Molybdenum Carbonyl Complexes of Diphenylphosphinous Acid and Diphenylphosphinous Acid Derivatives.
Crystal and Molecular Structures of $[Et_4N][Mo(CO)_4(PPh_2O)_2H] \cdot 0.37\ CH_2Cl_2$, $Mo(CO)_4(PPh_2OH)(PPh_2OCH_2CH_2NMe_2) \cdot H_2O$ and $Mo(CO)_4(PPh_2SPPh_2)$

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Crystal and molecular structures for the three complexes $[Et_4N][Mo(CO)_4(PPh_2O)_2H] \cdot 0.37CH_2Cl_2$ *(1),* $[Mo(CO)_4(PPh_2OH)(PPh_2OCH_2CH_2NMe_2)] \cdot H_2O$ *(2) and* $[Mo(CO)_4(PPh_2SPPh_2)]$ *(3) are reported. The octahedral coordination sphere at molybdenum consists of four carbonyl groups and two* cis *oriented phosphorus donor ligands. The unlocated hydrogen atom in* 1 *forms a strong hydrogen bridge between the two* Ph_2PO^- *ligands as evidenced by a short O–O distance of 2.415(4) Å. In complex* 2*, the acidic proton of the* PPh_2OH *ligand forms a strong hydrogen bond to the tertiary amine with a N–O distance of 2.77 Å. Complex* 3 *has essentially* C_{2v} *symmetry; the P–S–P bond angle is 86.9°. The P–M–P angles are 88.06(4)°, 86.36(7)° and 72.02(7)° for* 1, 2 *and* 3, *respectively. The average M–C distance over all these compounds is 2.010(6) Å; the M–P distances range from 2.487(2) to 2.563(2) Å and average to 2.51(1) Å. Compound* 1 *crystallizes in space group* $P\bar{1}$ *with* a *= 12.456(2) Å,* b *= 13.757(3) Å,* c *= 11.892(3) Å,* α *= 95.51(2)°,* β *= 108.30(2)°,* γ *= 91.91(1)°,* V *= 1922(2) Å*^{3}*,* Z *= 2. Compound* 2 *crystallizes in space group* Pbca *with* a *= 20.901(3) Å,* b *= 16.032(3) Å,* c *= 19.686(5) Å,* V *= 6597(2) Å*^{3}*,* Z *= 8. Compound* 3 *crystallizes in space group* $P2_12_12_1$ *with* a *= 11.014(1) Å,* b *= 14.244(2) Å,* c *= 17.233(1) Å,* V *= 2704(1) Å*^{3}*,* Z *= 4.*

Introduction

Metal complexes containing coordination-stabilized organophosphorus acid ligands such as diphenylphosphinous acid, Ph_2POH, are becoming increasingly common [1–9]. One particularly interesting class of complexes derived from these ligands contains the presumably symmetrical $\overline{M{-}PR_2O\cdots H\cdots O{-}P}R_2$ ring system which arises from hydrogen bridging between *cis*-coordinated R_2POH and R_2PO^- ligands. Crystal structures for the two complexes $[Pd_2(\mu\text{-}NCS)_2(PPh_2O)_2H]$ [8, 9] and $[Pd(S_2PMe_2)((PPh_2O)_2H)]$ [7] have been determined although the position of the bridging proton could not be determined. Multinuclear NMR and IR evidence for the same ring system in several six-coordinate molybdenum complexes has been reported [1]. A structural determination of $[Et_4N][Mo(CO)_4(PPh_2O)_2H]$, *1*, now proves this to be the case.

Because Ph_2POH can hydrogen bond intramolecularly to a Lewis base site or transfer the acid proton to a Lewis base the question of the mode of bonding of the acidic proton in the unsymmetrical complex $[Mo(CO)_4(PPh_2OH)(PPh_2OCH_2CH_2NMe_2)]$, *2*, [1], was of interest. Potential modes include intramolecular hydrogen bonding to either the oxygen or nitrogen of the 2-N,N-dimethylaminoethoxy moiety or proton transfer to nitrogen. Although, the acid proton has not been located, the molecular structure can be interpreted as involving a strong hydrogen bond between the acid hydrogen and the terminal nitrogen.

Complexes of tetraphenyldiphosphoxane, the acid anhydride of diphenylphosphinous acid, are also known and recently Wong and his coworkers [10, 11] have obtained the crystal and molecular structure of $[cis\text{-}Mo(CO)_4(PPh_2OPPh_2)]$. In this paper, we report the crystal and molecular structure of the thio-analog *cis*-$Mo(CO)_4(PPh_2SPPh_2)$, *3*.

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TABLE I. Summary of Crystal Data, Data Collection Parameters, and Least-Squares Residuals for $(NEt_4)[Mo(CO)_4(PPh_2O)_2H] \cdot 0.37CH_2Cl_2$, *1*; $Mo(CO)_4(PPh_2OH)(PPh_2OCH_2CH_2N(CH_3)_2 \cdot H_2O$, *2*; and $Mo(CO)_4(PPh_2)_2S$, *3*.

	1	*2*	*3*
Formula	$MoC_{36}H_{41}NO_6P_2 \cdot 0.37CH_2Cl_2$	$MoC_{32}H_{33}O_7NP_2$	$MoC_{28}H_{20}O_4P_2S$
Formula weight	773.04	701.50	610.41
Space group	$P\bar{1}$	*Pbca*	$P2_12_12_1$
a, Å	12.456(2)	20.901(3)	11.014(1)
b, Å	13.757(3)	16.032(3)	14.244(2)
c, Å	11.892(3)	19.686(5)	17.233(1)
α, degrees	95.51(2)	–	–
β, degrees	108.30(2)	–	–
γ, degrees	91.91(1)	–	–
V, Å^3	1922(2)	6597(2)	2704(1)
Z	2	8	4
d_{calc}, g/cm^3	1.34	1.41	1.50
Crystal size, mm	0.15 × 0.15 × 0.20	0.15 × 0.25 × 0.75	0.15 × 0.15 × 0.30
μ(MoKα), cm^{-1}	5.17	5.37	7.03
Data collection instrument	Enraf-Nonius CAD-4	Syntex $P\bar{1}$	CAD-4
Radiation	Mo Kα ($\lambda\bar{\alpha}$ = 0.71073 Å), graphite-monochromated		
Scan method	$2\theta - \omega$	$2\theta - \omega$	$2\theta - \omega$
Data collection range	$4° \leq 2\theta \leq 50°$	$4° \leq 2\theta \leq 50°$	$4° \leq 2\theta \leq 50°$
No. unique data, $F_o^2 \geq 3\sigma(F_o^2)$	4417	2032	1843
Number of parameters refined	436	388	325
R^a	0.0538	0.0409	0.0375
$R_w{}^b$	0.0700	0.0594	0.0462
Quality-of-fit indicator^c	1.751	1.529	1.214
Largest shift/esd, final cycle	0.28	0.43	0.12

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

Experimental Section

The syntheses of the title compounds have been previously reported [1]. Crystals of *1* (CH_2Cl_2/hexane) and *3* (diethyl ether/hexane) were obtained by standard mixed solvent recrystallization procedures. Complex *2* was originally characterized as a CH_3OH solvate (from CH_2Cl_2/CH_3OH) based on an elemental analysis and ^1H NMR. The crystals of *2* examined in this work were obtained by recrystallization from reagent grade CH_3OH and apparently precipitated as the thermodynamically more stable hydrate.

X-ray Data Collection, Structure Solution, and Refinement

$(NEt_4)[Mo(CO)_4(PPh_2O)_2H] \cdot 0.37CH_2Cl_2$, 1. A pale yellow crystal of approximate dimensions 0.20 × 0.15 × 0.15 mm was attached with epoxy cement to the end of a thin glass fiber. All geometric and intensity data were taken from this crystal by an automated 4-circle diffractometer (Enraf-Nonius CAD-4) equipped with a molybdenum X-ray tube (λ_α = 0.71073 Å) and a graphite monochromator.

The unit-cell constants and crystal orientation matrix were refined by a least-squares fit to the angular positions of 25 accurately located reflections in the range $12° < 2\theta < 32°$. The cell constants are given in Table I, along with a summary of other crystal data.

Scans of 7115 data points in the range $4° \leq 2\theta \leq 50°$ were made with a $2\theta - \omega$ motion. The scan width in omega was calculated for each reflection as $(0.70 + 0.35 \tan \theta)°$, and the scan speed in omega varied between 4 and 20 deg/min.

The data were processed by routine computational procedures [12]. After derivation of structure factors and averaging of equivalent reflections, there were 4417 unique data with $F_o^2 \geq 3\sigma(F_o^2)$ for use in structure solution and refinement. Although the crystal had taken on a dark brown color by the end of data collection, three reflections used as standards had not changed significantly in intensity, and therefore no

TABLE II. Table of Positional and Isotropic-equivalent Thermal Parameters and Their Estimated Standard Deviations for $(NEt_4)[Mo(CO)_4(PPh_2O)_2H] \cdot 0.37CH_2Cl_2$, *1*.

Atom	*x*	*y*	*z*	B ($Å^2$)
Mo1	0.15904(4)	0.23215(4)	0.22924(5)	3.15(1)
Cl1	0.000	0.500	0.000	14.3(5)*
Cl2	−0.162(2)	0.449(2)	0.087(2)	12.8(6)*
Cl3	−0.136(2)	0.526(1)	0.061(2)	12.7(5)*
Cl4	0.037(1)	0.511(1)	−0.034(2)	13.4(6)*
P1	0.2800(1)	0.2419(1)	0.4449(1)	3.46(4)
P2	0.3263(1)	0.1710(1)	0.1737(1)	3.40(3)
O1	0.0099(5)	0.2246(4)	−0.0383(4)	7.5(2)
O2	0.2743(5)	0.4449(4)	0.2427(5)	8.0(2)
O3	−0.0480(4)	0.3154(5)	0.2929(5)	8.4(2)
O4	0.0681(4)	0.0156(3)	0.2333(5)	6.2(1)
O5	0.4076(3)	0.2228(3)	0.4672(3)	4.0(1)
O6	0.4400(3)	0.1718(3)	0.2812(3)	4.2(1)
N1	0.2529(4)	0.7688(4)	0.3835(5)	4.9(1)
C1	0.0670(5)	0.2273(5)	0.0581(6)	4.7(2)
C2	0.2295(6)	0.3691(5)	0.2358(6)	5.1(2)
C3	0.0305(5)	0.2862(5)	0.2723(6)	4.8(2)
C4	0.1015(5)	0.0929(5)	0.2334(5)	3.8(1)
C5	0.2843(5)	0.3615(5)	0.5307(5)	3.9(1)
C6	0.1874(6)	0.3933(5)	0.5569(6)	5.4(2)
C7	0.1920(7)	0.4852(6)	0.6240(6)	6.3(2)
C8	0.2931(7)	0.5445(5)	0.6621(7)	6.5(2)
C9	0.3869(7)	0.5144(5)	0.6329(7)	6.3(2)
C10	0.3844(6)	0.4220(5)	0.5664(6)	5.3(2)
C11	0.2348(5)	0.1657(4)	0.5418(5)	3.3(1)
C12	0.1216(5)	0.1409(5)	0.5234(5)	4.4(2)
C13	0.0878(6)	0.0876(5)	0.6054(6)	5.1(2)
C14	0.1689(6)	0.0570(5)	0.7015(6)	5.5(2)
C15	0.2819(7)	0.0780(6)	0.7187(7)	6.2(2)
C16	0.3179(6)	0.1328(5)	0.6389(6)	5.0(2)
C17	0.3132(5)	0.0490(4)	0.0932(5)	3.5(1)
C18	0.2096(5)	0.0048(5)	0.0212(5)	4.3(2)
C19	0.2038(6)	−0.0883(5)	−0.0413(6)	5.0(2)
C20	0.3028(6)	−0.1371(5)	−0.0289(6)	5.6(2)
C21	0.4065(7)	−0.0945(6)	0.0439(7)	6.4(2)
C22	0.4119(6)	−0.0009(5)	0.1047(7)	5.5(2)
C23	0.3674(5)	0.2446(4)	0.0710(5)	3.9(1)
C24	0.4709(6)	0.2975(5)	0.1093(7)	5.7(2)
C25	0.5029(8)	0.3566(6)	0.0340(7)	7.5(2)
C26	0.4300(7)	0.3633(6)	−0.0767(7)	8.0(2)
C27	0.3254(8)	0.3099(7)	−0.1186(7)	8.1(2)
C28	0.2912(7)	0.2486(6)	−0.0433(6)	6.2(2)
C29	0.2546(7)	0.8728(6)	0.3505(8)	7.5(2)
C30	0.3746(8)	0.9292(6)	0.409(1)	9.1(3)
C31	0.2956(7)	0.7645(6)	0.5178(7)	6.3(2)
C32	0.2283(9)	0.8211(8)	0.5864(8)	9.9(3)
C33	0.3341(6)	0.7053(6)	0.3373(7)	6.4(2)
C34	0.3089(9)	0.700(1)	0.2022(9)	11.2(4)
C35	0.1271(6)	0.7298(7)	0.3292(8)	7.1(2)
C36	0.1052(7)	0.6262(8)	0.354(1)	9.5(3)
C37	−0.071(4)	0.455(3)	0.073(4)	6(1)*
C38	−0.002(4)	0.526(3)	0.060(4)	7(1)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^{*2}\beta(1,1) + b^{*2}\beta(2,2) + c^{*2}\beta(3,3) + ab(\cos \gamma)^{*}\beta(1,2) + ac(\cos \beta)^{*}\beta(1,3) + bc(\cos \alpha)^{*}\beta(2,3)]$.

TABLE III. Table of Bond Distances in Angstroms for $(NEt_4)[Mo(CO)_4(PPh_2O)_2H]\cdot 0.37CH_2Cl_2$, *1*.

Atom 1	Atom 2	Distance[a]
Mo1	P1	2.522(1)
Mo1	P2	2.522(1)
Mo1	C1	1.991(6)
Mo1	C2	2.036(6)
Mo1	C3	1.975(6)
Mo1	C4	2.033(6)
P1	O5	1.562(3)
P1	C5	1.841(5)
P1	C11	1.829(5)
P2	O6	1.581(3)
P2	C17	1.826(5)
P2	C23	1.837(5)
O1	C1	1.140(6)
O2	C2	1.149(6)
O3	C3	1.155(6)
O4	C4	1.129(6)
N1	C29	1.521(7)
N1	C31	1.525(7)
N1	C33	1.551(7)
N1	C35	1.550(7)
C5	C6	1.411(7)
C5	C10	1.399(7)
C6	C7	1.419(8)
C7	C8	1.400(9)
C8	C9	1.385(9)
C9	C10	1.425(8)
C11	C12	1.383(6)
C11	C16	1.411(7)
C12	C13	1.429(7)
C13	C14	1.378(8)
C14	C15	1.374(8)
C15	C16	1.432(8)
C17	C18	1.387(6)
C17	C22	1.404(7)
C18	C19	1.405(7)
C19	C20	1.397(8)
C20	C21	1.383(8)
C21	C22	1.404(8)
C23	C24	1.380(7)
C23	C28	1.400(7)
C24	C25	1.402(9)
C25	C26	1.357(11)
C26	C27	1.394(11)
C27	C28	1.433(9)
C29	C30	1.577(10)
C31	C32	1.525(10)
C33	C34	1.531(11)
C35	C36	1.517(10)
Cl1	C37	1.57(5)
Cl2	C37	1.20(4)
Cl3	C38	1.67(6)
Cl4	C38	1.35(5)

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[a] Numbers in parentheses are the estimated standard deviations in the least significant digits.

TABLE IV. Table of Bond Angles in Degrees for $(NEt_4)[Mo(CO)_4(PPh_2O)_2H]\cdot 0.37CH_2Cl_2$, *1*.

Atom 1	Atom 2	Atom 3	Angle[a]
P1	Mo1	P2	88.06(4)
P1	Mo1	C1	178.2(2)
P1	Mo1	C2	84.7(2)
P1	Mo1	C3	92.0(2)
P1	Mo1	C4	91.0(1)
P2	Mo1	C1	91.0(2)
P2	Mo1	C2	86.2(2)
P2	Mo1	C3	177.4(2)
P2	Mo1	C4	91.1(1)
C1	Mo1	C2	93.7(2)
C1	Mo1	C3	88.8(2)
C1	Mo1	C4	90.6(2)
C2	Mo1	C3	91.2(2)
C2	Mo1	C4	175.0(2)
C3	Mo1	C4	91.5(2)
Mo1	P1	O5	115.6(1)
Mo1	P1	C5	114.0(2)
Mo1	P1	C11	118.1(2)
O5	P1	C5	104.0(2)
O5	P1	C11	104.9(2)
C5	P1	C11	98.0(2)
Mo1	P2	O6	115.2(1)
Mo1	P2	C17	118.9(2)
Mo1	P2	C23	113.3(2)
O6	P2	C17	104.0(2)
O6	P2	C23	103.1(2)
C17	P2	C23	100.2(2)
C29	N1	C31	112.6(5)
C29	N1	C33	112.2(5)
C29	N1	C35	104.5(5)
C31	N1	C33	103.6(4)
C31	N1	C35	111.2(5)
C33	N1	C35	113.0(5)
Mo1	C1	O1	176.8(5)
Mo1	C2	O2	176.6(5)
Mo1	C3	O3	176.9(5)
Mo1	C4	O4	178.5(5)
P1	C5	C6	120.7(4)
P1	C5	C10	118.9(4)
C6	C5	C10	120.4(5)
C5	C6	C7	120.2(6)
C6	C7	C8	119.2(6)
C7	C8	C9	120.4(6)
C8	C9	C10	121.3(6)
C5	C10	C9	118.5(6)
P1	C11	C12	121.8(4)
P1	C11	C16	118.8(4)
C12	C11	C16	119.4(5)
C11	C12	C13	120.8(5)
C12	C13	C14	119.8(5)
C13	C14	C15	120.1(5)
C14	C15	C16	121.1(5)
C11	C16	C15	118.7(5)

(continued on facing page)

TABLE IV. *(continued)*

Atom 1	Atom 2	Atom 3	Angle[a]
P2	C17	C18	122.2(4)
P2	C17	C22	118.4(4)
C18	C17	C22	119.4(5)
C17	C18	C19	120.2(5)
C18	C19	C20	119.8(5)
C19	C20	C21	120.6(6)
C20	C21	C22	119.3(6)
C17	C22	C21	120.6(5)
P2	C23	C24	119.5(4)
P2	C23	C28	119.2(4)
C24	C23	C28	121.3(5)
C23	C24	C25	120.6(6)
C24	C25	C26	119.4(7)
C25	C26	C27	121.3(7)
C26	C27	C28	120.2(7)
C23	C28	C27	117.2(6)
N1	C29	C30	112.3(5)
N1	C31	C32	114.5(6)
N1	C33	C34	113.2(6)
N1	C35	C36	113.5(5)
Cl1	C37	Cl2	144(3)
Cl3	C38	Cl4	129(3)

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits.

decay correction was applied. The small linear absorption coefficient (5.17 cm^{-1}) obviated the need for an absorption correction, and none was made.

The position of the unique molybdenum atom was derived from the Patterson map, and the remaining non-hydrogen atoms of the [$Mo(CO)_4(PPh_2O)_2H^-$] and $(NEt_4)^+$ units were located and refined through alternate least-squares cycles and difference Fourier maps. One difference map revealed peaks with densities of about 3.7, 1.8 and 1.3 e/Å^3, the highest of which was on a special position. These were assigned as two disordered CH_2Cl_2 molecules; the assignment was supported by the identification of CH_2Cl_2 in the ^1H NMR spectrum at δ = 5.28 ppm. The refinement settled down with site occupancies of 0.17 and 0.20 for these groups. While some of the derived parameters for the CH_2Cl_2 groups were not ideal, no special effort was made to improve their refinement, since they are of little importance.

The structural refinement converged with final residuals (defined and summarized in Table I) R = 0.0538 and R_w = 0.0700. The last least-squares cycle did not shift any parameter by more than 0.28 times its estimated standard deviation. The strongest peak on a difference Fourier map after refinement had a density of 0.5 e/Å^3.

Positional parameters for compound *1* are given in Table II, and bond distances and angles are in Tables III and IV, respectively. The structure and labelling scheme of the complex anion are shown in Fig. 1.

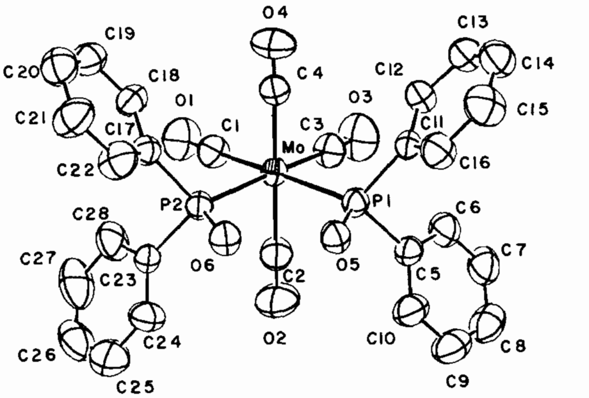

Fig. 1. ORTEP plot of the complex anion [$Mo(CO)_4(PPh_2O)_2H$] of compound *1*. Atoms are represented by their 50% probability ellipsoids.

$Mo(CO)_4(PPh_2OH)(PPh_2OCH_2CH_2N(CH_3)_2 \cdot H_2O$, 2. A pale yellow crystal of approximate dimensions 0.15 × 0.25 × 0.75 mm, mounted in a random orientation on a glass fiber, was used for collection of geometric and intensity data by a Syntex P$\bar{1}$ autodiffractometer. The unit-cell parameters and crystal orientation matrix were determined by routine procedures, and refined by a least-squares fit to the goniometer settings of 15 accurately located reflections in the range 26° $\leqslant 2\theta \leqslant$ 30°. The cell dimensions and other pertinent data are summarized in Table I.

Intensity data collection consisted of $2\theta-\omega$ scans of 2077 possible data points, with ranges from 1.0° above to 1.0° below the Kα_1, α_2 doublet, and with scan speeds variable between 1.8 and 24.0°/min. Three standard reflections did not change significantly in intensity during the course of data collection. After reduction of the data and averaging of equivalent reflections, there were 2032 unique data for use in structure solution and refinement. The data were not corrected for absorption (μ(MoKα) = 5.37 cm^{-1}). Systematic absences (0kl): k = 2n + 1, (h0l): l = 2n + 1, and (hk0):h = 2n + 1 established the space group as *Pbca*. The unit-cell volume was consistent with Z = 8.

The structure was solved by Patterson methods and was developed and refined by an alternating sequence of difference Fourier maps and least-squares cycles. The final refinement cycle included positional and thermal parameters for all 43 non-hydrogen atoms and an overall scale factor – 388 parameters in all. The refinement converged with residuals (Table I) R = 0.0409 and R_w = 0.0594. A difference map following the refinement showed no features of chemical significance.

TABLE V. Table of Positional and Isotropic-equivalent Thermal Parameters and Their Estimated Standard Deviations for $Mo(CO)_4(PPh_2OH)(PPh_2OCH_2CH_2N(CH_3)_2 \cdot H_2O$, *2*.

Atom	*x*	*y*	*z*	B (A^2)[a]
Mo	0.40559(4)	0.73065(5)	0.30081(4)	3.13(1)
P1	0.3363(1)	0.6051(1)	0.3108(1)	3.06(5)
P2	0.3508(1)	0.7558(1)	0.1861(1)	3.15(5)
O1	0.4830(4)	0.6859(5)	0.4314(3)	6.9(2)
O2	0.3180(4)	0.8479(5)	0.3889(4)	7.0(2)
O3	0.4962(4)	0.8858(5)	0.2878(4)	7.9(2)
O4	0.5036(4)	0.6260(5)	0.2121(4)	8.4(2)
O5	0.3165(3)	0.5734(4)	0.2345(3)	4.4(1)
O6	0.3711(3)	0.6947(4)	0.1285(3)	3.9(1)
O7	0.4793(5)	0.6797(7)	0.0466(6)	12.3(3)
N1	0.3477(4)	0.5408(5)	0.1007(4)	5.4(2)
C1	0.4534(5)	0.7013(6)	0.3856(5)	4.4(2)
C2	0.3474(4)	0.8025(6)	0.3559(5)	4.6(2)
C3	0.4615(4)	0.8306(6)	0.2906(5)	4.8(2)
C4	0.4682(4)	0.6643(6)	0.2444(5)	4.3(2)
C5	0.3076(6)	0.4902(6)	0.2125(5)	6.2(3)
C6	0.2957(6)	0.4935(7)	0.1368(5)	6.9(3)
C7	0.4099(7)	0.4977(8)	0.1046(9)	10.6(5)
C8	0.3254(8)	0.5539(8)	0.0294(6)	9.4(4)
C9	0.3659(4)	0.5099(5)	0.3525(4)	3.2(2)
C10	0.3228(4)	0.4540(5)	0.3817(5)	4.3(2)
C11	0.3449(5)	0.3784(6)	0.4104(5)	5.1(3)
C12	0.4100(5)	0.3625(6)	0.4102(6)	5.5(3)
C13	0.4547(5)	0.4183(6)	0.3789(6)	5.9(3)
C14	0.4317(5)	0.4923(6)	0.3510(5)	5.0(2)
C15	0.2587(4)	0.6176(5)	0.3519(5)	3.9(2)
C16	0.2602(5)	0.6493(6)	0.4196(5)	5.2(2)
C17	0.2004(5)	0.6594(6)	0.4545(6)	7.6(3)
C18	0.1441(5)	0.6397(7)	0.4218(7)	8.9(4)
C19	0.1448(5)	0.6090(8)	0.3557(7)	8.3(3)
C20	0.2023(4)	0.5967(7)	0.3186(6)	6.5(3)
C21	0.3652(4)	0.8603(5)	0.1489(5)	3.6(2)
C22	0.3690(4)	0.9305(5)	0.1896(5)	4.1(2)
C23	0.3819(5)	1.0096(6)	0.1599(5)	4.8(2)
C24	0.3906(5)	1.0152(6)	0.0889(6)	5.3(3)
C25	0.3860(5)	0.9451(6)	0.0478(5)	5.5(3)
C26	0.3722(4)	0.8648(6)	0.0775(5)	4.4(2)
C27	0.2623(4)	0.7563(5)	0.1835(4)	3.5(2)
C28	0.2251(4)	0.7799(5)	0.2382(5)	4.2(2)
C29	0.1567(5)	0.7779(6)	0.2323(5)	4.9(2)
C30	0.1288(5)	0.7539(6)	0.1716(5)	4.9(2)
C31	0.1660(5)	0.7319(6)	0.1164(5)	4.8(2)
C32	0.2330(4)	0.7310(6)	0.1208(5)	4.4(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^{*2}\beta(1,1) + b^{*2}\beta(2,2) + c^{*2}\beta(3,3) + ab(\cos \gamma)^{*}\beta(1,2) + ac(\cos \beta)^{*}\beta(1,3) + bc(\cos \alpha)^{*}\beta(2,3)]$.

Positional and isotropic-equivalent thermal parameters are listed in Table V; and bond distances and angles are given in Tables VI and VII, respectively. An ORTEP plot of the molecule is shown in Fig. 2.

$Mo(CO)_4(PPh_2)_2S$, 3. A yellow crystal of approximate dimensions 0.15 × 0.15 × 0.30 mm, attached to the end of a glass fiber, was used for all geometric and intensity data collection. The data were gathered by an automated CAD-4 diffractometer equipped with a Mo X-ray source and graphite-crystal monochromator. The general procedures for data collection, structure solution and refinement were the same as those described for $(NEt_4)[Mo(CO)_4(PPh_2O)_2H] \cdot 0.37CH_2Cl_2$ (*vide supra*). The relevant crystal parameters are summarized in Table I. Systematic

TABLE VI. Table of Bond Distances in Angstroms for Mo-$(CO)_4(PPh_2OH)(PPh_2OCH_2CH_2N(CH_3)_2 \cdot H_2O$, *2*.

Atom 1	Atom 2	Distance[a]
Mo	P1	2.487(2)
Mo	P2	2.563(2)
Mo	C1	2.001(9)
Mo	C2	1.997(10)
Mo	C3	1.994(9)
Mo	C4	2.018(10)
P1	O5	1.638(5)
P1	C9	1.840(7)
P1	C15	1.823(8)
P2	O6	1.556(5)
P2	C21	1.854(8)
P2	C27	1.850(8)
O1	C1	1.122(9)
O2	C2	1.152(9)
O3	C3	1.144(9)
O4	C4	1.155(9)
O5	C5	1.415(9)
N1	C6	1.505(12)
N1	C7	1.473(14)
N1	C8	1.492(11)
C5	C6	1.512(12)
C9	C10	1.393(10)
C9	C14	1.405(11)
C10	C11	1.414(11)
C11	C12	1.384(12)
C12	C13	1.432(12)
C13	C14	1.394(11)
C15	C16	1.428(11)
C15	C20	1.389(11)
C16	C17	1.437(13)
C17	C18	1.38(2)
C18	C19	1.39(2)
C19	C20	1.420(15)
C21	C22	1.382(10)
C21	C26	1.416(11)
C22	C23	1.423(11)
C23	C24	1.412(12)
C24	C25	1.389(12)
C25	C26	1.443(11)
C27	C28	1.381(10)
C27	C32	1.436(10)
C28	C29	1.436(11)
C29	C30	1.383(12)
C30	C31	1.383(12)
C31	C32	1.402(11)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

absences (h00): h = 2n + 1, (0k0): k = 2n + 1, and (00l): l = 2n + 1, established the space group as $P2_12_12_1$. No decay or absorption correction was found necessary.

The 1843 unique reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$ were used for structure solution and refinement. The position of the molybdenum atom was derived

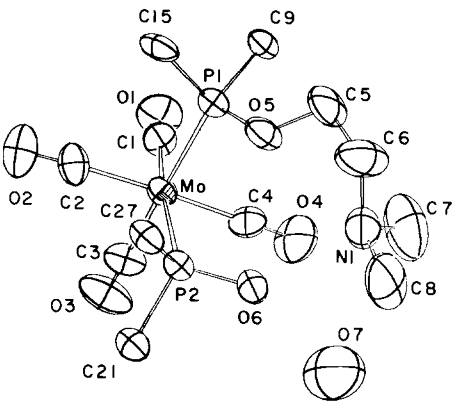

Fig. 2. Molecular structure and labelling scheme for $Mo(CO)_4(PPh_2OH)(PPh_2OCH_2CH_2N(CH_3)_2$, compound *2*. Atoms are represented by their 50% probability ellipsoids.

TABLE VII. Table of Bond Angles in Degrees for $Mo(CO)_4$-$(PPh_2OH)(PPh_2OCH_2CH_2N(CH_3)_2 \cdot H_2O$, *2*.

Atom 1	Atom 2	Atom 3	Angle[a]
P1	Mo	P2	86.36(7)
P1	Mo	C1	92.0(3)
P1	Mo	C2	94.0(3)
P1	Mo	C3	178.7(3)
P1	Mo	C4	89.7(2)
P2	Mo	C1	174.0(3)
P2	Mo	C2	96.6(3)
P2	Mo	C3	92.7(3)
P2	Mo	C4	83.6(3)
C1	Mo	C2	89.3(4)
C1	Mo	C3	88.9(4)
C1	Mo	C4	90.7(4)
C2	Mo	C3	87.1(4)
C2	Mo	C4	176.3(3)
C3	Mo	C4	89.3(4)
Mo	P1	O5	109.1(2)
Mo	P1	C9	120.7(3)
Mo	P1	C15	117.6(3)
O5	P1	C9	103.7(3)
O5	P1	C15	102.4(4)
C9	P1	C15	101.0(4)
Mo	P2	O6	114.9(2)
Mo	P2	C21	114.7(3)
Mo	P2	C27	118.1(3)
O6	P2	C21	103.7(3)
O6	P2	C27	104.7(3)
C21	P2	C27	98.5(3)
P1	O5	C5	127.4(5)
C6	N1	C7	112.1(9)
C6	N1	C8	106.8(9)
C7	N1	C8	113(1)
Mo	C1	O1	176.4(9)
Mo	C2	O2	174.5(8)
Mo	C3	O3	175.6(8)

(continued on facing page)

TABLE VII. *(continued)*

Atom 1	Atom 2	Atom 3	Angle[a]
Mo	C4	O4	179.5(9)
O5	C5	C6	106.9(7)
N1	C6	C5	111.4(9)
P1	C9	C10	120.1(6)
P1	C9	C14	119.0(6)
C10	C9	C14	120.8(8)
C9	C10	C11	120.3(8)
C10	C11	C12	118.6(9)
C11	C12	C13	121.8(8)
C12	C13	C14	118.4(9)
C9	C14	C13	120.0(9)
P1	C15	C16	115.7(7)
P1	C15	C20	121.3(8)
C16	C15	C20	123.0(9)
C15	C16	C17	118(1)
C16	C17	C18	120(1)
C17	C18	C19	121(1)
C18	C19	C20	123(1)
C15	C20	C19	116(1)
P2	C21	C22	121.1(7)
P2	C21	C26	117.1(6)
C22	C21	C26	121.8(8)
C21	C22	C23	120.0(8)
C22	C23	C24	119.1(8)
C23	C24	C25	121.1(9)
C24	C25	C26	120.0(9)
C21	C26	C25	117.9(9)
P2	C27	C28	122.8(6)
P2	C27	C32	116.7(6)
C28	C27	C32	120.5(7)
C27	C28	C29	119.4(8)
C28	C29	C30	119.7(8)
C29	C30	C31	120.8(8)
C30	C31	C32	121.0(9)
C27	C32	C31	118.4(8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

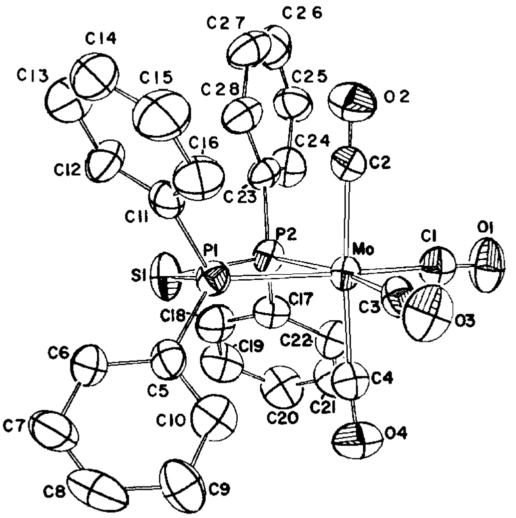

Fig. 3. ORTEP plot of $Mo(CO)_4(PPh_2)_2S$, compound *3*, showing 50% probability ellipsoids and atom labelling scheme.

from the Patterson function, and subsequent iterations of difference Fourier maps and least-squares refinement cycles led to the complete development and refinement of the structure. The final refinement, in which positional and anisotropic thermal parameters were refined for all atoms, converged with residuals (Table I) $R = 0.0375$ and $R_w = 0.0462$. The last least-squares cycle did not shift any parameter by more than 0.12 times its estimated standard deviation. A difference map following convergence showed no peak more dense than 0.49 e/Å^3. The enantiomorph was chosen on the basis of a slightly lower weighted R-factor.

Positional parameters, bond lengths and bond angles for *3* are given in Tables VIII, IX and X,

TABLE VIII. Table of Positional and Isotropic-equivalent Thermal Parameters for $Mo(CO)_4(PPh_2)_2S$, *3*.

Atom	x	y	z	B (Å^2)[a]
Mo	0.99356(6)	0.88141(4)	0.54062(4)	2.80(1)
S1	0.8741(2)	1.1084(2)	0.5030(2)	4.27(5)
P1	1.0496(2)	1.0498(2)	0.5222(1)	3.10(4)
P2	0.8081(2)	0.9678(2)	0.4992(1)	3.00(4)
O1	0.8674(6)	0.6851(4)	0.5562(4)	5.7(2)
O2	1.0777(7)	0.8364(5)	0.3695(4)	6.1(2)
O3	1.2435(5)	0.8080(5)	0.6043(4)	5.7(2)
O4	0.9326(7)	0.9030(5)	0.7180(4)	6.4(2)
C1	0.9145(7)	0.7552(6)	0.5495(5)	3.9(2)
C2	1.0454(8)	0.8539(6)	0.4297(5)	3.9(2)
C3	1.1545(7)	0.8326(5)	0.5802(5)	3.4(2)

(continued on facing page)

TABLE VIII. *(continued)*

Atom	*x*	*y*	*z*	B (Å^2)[a]
C4	0.9533(8)	0.8989(6)	0.6535(5)	3.8(2)
C5	1.1145(7)	1.1232(6)	0.5979(5)	3.6(2)
C6	1.123(1)	1.2193(7)	0.5888(5)	6.1(3)
C7	1.176(1)	1.2729(8)	0.6475(6)	7.1(3)
C8	1.223(1)	1.2317(8)	0.7131(6)	6.3(3)
C9	1.2154(9)	1.1330(7)	0.7253(6)	5.2(2)
C10	1.1581(8)	1.0810(7)	0.6651(6)	4.7(2)
C11	1.1395(8)	1.0886(5)	0.4381(5)	3.5(2)
C12	1.098(1)	1.1550(7)	0.3848(5)	5.3(2)
C13	1.174(1)	1.1828(8)	0.3241(6)	6.4(3)
C14	1.291(1)	1.1454(8)	0.3183(6)	6.8(3)
C15	1.333(1)	1.0765(9)	0.3713(6)	7.2(3)
C16	1.254(1)	1.0468(8)	0.4312(6)	5.6(2)
C17	0.6707(7)	0.9734(6)	0.5568(4)	3.4(2)
C18	0.5956(8)	1.0530(7)	0.5563(5)	4.8(2)
C19	0.4862(9)	1.0532(7)	0.6007(5)	5.1(2)
C20	0.4574(8)	0.9727(7)	0.6432(6)	5.5(3)
C21	0.5294(8)	0.8953(8)	0.6434(6)	5.8(3)
C22	0.6376(8)	0.8954(6)	0.6008(5)	4.0(2)
C23	0.7475(7)	0.9500(6)	0.4022(4)	3.2(2)
C24	0.6327(8)	0.9115(6)	0.3913(5)	4.3(2)
C25	0.5958(9)	0.8851(7)	0.3164(5)	4.8(2)
C26	0.671(1)	0.9005(7)	0.2535(6)	5.5(2)
C27	0.783(1)	0.9401(8)	0.2637(5)	5.5(3)
C28	0.8250(9)	0.9679(7)	0.3393(5)	4.6(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^{*2}\beta(1,1) + b^{*2}\beta(2,2) + c^{*2}\beta(3,3) + ab(\cos \text{gamma})^{*}\beta(1,2) + ac(\cos \text{beta})^{*}\beta(1,3) + bc(\cos \text{alpha})^{*}\beta(2,3)]$.

TABLE IX. Table of Bond Distances in Angstroms for $Mo(CO)_4(PPh_2)_2S$, *3*.

Atom 1	Atom 2	Distance[a]
Mo	P1	2.498(2)
Mo	P2	2.489(2)
Mo	C1	2.004(9)
Mo	C2	2.032(9)
Mo	C3	2.023(9)
Mo	C4	2.010(9)
S1	P1	2.131(3)
S1	P2	2.131(3)
P1	C5	1.818(9)
P1	C11	1.840(9)
P2	C17	1.812(8)
P2	C23	1.817(8)
O1	C1	1.131(10)
O2	C2	1.126(10)
O3	C3	1.121(10)
O4	C4	1.137(10)
C5	C6	1.381(13)
C5	C10	1.390(12)
C6	C7	1.392(14)
C7	C8	1.38(2)
C8	C9	1.42(2)
C9	C10	1.422(13)
C11	C12	1.396(12)
C11	C16	1.404(14)
C12	C13	1.399(14)
C13	C14	1.40(2)
C14	C15	1.42(2)
C15	C16	1.411(14)
C17	C18	1.404(12)
C17	C22	1.393(12)
C18	C19	1.427(13)
C19	C20	1.397(14)
C20	C21	1.358(13)
C21	C22	1.401(12)
C23	C24	1.390(12)
C23	C28	1.404(12)
C24	C25	1.405(12)
C25	C26	1.384(14)
C26	C27	1.361(15)
C27	C28	1.438(13)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

TABLE X. Table of Bond Angles in Degrees for $Mo(CO)_4(PPh_2)_2S$, *3*.

Atom 1	Atom 2	Atom 3	Angle[a]
P1	Mo	P2	72.02(7)
P1	Mo	C1	168.3(2)
P1	Mo	C2	89.8(2)
P1	Mo	C3	99.0(2)
P1	Mo	C4	93.4(3)
P2	Mo	C1	96.3(2)
P2	Mo	C2	93.2(3)
P2	Mo	C3	170.3(2)
P2	Mo	C4	92.0(3)
C1	Mo	C2	91.2(4)
C1	Mo	C3	92.7(3)
C1	Mo	C4	86.6(4)
C2	Mo	C3	90.2(4)
C2	Mo	C4	174.5(4)
C3	Mo	C4	84.8(4)
P1	S1	P2	86.9(1)
Mo	P1	S1	99.9(1)
Mo	P1	C5	123.9(3)
Mo	P1	C11	121.4(3)
S1	P1	C5	104.1(3)
S1	P1	C11	104.4(3)
C5	P1	C11	100.4(4)
Mo	P2	S1	100.1(1)
Mo	P2	C17	123.3(3)
Mo	P2	C23	119.8(3)
S1	P2	C17	103.1(3)
S1	P2	C23	106.6(3)
C17	P2	C23	101.7(4)
Mo	C1	O1	177.9(8)
Mo	C2	O2	177.2(8)
Mo	C3	O3	177.4(8)
Mo	C4	O4	175.7(8)
P1	C5	C6	121.0(8)
P1	C5	C10	119.1(7)
C6	C5	C10	119.9(9)
C5	C6	C7	119(1)
C6	C7	C8	121(1)
C7	C8	C9	121(1)
C8	C9	C10	116(1)
C5	C10	C9	122.4(9)
P1	C11	C12	122.9(8)
P1	C11	C16	115.1(7)
C12	C11	C16	122.0(9)
C11	C12	C13	119(1)
C12	C13	C14	120(1)
C13	C14	C15	121(1)
C14	C15	C16	119(1)
C11	C16	C15	119(1)
P2	C17	C18	121.6(7)
P2	C17	C22	118.8(7)
C18	C17	C22	119.6(8)
C17	C18	C19	119.7(9)
C18	C19	C20	118.1(9)
C19	C20	C21	122.4(9)
C20	C21	C22	120(1)
C17	C22	C21	120.7(9)
P2	C23	C24	120.9(7)
P2	C23	C28	117.5(6)
C24	C23	C28	121.3(8)
C23	C24	C25	119.5(9)
C24	C25	C26	120.2(9)
C25	C26	C27	120(1)
C26	C27	C28	122(1)
C23	C28	C27	116.9(9)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

respectively. A plot of the molecular structure, showing the atom labelling scheme, is shown in Fig. 3.

Discussion

The structures of the three complexes are qualitatively similar with the central Mo atom in each case surrounded by an octahedral coordination shell composed of four carbonyl groups and two phosphorus ligands *cis* to each other. In each case the entire molecule constitutes the crystallographic asymmetric unit and has no imposed symmetry. The average Mo–C distance, over all three compounds, is 2.010[6] Å*; the Mo–P distances range from 2.487(2) to 2.563(2) Å, with an average value of 2.51[1] Å. The P–Mo–P angles are 88.06(4)° and 86.36(7)° in compounds *1* and *2*, respectively; and the P–Mo–P chelate bite angle is 72.02(7)° in compound *3*.

In the complex anion $[Mo(CO)_4(PPh_2O)_2H]^-$ of *1* the intramolecular contact between atoms O(5) and O(6), 2.415(4) Å, is indicative of a rather strong hydrogen bond. Although the hydrogen atoms were not located for this structure, the close O···O contact [13] and its symmetrical environment support the notion that the hydrogen atom symmetrically, or very nearly symmetrically, bridges the two oxygen atoms. That the O(5)–O(6) distance is identical to the O–O separation in the two above-mentioned Pd(II) complexes [7–9] seems to be significant. This common observation suggests that the proton itself determines the O(5)–O(6) distance in complexes of this type and not other factors such as the metal or auxiliary ligands and their associated electronic and steric factors.

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*The estimated deviation in brackets is calculated as $[\ ] = [\Sigma_i \Delta_i^2/n(n-1)]^{1/2}$ in which Δ_i is the deviation of the i^{th} value from the mean of the n values in the sample.

In compound *2*, the two Mo–P distances (Mo–P(1), 2.487(2) Å and Mo–P(2), 2.563(2) Å) are significantly different, as are the two P–O distances P(1)–O(5), 1.638(5) Å; P(2)–O(6), 1.556(5) Å). Atom P(1), which is more strongly bound to the central molybdenum, at the same time forms a weaker bond to atom O(5) of the 2-(dimethylamino)-ethoxy moiety.

There is a set of close contacts involving atoms O(6), O(5), N(1) and O(7) of structure *2*. Since the hydrogen atoms present in this region have not been located, the interpretation of these contacts is necessarily speculative. We propose the following explanation. The O(7)···O(6) (2.790(11) Å) hydrogen bond is formed by a hydrogen atom of the $H_2O(7)$ water molecule. The P(2)–O(6) distance suggests that we have here a P–OH group which is then strongly hydrogen bonded to N(1). This O(6)–H··· N(1) hydrogen bond (O(6)···N(1), 2.575(9) Å) positions N(1) close (2.77 Å) to O(5). The O(5) to O(6) distance, 3.073(7) Å, and the O(7) to N(1) distance, 3.70(1) Å, indicate that there are no hydrogen bonds between these pairs of atoms.

The structure of compound *3* shows no remarkable features. The four-membered chelate ring is essentially planar and, except for the phenyl ring orientations, the molecule has essentially C_{2v} symmetry. All bond lengths are within normal ranges. The bond angles of the four-membered chelate rings in *3* and $[Mo(CO)_4(PPh_2OPPh_2)]$ are quite different. Especially obvious is the difference in the P–S–P (86.9°) and P–O–P (103.3°) angles. Although the acute P–S–P angle may be reflective of the effects of long P–S bonds and angle compression required for chelation, more important and perhaps controlling factors are the natural bond angles of sulfur and oxygen. Typically, the bond angles in covalent sulfides such as H_2S, RSH and RSR tend to be smaller by 10–12° than in the oxygen analogs [14].

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Supplementary Material

Tables of anisotropic thermal parameters (B's) and observed and calculated structures factors for all three structures (42 pages). Available on request from F.A.C.

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