measurement of Intensity Data

Radiation: Mo K$\alpha$
Filter(s): Nb foil at counter aperture (~47% transmission of Mo K$\alpha$)
Attenuators: Cu foil; used if *I*(peak) > $10^4$ counts/s
Takeoff angle: 3.0°
Detector aperture: 6.3 mm × 6.3 mm
Crystal-detector dist: 330 mm
Crystal orientation: $\phi$ axis is offset from [100] by 0.05°
Reflections measd: $h, k, \pm l$, except $0kl$ for $l \geqslant 0$ only
Max $2\theta$: 50°
Scan type: coupled $\theta$(crystal)–$2\theta$(counter)
Scan speed: 1.0°/min
Scan length: $\Delta(2\theta) = (1.0 + 0.692 \tan\theta)°$, starting 0.5° below the Mo K$\alpha_1$ peak
Bckgd measurement: stationary-crystal, stationary-counter; 20 s each at beginning and end of $2\theta$ scan
Standard reflections: 3 remeasured after every 47 reflections; root-mean-square deviations[c] were 0.81% for $20\bar{6}$, 0.35% for 080, 0.83% for 402
Reflections collected: 4670 measurements including 307 duplicate or equivalent measurements (averaged into primary data set) and 116 systematic absences

(C) Treatment of Intensity Data

Conversion to $|F_o|$ and $\sigma(|F_o|)$: as in ref 2, using an "ignorance factor" of $p = 0.025$
Absorption coeff: $\mu = 4.516$ cm$^{-1}$; maximum and minimum transmission factors[d] were 0.9098, 0.8428, respectively

[a] Unit-cell parameters are from a least-squares fit to the setting angles of the resolved Mo K$\alpha_1$ peaks ($\lambda$ 0.709 300 Å) of 12 reflections with $2\theta = 39$–$50°$. [b] The density was measured by neutral buoyancy in hexane/$CCl_4$. [c] Data reduction and analysis, including decay correction, were performed using the Fortran IV program RDUS2, by B. G. DeBoer. [d] Absorption corrections were applied using the program DRABZ, by B. G. DeBoer.

## Determination and Refinement of the Crystal Structure

All calculations were performed on an IBM 370/158 computer at the University of Illinois at Chicago Circle. Programs used were FORDAP (Fourier synthesis, by A. Zalkin), LSHF (structure factor calculations and full-matrix least-squares refinement, by B. G. DeBoer), STAN1 (distances, angles, and their esd's, by B. G. DeBoer), PLOD (least-squares planes and lines, by B. G. DeBoer), and ORTEP (thermal ellipsoid plotting program, by C. K. Johnson).

Scattering factors for all nonhydrogen atoms (zero valence state) were taken from the compilation of Cromer and Waber;[3] Stewart's "best-floated spherical H atom" values[4] were used for hydrogen. The real and imaginary anomalous dispersion terms ($\Delta f'$ and $i\Delta f''$) were

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included for all nonhydrogen atoms, using the values of Cromer and Liberman.[5]

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = (\sigma(|F_o|))^{-2}$. Discrepancy indices used below are defined in eq 1 and 2. The "goodness-of-fit" (GOF) is

$$R_F = \left[\frac{\Sigma ||F_o| - |F_c||}{\Sigma |F_o|}\right] \times 100\ (\%) \qquad (1)$$

$$R_{wF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w |F_o|^2}\right]^{1/2} \times 100\ (\%) \qquad (2)$$

$$\mathrm{GOF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\mathrm{NO} - \mathrm{NV}}\right]^{1/2} \qquad (3)$$

defined in eq 3; here NO is the number of observations and NV is the number of variable parameters.

A three-dimensional Patterson map yielded the positions of atoms in the $MoP_4$ core of the molecule; the noncentrosymmetric space group *Cc* was also clearly indicated. The *x* and *z* coordinates of the molybdenum atom were set at $x = {}^1/_2$ and $z = {}^1/_4$ and were not thereafter varied. A series of structure factor calculations and Fourier syntheses led to the location of the 62 nonhydrogen atoms in the $Mo(diphos)_2$ moiety and the $BF_4^-$ anion. Two cycles of full-matrix least-squares refinement of positional and isotropic thermal parameters yielded discrepancy indices of $R_F = 17.4\%$ and $R_{wF} = 19.8\%$. A difference-Fourier synthesis now revealed two large peaks (of height 7.08 and 6.42 e $Å^{-3}$) lying above and below the $MoP_4$ plane at distances of ~2 Å from the metal atom; no other notable features (i.e., solvent molecules, hydrogen atoms, etc.) were discernible from this map. These two "axial features" were input into the structure factor calculation as fluorine atoms. (This was done without prejudice and for convenience only, since the scattering factors for fluorine were already in our computer program deck.) Four cycles of full-matrix least-squares refinement of the scale factor, positional parameters for all 64 nonhydrogen atoms, anisotropic thermal parameters for Mo, P, and F atoms, and isotropic thermal parameters for carbon atoms converged with $R_F = 6.39\%$ and $R_{wF} = 6.80\%$.

At this juncture we carefully considered the nature of the two axial ligands and concluded, on the basis of the evidence listed below, that one ligand (identified hereafter as O(A)) was an oxide ion involved in a Mo═O system and that the other ligand (O(B)) was a hydroxide ligand. Our conclusion was based upon the following considerations.

(i) The peak heights of these atoms, taken in conjunction with their behavior under refinement and their chemical environment, are consistent with their being fluoride ions or oxygen-bonded ligands (═O, –OH, or (most unlikely) $-OH_2$).

(ii) Elemental analysis indicates only four fluorine atoms per formula unit. These are believed to be in the $BF_4^-$ anion. (There is a remote possibility that this could be a $BF_3OH^-$ ion. It is unlikely that we would be able to distinguish crystallographically between $BF_4^-$ and $BF_3OH^-$ ions, particularly if the former were disordered. The equilibrium constant for the reaction $BF_4^- + H_2O \rightleftharpoons BF_3OH^- + HF$ is $2.3 \times 10^{-3}$; however, this pertains to *aqueous solutions* and is valid only at low pH values.)

(iii) $^{31}P$ and $^{19}F$ NMR spectra gave no indications of fluoride ions attached to the molybdenum atom—i.e., *no* $^{31}P-^{19}F$ coupling was detected.

(iv) NMR spectra are sharp, so the complex is diamagnetic. It is most likely to be a Mo(IV) species, although Mo(II) must also be considered.

(v) The axial ligands are nonequivalent, with Mo–O(A) = 1.83 Å, Mo–O(B) = 1.95 Å, and O(A)–Mo–O(B) = 178°. This difference is easily explained if we have Mo═O and Mo—OH linkages. (This also produces a Mo(IV) species, which is otherwise only obtained by having Mo═O and Mo—F linkages.)

(vi) Incorporation of O(A) and O(B) into the structure as oxygen atoms and refinement to convergence provide the ex post facto result that these atoms behave sensibly, yielding equivalent isotropic thermal parameters of 3.27 and 2.75 $Å^2$ (respectively) as opposed to 3.46 $Å^2$ for molybdenum and 3.11–3.49 $Å^2$ for phosphorus atoms.

These two axial ligands were thus entered into the structure factor calculations as oxygen atoms. All hydrogen atoms of the diphos ligands were also included in idealized positions with $d$(C–H) = 0.95 Å[6] and the appropriate $sp^2$ or $sp^3$ geometry about carbon. The isotropic thermal parameters for the hydrogen atoms were set as $B(H_i) = B(C_i) + 1.0\ Å^2$. In subsequent refinement, all hydrogen atom parameters were coupled to those of their attached carbon atoms—i.e., each CH or $CH_2$ unit was treated as a rigid, nonrotating, group.

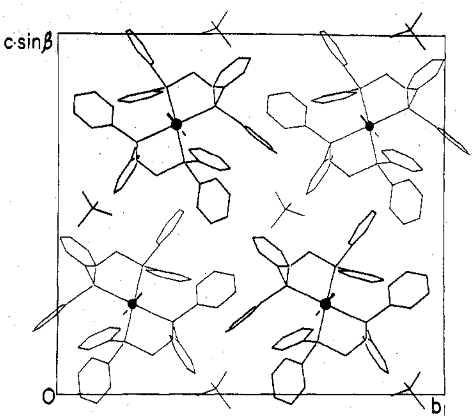

**Figure 1.** Packing of $Mo(diphos)_2(O)(OH)^+$ cations $BF_4^-$ anions within the unit cell, as viewed down *a*.

Three cycles of full-matrix least-squares refinement of the scale factor, positional parameters for all nonhydrogen atoms, anisotropic thermal parameters for Mo, P, F, and O atoms, and isotropic thermal parameters for carbon atoms led to convergence with $R_F = 5.89\%$, $R_{wF} = 6.15\%$, and GOF = 2.51.

The chirality of the noncentrosymmetric crystal was now tested by inverting the structure and refining to convergence $[(\Delta/\sigma)_{max} < 0.1]$ once again. The resulting discrepancy indices ($R_F = 5.83\%$, $R_{wF} = 6.09\%$, and GOF = 2.43) show that the inverted structure defines the correct enantiomorph.

The number of independent observations was 4247 and the number of variables was 310, giving a data-to-parameter ratio of 13.70:1.0. The function $\sum w(|F_o| - |F_c|)^2$ was essentially independent of $|F_o|$ or $(\sin\theta)/\lambda$; the weighting scheme is thus reasonable. There was no evidence for secondary extinction.

A final difference-Fourier synthesis had as its three highest features (1) a peak of 0.49 e $Å^{-3}$ at 0.300, 0.165, 0.225 (close to Mo), (2) a peak of 0.35 e $Å^{-3}$ at 0.690, 0.210, 0.270 (close to O(A)), and (3) a peak of 0.26 e $Å^{-3}$ at 0.510, 0.195, 0.255 (close to Mo); all other features were below 0.25 e $Å^{-3}$ in height.

No evidence for the hydrogen atom attached to O(B) was found from this map nor from any of a series of difference-Fourier maps synthesized using increasingly severe cutoffs of data as a function of $(\sin\theta)/\lambda$, down to $(\sin\theta)/\lambda < 0.30$.

Final positional and isotropic thermal parameters are collected in Table II; anisotropic thermal parameters for the heavier atoms are given in Table III. A table of observed and calculated structure factor amplitudes is available as supplementary material.

## Results and Discussion

Intramolecular distances and angles are collected, with their esd's, in Tables IV and V.

The crystal consists of discrete $Mo(diphos)_2(O)(OH)^+$ and $BF_4^-$ ions, which are separated by normal van der Waals distances. Figure 1 shows the crystal structure viewed down *a*. The schemes used for labeling atoms within the $Mo(diphos)_2(O)(OH)^+$ cation and the $BF_4^-$ anion are illustrated in Figures 2 and 3.

The cation is a Mo(IV) derivative, in which the molybdenum atom is in octahedral coordination to two chelating diphos ($Ph_2P(CH_2)_2PPh_2$) ligands, an oxide ion (O(A)), and a hydroxide ion (the oxygen atom of which is labeled O(B)). The coordination environment about the molybdenum atom is illustrated in Figure 4.

The Mo═O distance (Mo–O(A) = 1.833 (5) Å) is 0.119 (7) Å shorter than the Mo—OH distance (Mo–O(B) = 1.952 (5) Å) and the O═Mo—OH angle is 178.09 (26)°. To our knowledge, the only other species with a trans O═Mo—OH system that has been subjected to crystallographic examination is $Mo(O)(OH)(CN)_4^{3-}$. In this anionic species, the reported[7]

**Table II.** Final Positional Parameters and Their Esd's[a] for $[Mo(diphos)_2(O)(OH)][BF_4]$

| Atom | $x$ | $y$ | $z$ | $B_{iso}$, Å$^2$ | Atom | $x$ | $y$ | $z$ | $B_{iso}$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| (A) Atoms of the $Mo(diphos)_2(O)(OH)^+$ Ion | | | | | | | | | |
| Mo | 0.5 | 0.194974 (28) | 0.25 | 3.458[b] | C(25)B | 0.9969 (11) | 0.1350 (5) | 0.1836 (5) | 6.53 (23) |
| P(1) | 0.48712 (20) | 0.29645 (8) | 0.19970 (9) | 3.19 | C(26)B | 0.8715 (9) | 0.1625 (4) | 0.1802 (4) | 5.45 (20) |
| P(2) | 0.59986 (21) | 0.17341 (9) | 0.14410 (9) | 3.11 | C(3) | 0.3726 (9) | 0.1508 (4) | 0.3950 (4) | 4.56 (17) |
| P(3) | 0.39798 (22) | 0.21982 (10) | 0.35450 (10) | 3.49 | C(31)A | 0.4912 (8) | 0.2615 (4) | 0.4150 (4) | 4.25 (16) |
| P(4) | 0.49773 (21) | 0.09324 (9) | 0.30158 (9) | 3.22 | C(32)A | 0.6258 (9) | 0.2535 (4) | 0.4222 (5) | 5.00 (18) |
| O(A) | 0.6707 (5) | 0.2152 (2) | 0.2779 (2) | 3.27 | C(33)A | 0.6998 (11) | 0.2813 (5) | 0.4727 (5) | 6.48 (23) |
| O(B) | 0.3200 (4) | 0.1706 (2) | 0.2204 (2) | 2.75 | C(34)A | 0.6340 (13) | 0.3146 (5) | 0.5117 (6) | 7.64 (28) |
| C(1) | 0.6357 (8) | 0.2976 (3) | 0.1511 (4) | 3.68 (14) | C(35)A | 0.5040 (14) | 0.3258 (6) | 0.5075 (6) | 8.29 (30) |
| C(11)A | 0.3411 (8) | 0.3117 (4) | 0.1482 (4) | 3.81 (15) | C(36)A | 0.4247 (11) | 0.2985 (4) | 0.4571 (5) | 5.95 (21) |
| C(12)A | 0.2174 (9) | 0.2900 (4) | 0.1618 (4) | 4.53 (17) | C(31)B | 0.2365 (8) | 0.2566 (4) | 0.3439 (4) | 4.35 (16) |
| C(13)A | 0.1023 (10) | 0.3027 (4) | 0.1245 (4) | 5.38 (19) | C(32)B | 0.1146 (12) | 0.2268 (6) | 0.3429 (6) | 7.47 (27) |
| C(14)A | 0.1124 (10) | 0.3358 (4) | 0.0724 (4) | 5.26 (18) | C(33)B | −0.0058 (16) | 0.2591 (8) | 0.3278 (7) | 10.27 (41) |
| C(15)A | 0.2340 (10) | 0.3573 (4) | 0.0559 (5) | 5.95 (21) | C(34)B | 0.0022 (16) | 0.3157 (7) | 0.3112 (7) | 9.39 (37) |
| C(16)A | 0.3488 (10) | 0.3459 (4) | 0.0937 (4) | 5.18 (18) | C(35)B | 0.1140 (12) | 0.3474 (6) | 0.3175 (5) | 7.52 (27) |
| C(11)B | 0.5124 (9) | 0.3614 (3) | 0.2493 (4) | 3.43 (12) | C(36)B | 0.2343 (11) | 0.3166 (4) | 0.3307 (5) | 6.10 (22) |
| C(12)B | 0.6039 (8) | 0.3575 (4) | 0.2996 (4) | 4.48 (16) | C(4) | 0.3537 (8) | 0.0976 (4) | 0.3517 (4) | 4.58 (17) |
| C(13)B | 0.6276 (10) | 0.4039 (4) | 0.3411 (5) | 5.42 (19) | C(41)A | 0.6368 (7) | 0.0706 (3) | 0.3544 (4) | 3.61 (14) |
| C(14)B | 0.5562 (9) | 0.4564 (4) | 0.3309 (4) | 5.25 (19) | C(42)A | 0.6229 (11) | 0.0227 (5) | 0.3940 (5) | 6.44 (23) |
| C(15)B | 0.4664 (10) | 0.4601 (5) | 0.2825 (4) | 5.70 (20) | C(43)A | 0.7276 (11) | 0.0047 (5) | 0.4344 (5) | 7.00 (24) |
| C(16)B | 0.4426 (9) | 0.4140 (4) | 0.2401 (4) | 4.68 (17) | C(44)A | 0.8460 (10) | 0.0329 (4) | 0.4343 (4) | 5.34 (19) |
| C(2) | 0.6353 (8) | 0.2458 (4) | 0.1062 (4) | 4.15 (16) | C(45)A | 0.8640 (10) | 0.0787 (4) | 0.3956 (4) | 5.49 (19) |
| C(21)A | 0.5061 (8) | 0.1329 (4) | 0.0832 (4) | 3.79 (15) | C(46)A | 0.7571 (9) | 0.0984 (4) | 0.3549 (4) | 4.77 (17) |
| C(22)A | 0.4117 (8) | 0.0908 (4) | 0.0997 (4) | 4.43 (16) | C(41)B | 0.4651 (7) | 0.0274 (3) | 0.2530 (4) | 3.56 (14) |
| C(23)A | 0.3470 (9) | 0.0557 (4) | 0.0540 (4) | 5.06 (18) | C(42)B | 0.3361 (8) | 0.0066 (4) | 0.2411 (4) | 4.23 (15) |
| C(24)A | 0.3752 (9) | 0.0622 (4) | −0.0076 (5) | 5.28 (19) | C(43)B | 0.3129 (9) | −0.0407 (4) | 0.1993 (4) | 4.90 (18) |
| C(25)A | 0.4631 (10) | 0.1045 (4) | −0.0248 (5) | 5.67 (20) | C(44)B | 0.4195 (10) | −0.0661 (4) | 0.1705 (4) | 5.32 (19) |
| C(26)A | 0.5320 (9) | 0.1397 (4) | 0.0196 (4) | 4.72 (17) | C(45)B | 0.5482 (9) | −0.0452 (4) | 0.1840 (4) | 5.18 (18) |
| C(21)B | 0.7614 (8) | 0.1364 (4) | 0.1480 (4) | 4.07 (16) | C(46)B | 0.5711 (8) | 0.0020 (4) | 0.2252 (4) | 4.35 (16) |
| C(22)B | 0.7800 (9) | 0.0814 (4) | 0.1220 (4) | 5.11 (18) | | | | | |
| C(23)B | 0.9072 (10) | 0.0537 (5) | 0.1264 (5) | 6.43 (23) | | | | | |
| C(24)B | 1.0079 (11) | 0.0819 (5) | 0.1566 (5) | 6.83 (24) | | | | | |
| (B) Atoms in $BF_4^-$ Ion | | | | | | | | | |
| B | 0.6732 (11) | 0.4098 (5) | 0.0153 (5) | 4.85 (21) | F(3) | 0.7983 (7) | 0.3963 (4) | 0.0332 (3) | 9.81 |
| F(1) | 0.6744 (6) | 0.4468 (3) | −0.0370 (3) | 7.64 | F(4) | 0.6082 (6) | 0.4380 (3) | 0.0627 (2) | 6.83 |
| F(2) | 0.6015 (7) | 0.3600 (3) | −0.0036 (3) | 7.61 | | | | | |
| (C) Calculated Positions for Hydrogen Atoms | | | | | | | | | |
| H(1)A | 0.6357 | 0.3341 | 0.1279 | 4.68 | H(32)A | 0.6684 | 0.2289 | 0.3928 | 6.00 |
| H(1)B | 0.7138 | 0.2953 | 0.1775 | 4.68 | H(33)A | 0.7939 | 0.2757 | 0.4786 | 7.48 |
| H(12)A | 0.2116 | 0.2664 | 0.1986 | 5.53 | H(34)A | 0.6846 | 0.3329 | 0.5454 | 8.64 |
| H(13)A | 0.0169 | 0.2879 | 0.1347 | 6.38 | H(35)A | 0.4642 | 0.3510 | 0.5371 | 9.29 |
| H(14)A | 0.0342 | 0.3445 | 0.0467 | 6.26 | H(36)A | 0.3306 | 0.3048 | 0.4515 | 6.95 |
| H(15)A | 0.2394 | 0.3801 | 0.0185 | 6.95 | H(32)B | 0.1151 | 0.1858 | 0.3527 | 8.47 |
| H(16)A | 0.4338 | 0.3609 | 0.0832 | 6.18 | H(33)B | −0.0902 | 0.2396 | 0.3277 | 11.27 |
| H(12)B | 0.6524 | 0.3216 | 0.3060 | 5.48 | H(34)B | −0.0809 | 0.3341 | 0.2995 | 10.39 |
| H(13)B | 0.6914 | 0.4000 | 0.3756 | 6.42 | H(35)B | 0.1111 | 0.3886 | 0.3089 | 8.52 |
| H(14)B | 0.5702 | 0.4890 | 0.3587 | 6.25 | H(36)B | 0.3172 | 0.3373 | 0.3311 | 7.10 |
| H(15)B | 0.4187 | 0.4962 | 0.2757 | 6.70 | H(4)A | 0.2741 | 0.1036 | 0.3263 | 5.58 |
| H(16)B | 0.3785 | 0.4174 | 0.2057 | 5.68 | H(4)B | 0.3460 | 0.0619 | 0.3752 | 5.58 |
| H(2)A | 0.5689 | 0.2528 | 0.0739 | 5.15 | H(42)A | 0.5399 | 0.0020 | 0.3935 | 7.44 |
| H(2)B | 0.7213 | 0.2432 | 0.0884 | 5.15 | H(43)A | 0.7172 | −0.0276 | 0.4624 | 8.00 |
| H(22)A | 0.3932 | 0.0866 | 0.1429 | 5.43 | H(44)A | 0.9180 | 0.0199 | 0.4618 | 6.34 |
| H(23)A | 0.2841 | 0.0266 | 0.0656 | 6.06 | H(45)A | 0.9488 | 0.0980 | 0.3964 | 6.49 |
| H(24)A | 0.3308 | 0.0383 | −0.0391 | 6.28 | H(46)A | 0.7675 | 0.1311 | 0.3275 | 5.77 |
| H(25)A | 0.4792 | 0.1091 | −0.0682 | 6.67 | H(42)B | 0.2626 | 0.0244 | 0.2607 | 5.23 |
| H(26)A | 0.5958 | 0.1683 | 0.0077 | 5.72 | H(43)B | 0.2245 | −0.0554 | 0.1908 | 5.90 |
| H(22)B | 0.7050 | 0.0627 | 0.1010 | 6.11 | H(44)B | 0.4033 | −0.0984 | 0.1424 | 6.32 |
| H(23)B | 0.9215 | 0.0161 | 0.1080 | 7.43 | H(45)B | 0.6221 | −0.0627 | 0.1644 | 6.18 |
| H(24)B | 1.0936 | 0.0635 | 0.1598 | 7.83 | H(46)B | 0.6596 | 0.0166 | 0.2337 | 5.35 |
| H(25)B | 1.0723 | 0.1531 | 0.2048 | 7.53 | | | | | |
| H(26)B | 0.8586 | 0.2003 | 0.1986 | 6.45 | | | | | |
| H(3)A | 0.2971 | 0.1547 | 0.4204 | 5.56 | | | | | |
| H(3)B | 0.4504 | 0.1430 | 0.4211 | 5.56 | | | | | |

[a] Esd's, shown in parentheses, are right adjusted to the last digit of the preceding number. [b] "Equivalent isotropic" thermal parameters are given for the heavier atoms. These correspond to the average mean-square displacement along the three principal axes of the anisotropic thermal vibration ellipsoid. For the full anisotropic thermal parameters, see Table III.

Mo═O and Mo—OH distances are 1.698 (7) and 2.077 (7) Å, respectively. However, this structure suffers from a disordered molybdenum atom and the quoted esd's are probably severely underestimated.

Robinson, Schlemper, and Murmann[7] have compiled a table which includes known Mo═O and Mo—OH bond lengths. Reported Mo═O bond lengths range from 1.668 (5) Å in $Mo(O)(H_2O)(CN)_4^{2-}$ to 1.834 (9) Å in $Mo(O)_2(CN)_4^{4-}$ and Mo—OH distances range from 1.96 (1) Å in $Mo_4O_{10}(OH)_2$ to 2.181 (3) Å in $MoO_3 \cdot 2H_2O$.

Differences between Mo═O and Mo—OH distances determined in the present $Mo(diphos)_2(O)(OH)^+$ ion and in

**Table III.** Anisotropic Thermal Parameters[a] of the Heavier Atoms

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ | $\langle U\rangle$[b] | | |
|---|---|---|---|---|---|---|---|---|---|
| Mo | 4.885 (31) | 2.697 (22) | 2.877 (23) | 0.195 (25) | 1.039 (20) | 0.149 (22) | 0.178 | 0.185 | 0.256 |
| P(1) | 3.55 (9) | 3.75 (8) | 3.30 (8) | −0.24 (7) | 0.45 (7) | 0.14 (6) | 0.18 | 0.20 | 0.22 |
| P(2) | 3.47 (9) | 3.13 (9) | 2.79 (8) | 0.14 (7) | 0.58 (6) | 0.10 (7) | 0.18 | 0.20 | 0.22 |
| P(3) | 4.03 (10) | 3.54 (10) | 2.95 (8) | −0.48 (8) | 0.74 (7) | −0.43 (7) | 0.18 | 0.20 | 0.24 |
| P(4) | 3.71 (9) | 3.00 (9) | 2.97 (8) | −0.39 (7) | 0.23 (6) | 0.33 (7) | 0.18 | 0.20 | 0.22 |
| O(A) | 2.84 (21) | 3.18 (22) | 3.81 (23) | −0.46 (18) | 0.43 (17) | 0.11 (18) | 0.18 | 0.21 | 0.22 |
| O(B) | 2.96 (20) | 2.48 (20) | 2.86 (20) | 0.41 (16) | 0.57 (16) | 0.33 (16) | 0.17 | 0.18 | 0.21 |
| F(1) | 8.48 (36) | 8.01 (36) | 6.56 (32) | −0.72 (29) | 1.70 (27) | 1.68 (27) | 0.24 | 0.34 | 0.34 |
| F(2) | 9.39 (39) | 6.77 (32) | 6.72 (31) | −2.11 (28) | 0.92 (27) | −1.14 (26) | 0.26 | 0.29 | 0.37 |
| F(3) | 6.39 (32) | 15.76 (66) | 7.01 (34) | 3.67 (38) | −2.38 (26) | −3.69 (39) | 0.23 | 0.29 | 0.49 |
| F(4) | 7.77 (33) | 7.43 (32) | 5.50 (26) | −0.91 (26) | 2.42 (24) | −1.95 (24) | 0.22 | 0.29 | 0.36 |

[a] These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameter and have units of Å². They enter the expression for the structure factor in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] These values correspond to the root-mean-square amplitudes of vibration (in Å) of the atom along the three principal axes (minor, median, major, respectively) of its vibration ellipsoid. For relative orientations, see figures.

**Table IV.** Interatomic Distances (Å) and Their Esd's

| | | | |
|---|---|---|---|
| (A) Molybdenum–Phosphorus Distances | | | |
| Mo–P(1) | 2.530 (2) | Mo–P(3) | 2.551 (2) |
| Mo–P(2) | 2.553 (2) | Mo–P(4) | 2.547 (2) |
| (B) Molybdenum–Oxygen Distances | | | |
| Mo–O(A) | 1.833 (5) | Mo–O(B) | 1.952 (5) |
| (C) Phosphorus–Bridging Carbon Distances | | | |
| P(1)–C(1) | 1.849 (8) | P(3)–C(3) | 1.805 (9) |
| P(2)–C(2) | 1.865 (8) | P(4)–C(4) | 1.833 (8) |
| (D) Phosphorus–Phenyl Carbon Distances | | | |
| P(1)–C(11)A | 1.811 (8) | P(1)–C(11)B | 1.818 (8) |
| P(2)–C(21)A | 1.808 (8) | P(2)–C(21)B | 1.812 (8) |
| P(3)–C(31)A | 1.813 (8) | P(3)–C(31)B | 1.816 (9) |
| P(4)–C(41)A | 1.815 (8) | P(4)–C(41)B | 1.831 (8) |
| (E) Bridging Carbon–Bridging Carbon Distances | | | |
| C(1)–C(2) | 1.509 (10) | C(3)–C(4) | 1.519 (12) |
| (F) Phenyl Carbon–Phenyl Carbon Distances | | | |
| C(11)A–C(12)A | 1.372 (11) | C(11)B–C(12)B | 1.372 (12) |
| C(12)A–C(13)A | 1.394 (12) | C(12)B–C(13)B | 1.384 (12) |
| C(13)A–C(14)A | 1.343 (13) | C(13)B–C(14)B | 1.394 (13) |
| C(14)A–C(15)A | 1.369 (13) | C(14)B–C(15)B | 1.332 (12) |
| C(15)A–C(16)A | 1.390 (12) | C(15)B–C(16)B | 1.391 (13) |
| C(16)A–C(11)A | 1.397 (12) | C(16)B–C(11)B | 1.386 (11) |
| C(21)A–C(22)A | 1.396 (11) | C(21)B–C(22)B | 1.376 (12) |
| C(22)A–C(23)A | 1.387 (12) | C(22)B–C(23)B | 1.414 (13) |
| C(23)A–C(24)A | 1.362 (12) | C(23)B–C(24)B | 1.327 (13) |
| C(24)A–C(25)A | 1.359 (13) | C(24)B–C(25)B | 1.336 (15) |
| C(25)A–C(26)A | 1.391 (12) | C(25)B–C(26)B | 1.395 (13) |
| C(26)A–C(21)A | 1.396 (11) | C(26)B–C(21)B | 1.396 (12) |
| C(31)A–C(32)A | 1.356 (11) | C(31)B–C(32)B | 1.388 (14) |
| C(32)A–C(33)A | 1.419 (13) | C(32)B–C(33)B | 1.427 (17) |
| C(33)A–C(34)A | 1.318 (16) | C(33)B–C(34)B | 1.330 (19) |
| C(34)A–C(35)A | 1.320 (16) | C(34)B–C(35)B | 1.326 (16) |
| C(35)A–C(36)A | 1.439 (16) | C(35)B–C(36)B | 1.402 (15) |
| C(36)A–C(31)A | 1.413 (13) | C(36)B–C(31)B | 1.385 (13) |
| C(41)A–C(42)A | 1.382 (12) | C(41)B–C(42)B | 1.381 (10) |
| C(42)A–C(43)A | 1.380 (14) | C(42)B–C(43)B | 1.402 (11) |
| C(43)A–C(44)A | 1.342 (13) | C(43)B–C(44)B | 1.379 (12) |
| C(44)A–C(45)A | 1.340 (13) | C(44)B–C(45)B | 1.385 (13) |
| C(45)A–C(46)A | 1.410 (12) | C(45)B–C(46)B | 1.393 (12) |
| C(46)A–C(41)A | 1.353 (11) | C(46)B–C(41)B | 1.362 (11) |
| (G) Boron–Fluorine Distances | | | |
| B–F(1) | 1.391 (12) | B–F(3) | 1.321 (12) |
| B–F(2) | 1.382 (12) | B–F(4) | 1.380 (12) |

$Mo(O)(OH)(CN)_4^{3-}$[7] may be affected by one or more of the following factors: (1) a change (by 4 units) of the net charge on the ion; (2) the relative $\pi$ acidities of diphos and $CN^-$ ligands; (3) systematic errors in Mo═O and Mo—OH distances caused by disorder within the $Mo(O)(OH)(CN)_4^{3-}$ ion (see above); (4) the (remote) possibility of minor disorder between oxide and hydroxide ligands in our present $Mo(diphos)_2(O)(OH)^+$ cation. There is no clear evidence for this except that the thermal ellipsoid of the molybdenum atom defines (approximately) a prolate spheroid extended in a direction perpendicular to the $MoP_4$ plane. The extension is, however, slight; root-mean-square amplitudes of vibration of the molybdenum atom along its three principal axes are 0.178, 0.185, and 0.256 Å. The vibration ellipsoids of O(A) and O(B) are closer to spherical, root-mean-square amplitudes of vibration along the principal axes being 0.18, 0.21, and 0.22 Å for O(A) and 0.17, 0.18, and 0.21 Å for O(B).

The $MoP_4$ system is approximately planar, deviations of

**Table V.** Intramolecular Angles (deg) and Their Esd's

| | | | |
|---|---|---|---|
| (A) Oxygen-Molybdenum-Phosphorus and Oxygen-Molybdenum-Oxygen Angles | | | |
| O(A)-Mo-P(1) | 86.40 (16) | O(B)-Mo-P(1) | 95.32 (14) |
| O(A)-Mo-P(2) | 86.33 (16) | O(B)-Mo-P(2) | 93.17 (14) |
| O(A)-Mo-P(3) | 93.89 (16) | O(B)-Mo-P(3) | 86.68 (14) |
| O(A)-Mo-P(4) | 96.55 (16) | O(B)-Mo-P(4) | 81.76 (14) |
| O(A)-Mo-O(B) | 178.09 (26) | | |
| (B) Phosphorus-Molybdenum-Phosphorus Angles | | | |
| P(1)-Mo-P(2) | 79.29 (7) | P(3)-Mo-P(4) | 79.12 (7) |
| P(1)-Mo-P(3) | 98.89 (7) | P(2)-Mo-P(4) | 102.68 (7) |
| P(2)-Mo-P(3) | 178.15 (8) | P(1)-Mo-P(4) | 176.52 (7) |
| (C) Molybdenum-Phosphorus-Bridging Carbon Angles | | | |
| Mo-P(1)-C(1) | 103.0 (2) | Mo-P(3)-C(3) | 107.2 (3) |
| Mo-P(2)-C(2) | 107.7 (3) | Mo-P(4)-C(4) | 103.0 (3) |
| (D) Molybdenum-Phosphorus-Phenyl Carbon Angles | | | |
| Mo-P(1)-C(11)A | 116.8 (3) | Mo-P(1)-C(11)B | 118.9 (3) |
| Mo-P(2)-C(21)A | 121.2 (3) | Mo-P(2)-C(21)B | 115.6 (3) |
| Mo-P(3)-C(31)A | 121.3 (3) | Mo-P(3)-C(31)B | 112.5 (3) |
| Mo-P(4)-C(41)A | 119.9 (3) | Mo-P(4)-C(41)B | 119.7 (2) |
| (E) Bridging Carbon-Phosphorus-Phenyl Carbon Angles | | | |
| C(1)-P(1)-C(11)A | 107.6 (4) | C(1)-P(1)-C(11)B | 102.8 (4) |
| C(2)-P(2)-C(21)A | 103.7 (4) | C(2)-P(2)-C(21)B | 103.7 (4) |
| C(3)-P(3)-C(31)A | 100.9 (4) | C(3)-P(3)-C(31)B | 108.0 (4) |
| C(4)-P(4)-C(41)A | 104.6 (4) | C(4)-P(4)-C(41)B | 104.4 (4) |
| (F) Phenyl Carbon-Phosphorus-Phenyl Carbon Angles | | | |
| C(11)A-P(1)-C(11)B | 106.4 (4) | C(31)A-P(3)-C(31)B | 105.7 (4) |
| C(21)A-P(2)-C(21)B | 103.1 (4) | C(41)A-P(4)-C(41)B | 103.2 (4) |
| (G) Phosphorus-Bridging Carbon-Bridging Carbon Angles | | | |
| P(1)-C(1)-C(2) | 111.4 (5) | P(3)-C(3)-C(4) | 114.2 (6) |
| P(2)-C(2)-C(1) | 113.7 (5) | P(4)-C(4)-C(3) | 108.5 (6) |
| (H) Phenyl Carbon-Carbon-Carbon Angles | | | |
| C(16)A-C(11)A-C(12)A | 117.4 (8) | C(16)B-C(11)B-C(12)B | 118.5 (8) |
| C(11)A-C(12)A-C(13)A | 121.9 (8) | C(11)B-C(12)B-C(13)B | 122.2 (8) |
| C(12)A-C(13)A-C(14)A | 119.4 (9) | C(12)B-C(13)B-C(14)B | 118.4 (9) |
| C(13)A-C(14)A-C(15)A | 120.9 (10) | C(13)B-C(14)B-C(15)B | 119.5 (10) |
| C(14)A-C(15)A-C(16)A | 120.0 (10) | C(14)B-C(15)B-C(16)B | 122.7 (10) |
| C(15)A-C(16)A-C(11)A | 120.3 (9) | C(15)B-C(16)B-C(11)B | 118.8 (8) |
| C(26)A-C(21)A-C(22)A | 118.6 (7) | C(26)B-C(21)B-C(22)B | 117.4 (8) |
| C(21)A-C(22)A-C(23)A | 120.6 (8) | C(21)B-C(22)B-C(23)B | 120.8 (9) |
| C(22)A-C(23)A-C(24)A | 120.1 (9) | C(22)B-C(23)B-C(24)B | 118.4 (11) |
| C(23)A-C(24)A-C(25)A | 120.0 (9) | C(23)B-C(24)B-C(25)B | 124.2 (12) |
| C(24)A-C(25)A-C(26)A | 121.6 (9) | C(24)B-C(25)B-C(26)B | 118.1 (10) |
| C(25)A-C(26)A-C(21)A | 119.0 (8) | C(25)B-C(26)B-C(21)B | 121.2 (10) |
| C(36)A-C(31)A-C(32)A | 120.1 (8) | C(36)B-C(31)B-C(32)B | 117.7 (9) |
| C(31)A-C(32)A-C(33)A | 120.0 (9) | C(31)B-C(32)B-C(33)B | 118.9 (12) |
| C(32)A-C(33)A-C(34)A | 118.3 (11) | C(32)B-C(33)B-C(34)B | 119.3 (15) |
| C(33)A-C(34)A-C(35)A | 125.7 (14) | C(33)B-C(34)B-C(35)B | 123.6 (16) |
| C(34)A-C(35)A-C(36)A | 118.1 (13) | C(34)B-C(35)B-C(36)B | 117.3 (13) |
| C(35)A-C(36)A-C(31)A | 117.8 (10) | C(35)B-C(36)B-C(31)B | 122.0 (10) |
| C(46)A-C(41)A-C(42)A | 118.3 (8) | C(46)B-C(41)B-C(42)B | 120.9 (7) |
| C(41)A-C(42)A-C(43)A | 120.9 (10) | C(41)B-C(42)B-C(43)B | 119.9 (8) |
| C(42)A-C(43)A-C(44)A | 119.9 (11) | C(42)B-C(43)B-C(44)B | 119.5 (8) |
| C(43)A-C(44)A-C(45)A | 120.8 (10) | C(43)B-C(44)B-C(45)B | 119.6 (9) |
| C(44)A-C(45)A-C(46)A | 119.9 (9) | C(44)B-C(45)B-C(46)B | 120.9 (9) |
| C(45)A-C(46)A-C(41)A | 120.1 (9) | C(45)B-C(46)B-C(41)B | 119.3 (8) |
| (I) Fluorine-Boron-Fluorine Angles | | | |
| F(1)-B-F(2) | 106.3 (8) | F(2)-B-F(3) | 111.3 (9) |
| F(1)-B-F(3) | 108.9 (9) | F(2)-B-F(4) | 109.4 (8) |
| F(1)-B-F(4) | 109.2 (8) | F(3)-B-F(4) | 111.6 (8) |

individual atoms from the least-squares plane being 0.0285 (4) Å for Mo, −0.035 (2) Å for P(1), 0.020 (2) Å for P(2), 0.021 (2) Å for P(3), and −0.035 (2) Å for P(4) (see Table VI). Interatomic angles within this plane suffer from distortion caused by the chelating nature of the diphos ligands. Thus, the *intra*ligand angles P(1)–Mo–P(2) and P(3)–Mo–P(4) are 79.29 (7) and 79.12 (7)° (respectively), whereas the cis-*inter*ligand angles are P(1)–Mo–P(3) = 98.89 (7)° and P(2)–Mo–P(4) = 102.68 (7)°. The four independent molybdenum–phosphorus bond lengths are Mo–P(1) = 2.530 (2) Å, Mo–P(2) = 2.553 (2) Å, Mo–P(3) = 2.551 (2) Å, and Mo–P(4) = 2.547 (2) Å; the average value is 2.545 ± 0.010 Å.[8]

The five-membered $\overline{\mathrm{Mo{-}P{-}C{-}C{-}P}}$ chelate rings each have the expected puckered geometry. The absolute configurations of the two rings are opposite one from another (see Figure 4). The cation is thus correctly named as the δλ-Mo(diphos)$_2$(O)(OH)$^+$ isomer.

The phosphorus–phenyl distances range from 1.808 (8) to 1.831 (8) Å, averaging 1.816 ± 0.007 Å. This may be compared to the P–C(sp$^3$) distances which range from 1.805 (9) to 1.865 (8) Å averaging 1.838 ± 0.026 Å.

Distances and angles within the phenyl groups are all normal. Internal angles at the P-bonded carbon are mostly reduced from the regular trigonal angle, individual values being

**Table VI.** Least-Squares Planes and Deviations (Å) of Atoms Therefrom[a,b]

| Atom | Dev | Atom | Dev |
|---|---|---|---|
| I. MoP$_4$ Plane: $0.89499X + 0.18969Y + 0.40375Z = 7.1758$ | | | |
| Mo* | 0.0285 (4) | P(3)* | 0.021 (2) |
| P(1)* | −0.035 (2) | P(4)* | −0.035 (2) |
| P(2)* | 0.020 (2) | | |
| C(1) | 0.925 (8) | C(3) | −0.192 (9) |
| C(2) | 0.358 (8) | C(4) | −0.919 (9) |
| C(11)A | −1.666 (8) | C(31)A | 1.493 (8) |
| C(11)B | 0.848 (8) | C(31)B | −1.343 (8) |
| C(21)A | −1.455 (8) | C(41)A | 1.513 (8) |
| C(21)B | 1.333 (8) | C(41)B | −0.979 (7) |
| II. $-0.1842X + 0.8252Y + 0.5339Z = 6.8842$ | | | |
| C(11)A* | 0.007 (8) | C(15)A* | −0.009 (10) |
| C(12)A* | −0.013 (9) | C(16)A* | 0.003 (10) |
| C(13)A* | 0.006 (10) | P(1) | 0.050 (2) |
| C(14)A* | 0.005 (10) | | |
| III. $0.7456X + 0.3428Y - 0.5714Z = 3.3895$ | | | |
| C(11)B* | −0.002 (8) | C(15)B* | −0.009 (10) |
| C(12)B* | −0.001 (8) | C(16)B* | 0.006 (9) |
| C(13)B* | −0.001 (9) | P(1) | −0.052 (2) |
| C(14)B* | 0.006 (9) | | |
| IV. $0.7279X - 0.6782Y + 0.1011Z = 1.7440$ | | | |
| C(21)A* | 0.008 (8) | C(25)A* | −0.017 (10) |
| C(22)A* | −0.008 (8) | C(26)A* | 0.004 (9) |
| C(23)A* | −0.004 (9) | P(2) | 0.152 (2) |
| C(24)A* | 0.017 (10) | | |
| V. $-0.2821X - 0.4402Y + 0.8524Z = -0.7648$ | | | |
| C(21)B* | −0.012 (8) | C(25)B* | −0.005 (11) |
| C(22)B* | 0.005 (9) | C(26)B* | 0.012 (10) |
| C(23)B* | 0.003 (11) | P(2) | 0.004 (2) |
| C(24)B* | −0.003 (11) | | |
| VI. $0.1834X + 0.7924Y - 0.5818Z = 0.3816$ | | | |
| C(31)A* | −0.009 (8) | C(35)A* | 0.005 (14) |
| C(32)A* | 0.005 (9) | C(36)A* | 0.004 (10) |
| C(33)A* | 0.005 (11) | P(3) | −0.166 (2) |
| C(34)A* | −0.010 (13) | | |
| VII. $-0.1536X + 0.2067Y + 0.9663Z = 7.9649$ | | | |
| C(31)B* | −0.018 (8) | C(35)B* | 0.047 (12) |
| C(32)B* | 0.008 (12) | C(36)B* | −0.008 (10) |
| C(33)B* | 0.031 (16) | P(3) | −0.218 (2) |
| C(34)B* | −0.060 (15) | | |
| VIII. $-0.3360X + 0.6229Y + 0.7065Z = 4.2934$ | | | |
| C(41)A* | 0.007 (8) | C(45)A* | −0.007 (10) |
| C(42)A* | −0.011 (11) | C(46)A* | 0.002 (9) |
| C(43)A* | 0.006 (11) | P(4) | −0.019 (2) |
| C(44)A* | 0.004 (10) | | |
| IX. $0.0791X - 0.6440Y + 0.7610Z = 4.0396$ | | | |
| C(41)B* | −0.006 (7) | C(45)B* | 0.006 (9) |
| C(42)B* | 0.004 (8) | C(46)B* | 0.001 (8) |
| C(43)B* | 0.002 (9) | P(4) | −0.157 (2) |
| C(44)B* | −0.007 (10) | | |

[a] Cartesian (Å) coordinates ($X, Y, Z$) are related to the fractional cell coordinates ($x, y, z$) by the transformation

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & 0 & c\cos\beta \\ 0 & b & 0 \\ 0 & 0 & c\sin\beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

[b] Atoms marked with an asterisk were included in calculating the plane. All other atoms were assigned zero weight.

C(16)A–C(11)A–C(12)A = 117.4 (8)°, C(16)B–C(11)B–C(12)B = 118.5 (8)°, C(26)A–C(21)A–C(22)A = 118.6 (7)°, C(26)B–C(21)B–C(22)B = 117.4 (8)°, C(36)A–C(31)A–C(32)A = 120.1 (8)°, C(36)B–C(31)B–C(32)B = 117.7 (9)°, C(46)A–C(41)A–C(42)A = 118.3 (8)°, and C(46)B–C(41)B–C(42)B = 120.9 (7)°. This result is expected and has been discussed by Coulson et al.[9]

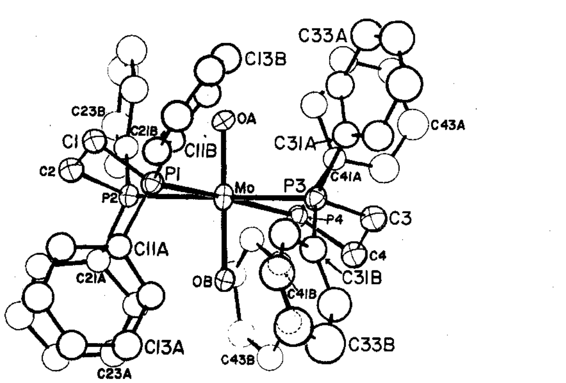

**Figure 2.** Labeling of atoms in the Mo(diphos)$_2$(O)(OH)$^+$ cation (ORTEP diagram; 30% ellipsoids).

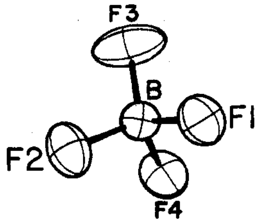

**Figure 3.** The BF$_4^-$ anion (ORTEP diagram; 30% ellipsoids).

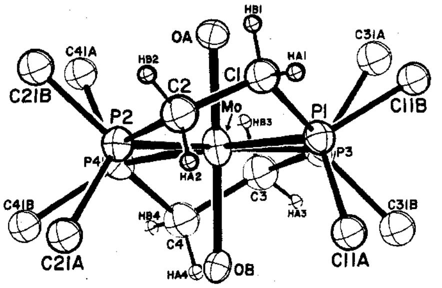

**Figure 4.** The Mo(C$_2$PCH$_2$CH$_2$PC$_2$)$_2$O$_2$ core of the molecule, showing the octahedral coordination geometry about the Mo(IV) atom and the conformations of the diphos ligands (ORTEP diagram).

The phenyl ring defined by atoms C(31)B–C(36)B appears to be slightly puckered. Each of the other phenyl rings is planar within the limits of experimental error (see Table VI) and has approximate $C_{2v}$ symmetry.

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**Registry No.** [Mo(diphos)$_2$(O)(OH)][BF$_4$], 65276-03-1.

**Supplementary Material Available:** Listing of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

## References and Notes

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