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cis-Tetracarbonylbis(triphenyl phosphite)-molybdenum(0)

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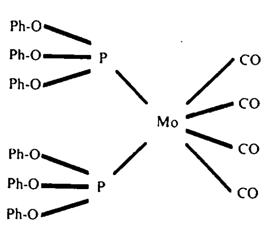
Abstract

The coordination environment of the Mo atom in the title compound, [$Mo(CO)_4\{P(C_6H_5O)_3\}_2$], is pseudo-octahedral, with principle dimensions Mo—P 2.442 (1), 2.443 (2), Mo—C(*trans* to P) 2.003 (6), 2.016 (6), Mo—C(*trans* to C) 2.032 (7), 2.042 (6) Å, P—Mo—P 89.55 (5), *trans*-P—Mo—C 178.0 (2), 173.9 (2), *trans*-C—Mo—C 175.5 (2)°. The geometry about the P atom is distorted from tetrahedral, with larger Mo—P—O angles [mean 117.3 (2)°] and smaller O—P—O angles [mean 100.5 (2)°]. The short Mo—P bond distances indicate the strong π-acceptor ability of $P(OPh)_3$, as also evidenced by the highly shielded $\delta(^{95}Mo)$ value (−1754 p.p.m.).

Comment

The title compound, (1), was synthesized as part of our studies of the nature of P^{III} ligands as probed by ^{95}Mo NMR spectroscopy (Alyea & Song, 1992, 1994). A search of the April 1993 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1993) for structures containing the $Mo(CO)_4P_2$ fragment revealed several structures of this type, but no phosphite structures. The only relevant structure found was for the corresponding phosphine derivative *cis*-$Mo(CO)_4(PPh_3)_2$, (2) (Cotton, Darensbourg, Klein & Kolthammer, 1982). Following our determination (Alyea, Ferguson, Gallagher & Song, 1994) that the *p*-F substitutent in *cis*-$Mo(CO)_4[P(C_6H_4F\text{-}p)_3]_2$, (3), causes considerable distortions compared to those reported for (2), we wished to examine the structural consequences of phenoxy substitutents.



(1)

A general view of molecule (1) is shown in Fig. 1 and the dimensions (Table 2) show that the Mo atom has a pseudo-octahedral coordination environment in the solid state. As expected, the average Mo—P bond distance in (1) [2.442 (2) Å] is considerably less than the average Mo—P bond distance in the triphenylphosphine analogue (2) [2.577 (2) Å]. In spite of the short Mo—P distance, distortion within the complex (as measured by the P—Mo—P angle) is less than that found in (2), which can be attributed to the smaller cone angle for $P(OPh)_3$ (128°) than for PPh_3 (145°) (Tolman, 1977). The P—Mo—P angle in (1) [89.55 (5)°] is nearly ideal compared to the corresponding angles in (2) [104.62 (7)°] and the (p-$FC_6H_5)_3P$ complex (3) [107.327 (13)°]. The resistance to deformation of the P—Mo—P angle may be enhanced by the shortened Mo—P bond distance, which is obviously a consequence of the greater π-acceptor ability of the phosphite ligand. The significantly greater shielding of the Mo nucleus in (1), as given by the $\delta(^{95}Mo)$ value of −1754 p.p.m., relative to −1556 p.p.m. for (2) (Alyea & Somogyvari, 1988), is consistent with $P(OPh)_3$ being a much better π-acceptor ligand than PPh_3.

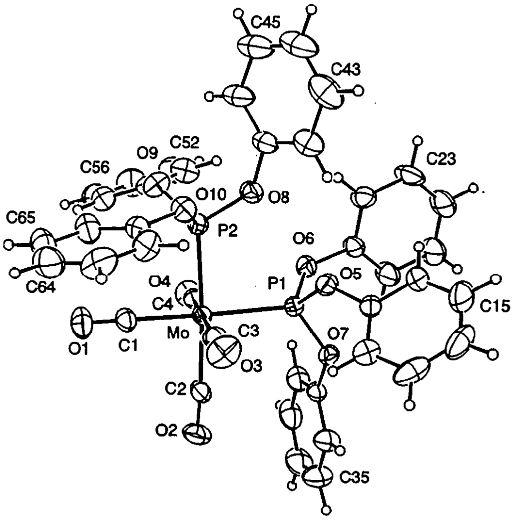


Fig. 1. A view of the title molecule with atomic numbering scheme; non-H atoms are shown with displacement ellipsoids at the 30% probability level and all H atoms are drawn as small spheres of arbitrary size.

Other angles around the Mo atom show significant departures from the values for idealized octahedral geometry; *cis*-P—Mo—C angles are 88.2 (2)-95.7 (2)° and *cis*-C—Mo—C angles are 87.5 (2)-92.0 (2)°. The *trans*-P—Mo—C angles [173.9 (2), 178.0 (2)°] and C—Mo—C angle [175.5 (2)°] are considerably less distorted from 180° than the analogous P—Mo—C [166.76 (5)°] and C—Mo—C [174.31 (8)°] angles in complex (3). The Mo,P1,P2,C1,C2 moiety is slightly nonplanar [the dihedral angle between the Mo,P1,P2 and Mo,C1,C2 planes is 4.5 (3)°].

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Intramolecular repulsions within molecule (1) are manifested by a bending of the angles Mo—C2—O2 [175.4 (5)°] and Mo—C4—O4 [175.1 (5)°] compared to the other two Mo—C—O angles [178.1 (5) and 178.2 (5)°]. Distortion of the tetrahedral geometry at the P atoms is shown by two of the Mo—P—O angles [121.9 (1) and 120.4 (2)°] being much larger than the other four [112.5 (1)-118.5 (2)°]. The O—P—O angles are also irregular and have values [96.9 (2)-104.4 (2)°] which are much less than the tetrahedral value.

The mean length of the Mo—C bonds *trans* to P [2.010 (6) Å] is shorter than the mean length of the Mo—C bonds *trans* to C [2.037 (6) Å]. The analogous average bond distances in molecules (2) and (3) differ by 0.034 and 0.044 Å, respectively. The smaller difference in molecule (1) is consistent with the $P(OPh)_3$ ligand being more effective than the triarylphosphine ligands in (2) and (3) at competing with the *trans* CO ligands, as a result of its greater π-acceptor ability.

Other bond distances and angles in (1) are normal and are available as supplementary material. Intermolecular contacts are of the van der Waals type.

Experimental

The compound was synthesized by adding the phosphite ligand (in a 2.2:1 ratio) to a dichloromethane solution of $Mo(CO)_4(piperidine)_2$ and stirring for 1 h. Filtration through Celite, reduction of the volume and addition of methanol gave colourless crystals. Recrystallization from dichloromethane-methanol gave crystals suitable for X-ray analysis. The infrared spectrum in the δ(CO) stretching region and the melting point were in good agreement with literature data (Darensbourg & Kump, 1978; Magee, Matthews, Wang & Wotiz, 1961).

Crystal data

$[Mo(CO)_4(C_{18}H_{15}O_3P)_2]$
$M_r = 828.55$
Monoclinic
$P2_1$
$a = 11.4069$ (18) Å
$b = 16.2441$ (8) Å
$c = 11.8091$ (17) Å
$\beta = 118.187$ (9)°
$V = 1928.7$ (4) Å^3
$Z = 2$
$D_x = 1.427$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 11.50$-19.50°
$\mu = 0.47$ mm^{-1}
$T = 293$ K
Plate
0.14 × 0.28 × 0.51 mm
Colourless

Data collection

Nonius CAD-4 diffractometer
θ-2θ scans
Absorption correction: empirical
$T_{min} = 0.945$, $T_{max} = 0.992$
4544 measured reflections
4344 independent reflections

2886 observed reflections [$I_{net} > 3.0\sigma(I_{net})$]
$R_{int} = 0.013$
$\theta_{max} = 26.91$°
$h = -14 \rightarrow 12$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F
$R = 0.028$
$wR = 0.035$
$S = 0.94$
2886 reflections
477 parameters
$w = 1/[\sigma^2(F) + 0.0008F^2]$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Mo	0.83997 (5)	0.75	0.75486 (4)	0.0425 (3)
P1	0.73942 (16)	0.70428 (10)	0.53161 (14)	0.0444 (10)
P2	0.84415 (17)	0.89086 (10)	0.68446 (15)	0.0477 (10)
O1	0.9756 (6)	0.8135 (4)	1.0403 (5)	0.088 (4)
O2	0.8213 (7)	0.5783 (4)	0.8705 (6)	0.093 (5)
O3	0.5497 (6)	0.7836 (4)	0.7144 (6)	0.093 (5)
O4	1.1218 (5)	0.6949 (4)	0.7909 (5)	0.074 (4)
O5	0.6090 (4)	0.7534 (4)	0.4344 (4)	0.060 (3)
O6	0.8370 (4)	0.7159 (3)	0.4697 (4)	0.055 (3)
O7	0.6815 (4)	0.6126 (3)	0.4897 (4)	0.052 (3)
O8	0.7939 (5)	0.9019 (3)	0.5339 (4)	0.062 (3)
O9	0.9787 (5)	0.9447 (3)	0.7523 (5)	0.068 (3)
O10	0.7460 (5)	0.9579 (3)	0.6960 (4)	0.062 (3)
C1	0.9244 (7)	0.7912 (4)	0.9362 (6)	0.057 (4)
C2	0.8284 (7)	0.6387 (4)	0.8245 (6)	0.059 (5)
C3	0.6541 (8)	0.7727 (4)	0.7302 (6)	0.059 (5)
C4	1.0221 (7)	0.7178 (4)	0.7756 (5)	0.048 (4)
C11	0.4817 (6)	0.7256 (3)	0.3515 (6)	0.051 (4)
C12	0.4021 (8)	0.6941 (5)	0.3982 (7)	0.071 (5)
C13	0.2722 (10)	0.6745 (5)	0.3147 (12)	0.097 (8)
C14	0.2255 (10)	0.6858 (6)	0.1853 (13)	0.113 (8)
C15	0.3053 (11)	0.7156 (7)	0.1407 (9)	0.109 (7)
C16	0.4344 (8)	0.7359 (6)	0.2231 (7)	0.081 (6)
C21	0.7950 (7)	0.7118 (5)	0.3360 (6)	0.057 (5)
C22	0.7795 (8)	0.7843 (5)	0.2722 (8)	0.072 (6)
C23	0.7398 (12)	0.7824 (6)	0.1418 (9)	0.094 (8)
C24	0.7202 (12)	0.7089 (8)	0.0807 (8)	0.101 (9)
C25	0.7367 (12)	0.6375 (6)	0.1446 (9)	0.102 (8)
C26	0.7758 (10)	0.6370 (5)	0.2769 (8)	0.086 (7)
C31	0.7458 (7)	0.5406 (4)	0.5519 (6)	0.053 (4)
C32	0.8775 (8)	0.5268 (4)	0.5901 (7)	0.066 (5)
C33	0.9336 (10)	0.4528 (6)	0.6448 (8)	0.087 (7)
C34	0.8624 (16)	0.3938 (7)	0.6621 (9)	0.118 (11)
C35	0.7304 (15)	0.4075 (6)	0.6240 (11)	0.115 (11)
C36	0.6696 (9)	0.4827 (5)	0.5672 (8)	0.079 (6)
C41	0.7485 (8)	0.9750 (4)	0.4607 (7)	0.062 (5)
C42	0.6230 (10)	0.9740 (6)	0.3624 (9)	0.087 (7)
C43	0.5783 (11)	1.0438 (9)	0.2842 (10)	0.112 (9)
C44	0.6561 (16)	1.1100 (8)	0.3067 (13)	0.114 (11)
C45	0.7802 (14)	1.1092 (6)	0.4053 (12)	0.106 (10)
C46	0.8293 (10)	1.0413 (5)	0.4854 (9)	0.086 (7)
C51	1.1045 (7)	0.9121 (4)	0.7809 (7)	0.061 (5)
C52	1.1331 (9)	0.8894 (6)	0.6854 (8)	0.078 (6)
C53	1.2578 (11)	0.8605 (7)	0.7165 (11)	0.101 (9)
C54	1.3522 (10)	0.8568 (7)	0.8407 (13)	0.098 (8)
C55	1.3255 (9)	0.8802 (7)	0.9365 (9)	0.094 (7)
C56	1.1950 (8)	0.9090 (5)	0.9061 (8)	0.075 (6)
C61	0.7383 (7)	0.9764 (4)	0.8076 (6)	0.058 (5)
C62	0.6096 (8)	0.9865 (5)	0.7915 (8)	0.080 (6)
C63	0.5972 (11)	1.0079 (6)	0.9004 (12)	0.100 (9)
C64	0.7058 (15)	1.0196 (6)	1.0130 (11)	0.105 (10)
C65	0.8279 (12)	1.0104 (6)	1.0276 (8)	0.098 (8)
C66	0.8448 (8)	0.9886 (5)	0.9242 (7)	0.076 (6)

Table 2. *Selected geometric parameters* (Å, °)

Mo—P1	2.4415 (14)	P2—O10	1.613 (4)
Mo—P2	2.4426 (15)	O1—C1	1.143 (7)

Mo—C1	2.003 (6)	O2—C2	1.143 (8)
Mo—C2	2.016 (6)	O3—C3	1.129 (9)
Mo—C3	2.032 (7)	O4—C4	1.127 (8)
Mo—C4	2.042 (6)	O5—C11	1.389 (6)
P1—O5	1.598 (4)	O6—C21	1.419 (7)
P1—O6	1.605 (4)	O7—C31	1.391 (7)
P1—O7	1.610 (4)	O8—C41	1.415 (7)
P2—O8	1.600 (4)	O9—C51	1.413 (8)
P2—O9	1.612 (4)	O10—C61	1.394 (7)
P1—Mo—P2	89.55 (5)	O5—P1—O7	97.71 (23)
P1—Mo—C1	177.96 (18)	O6—P1—O7	103.97 (21)
P1—Mo—C2	94.57 (16)	Mo—P2—O8	115.43 (16)
P1—Mo—C3	88.51 (16)	Mo—P2—O9	120.40 (18)
P1—Mo—C4	89.08 (15)	Mo—P2—O10	118.51 (17)
P2—Mo—C1	88.49 (18)	O8—P2—O9	104.38 (24)
P2—Mo—C2	173.94 (17)	O8—P2—O10	96.86 (22)
P2—Mo—C3	88.17 (16)	O9—P2—O10	97.34 (24)
P2—Mo—C4	95.65 (15)	P1—O5—C11	130.7 (4)
C1—Mo—C2	87.42 (24)	P1—O6—C21	124.0 (4)
C1—Mo—C3	92.00 (23)	P1—O7—C31	125.3 (3)
C1—Mo—C4	90.54 (23)	P2—O8—C41	127.5 (4)
C2—Mo—C3	87.50 (24)	P2—O9—C51	122.4 (4)
C2—Mo—C4	88.87 (24)	P2—O10—C61	125.6 (4)
C3—Mo—C4	175.47 (22)	Mo—C1—O1	178.1 (5)
Mo—P1—O5	115.25 (17)	Mo—C2—O2	175.4 (5)
Mo—P1—O6	112.49 (14)	Mo—C3—O3	178.2 (5)
Mo—P1—O7	121.91 (14)	Mo—C4—O4	175.1 (5)
O5—P1—O6	102.97 (20)		

The space group was determined as either $P2_1$ or $P2_1/m$ from the systematic absences ($0k0$ absent if $k = 2n + 1$); $P2_1$ was chosen and confirmed by the analysis. All H atoms were clearly visible in difference maps calculated at intermediate stages of refinement; they were then positioned on geometric grounds (C—H 0.95 Å) and included as riding atoms in the structure-factor calculations. Space group $P2_1$ is chiral and calculations with the coordinates as listed and with their inverse, clearly showed that the correct enantiomer had been chosen for the crystal selected for the analysis; the R and wR values for the other enantiomer were higher (0.0306 and 0.0387 compared with 0.0275 and 0.0345, respectively). There is no solvent of crystallization present in the lattice and an examination of the crystal structure using *PLATON* (Spek, 1990) revealed no potential volume for any solvent molecules. Data collection and cell refinement were performed using *CAD*-4 *Software* (Enraf-Nonius, 1989). *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) was used for data reduction, structure solution and refinement, and for preparation of the material for publication. The diagram was prepared using *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71838 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1120]

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Hydrogen Bonding in Ferrocene Derivatives: Structure of the 1:1 Adduct of Ferrocenyl(diphenyl)methanol and Dimethyl Sulfoxide

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Abstract

Ferrocenyl(diphenyl)methanol, $[(C_5H_5)Fe\{(C_5H_4)C(Ph_2)OH\}]$, forms a 1:1 adduct with dimethyl sulfoxide, $(CH_3)_2SO$. In this adduct, the hydrogen-bonded aggregate consists of one molecule of the ferrocene acting as hydrogen-bond donor and one molecule of DMSO acting as hydrogen-bond acceptor; the hydrogen-bonded O···O distance is 2.796 (2) Å.

Comment

The diol ferrocene-1,1′-diylbis(diphenylmethanol), $[Fe\{(C_5H_4)CPh_2OH\}_2]$ (I), forms hydrogen-bonded adducts with a wide range of hydrogen-bond donor and acceptor molecules (Ferguson, Gallagher, Glidewell & Zakaria, 1993*a*; Glidewell, Ferguson, Lough & Zakaria, 1994). These adducts exhibit a very wide range of structural types and, for certain hydrogen-bond acceptors, several distinct adducts of different stoichiometries are formed. Thus, for example, (I) forms two adducts with dimethyl sulfoxide (DMSO) which have