

Refinement

Refinement on F	$(\Delta/\sigma)_{\max} = 0.014$
$R = 0.0448$	$\Delta\rho_{\max} = 1.19 \text{ e } \text{\AA}^{-3}$ (ghost of Ag atom)
$wR = 0.0498$	$\Delta\rho_{\min} = -0.46 \text{ e } \text{\AA}^{-3}$
$S = 1.11$	Extinction correction: none
1044 reflections	Atomic scattering factors from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)
101 parameters	
H-atom parameters not refined	
$w = 1/[\sigma^2(F) + (0.02F)^2 + 1 - F]$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
W	0.7486	-0.13864 (4)	0.2506	0.0343 (2)
Ag	0.2464 (7)	-0.13737 (9)	0.2446 (4)	0.0570 (5)
S1	0.554 (1)	-0.0772 (3)	0.3179 (9)	0.062 (3)
S2	0.984 (1)	-0.1635 (3)	0.3986 (7)	0.050 (2)
S3	0.536 (1)	-0.2018 (3)	0.1944 (8)	0.056 (2)
S4	0.922 (1)	-0.1133 (4)	0.0965 (7)	0.058 (2)
O	0.325 (3)	-0.0746 (9)	0.829 (2)	0.067 (6)
N1	0.253 (4)	-0.0170 (9)	0.964 (2)	0.048 (6)
N2	0.552 (4)	-0.157 (1)	0.751 (2)	0.052 (7)
C1	0.313 (7)	0.008 (2)	1.075 (4)	0.10 (1)
C2	0.051 (7)	0.000 (2)	0.904 (4)	0.09 (1)
C3	0.368 (5)	-0.053 (1)	0.923 (3)	0.049 (8)
C11	0.796 (5)	-0.141 (1)	0.734 (3)	0.068 (9)
C12	0.801 (6)	-0.092 (2)	0.658 (3)	0.08 (1)
C21	0.547 (6)	-0.194 (1)	0.851 (3)	0.07 (1)
C22	0.322 (7)	-0.198 (2)	0.889 (4)	0.10 (1)
C31	0.419 (5)	-0.170 (1)	0.643 (3)	0.057 (9)
C32	0.519 (6)	-0.215 (1)	0.581 (3)	0.07 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

W—Ag	2.991 (6)	W—S4	2.211 (9)
W—Ag ⁱ	2.975 (6)	Ag—S1	2.545 (11)
W—S1	2.196 (9)	Ag—S2 ⁱⁱ	2.539 (11)
W—S2	2.211 (8)	Ag—S3	2.550 (10)
W—S3	2.192 (9)	Ag—S4 ⁱⁱ	2.552 (11)
Ag—W—Ag ⁱ	177.1 (2)	S1—Ag—S3	91.5 (4)
S1—W—S2	106.6 (4)	S1—Ag—S4 ⁱⁱ	123.0 (4)
S1—W—S3	112.5 (3)	S2 ⁱⁱ —Ag—S3	115.4 (4)
S1—W—S4	109.5 (4)	S2 ⁱⁱ —Ag—S4 ⁱⁱ	92.8 (3)
S2—W—S3	107.7 (4)	S3—Ag—S4 ⁱⁱ	121.3 (4)
S2—W—S4	113.0 (3)	W—S1—Ag	77.8 (3)
S3—W—S4	107.7 (4)	W—S2—Ag ⁱ	77.2 (3)
W—Ag—W ⁱⁱ	177.1 (2)	W—S3—Ag	77.8 (3)
S1—Ag—S2 ⁱⁱ	114.9 (4)	W—S4—Ag ⁱ	77.0 (3)

Symmetry codes: (i) $1 + x, y, z$; (ii) $x - 1, y, z$.

The structure and its enantiomorph were refined by full-matrix least-square methods; the absolute configuration was assigned to the enantiomorph that gave the better of the two sets of agreement factors (R , wR and S). H atoms were all located theoretically and not refined. Structure solution and refinement were carried out on a Compaq PROLINEA 4/50 computer.

Data collection: *CONTROL* (Molecular Structure Corporation, 1988). Cell refinement: *CONTROL*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *GCIF* (local program).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DE1020). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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***trans*-[Mo(CO)₄{P(OMe)₃]₂]**

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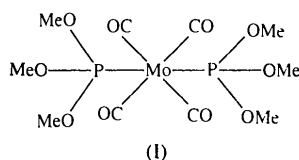
Abstract

Crystals of *trans*-tetracarbonylbis(trimethyl phosphite)-molybdenum(0) contain discrete [Mo(C₃H₉O₃P)₂(CO)₄] molecules whose metal atoms occupy crystallographic inversion centres. Valency angles at the Mo atom deviate from ideal octahedral values by no more than 3.3 (1)°. Mo–ligand bond lengths are normal, with an Mo–P distance of 2.4256 (8) and Mo–C distances of 2.041 (3) and 2.037 (4) Å.

Comment

The title complex, *trans*-tetracarbonylbis(trimethyl phosphite)molybdenum(0), (I), has been prepared previously in a mixture of [Mo(CO)_{6-n}{P(OMe)₃]_n] ($n =$

1–6) species (Andrews, Colquhoun, McFarlane & Grim, 1982). Until now, however, its structure has not been reported.



As part of a systematic study of Mo–phosphite complexes, we have prepared and isolated (I) by reaction of [Mo(CO)₆] with P(OMe)₃ in refluxing deoxygenated MeCN solution. While ³¹P and ⁹⁵Mo NMR spectroscopic studies on the isolated product indicate the presence of both (I) and *fac*-[Mo(CO)₃{P(OMe)₃}₃], cooling a pentane solution of this material yielded colourless blocks of (I). The X-ray structure analysis shows the Mo atom occupying a crystallographic inversion centre at (0,0,0), coordinated to four carbonyl ligands and two *trans*-P(OMe)₃ ligands, with an Mo–P distance of 2.4256 (8), and Mo–C distances of 2.041 (3) and 2.037 (4) Å (Fig. 1). The angles subtended by *cis* ligands around the Mo atom are in the range 86.7 (1)–93.3 (1)°, resulting in slightly distorted octahedral geometry. The Mo–P and Mo–C bond lengths are comparable with those observed

in related molybdenum(0)–phosphite species; for example, in [Mo(CO)₅{P(OCH₂)₃CMe}], with an Mo–P distance of 2.417 (1) and Mo–C distances in the range 2.025 (7)–2.052 (8) Å (Aroney, Davies, Hambly & Pierens, 1994), and *fac*-[Mo(CO)₃{P(OMe)₂O}]₃-SiMe₃-P,P',P''], with Mo–P distances in the range 2.4367 (8)–2.4504 (8) and Mo–C distances in the range 2.005 (3)–2.010 (3) Å (Greene, Taylor, Kee & Thornton-Pett, 1993).

Experimental

Suitable crystals of (I) were obtained by cooling a solution of the complex in pentane to 243 K. The selected crystal was coated with mineral oil and mounted on a glass fibre.

Crystal data

[Mo(C₃H₉O₃P)₂(CO)₄]

M_r = 456.13

Monoclinic

*P*2₁/*n*

a = 6.992 (3) Å

b = 13.356 (5) Å

c = 9.521 (3) Å

β = 104.05 (3)°

V = 862.5 (5) Å³

Z = 2

D_x = 1.756 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25

reflections

θ = 24.35–25.00°

μ = 0.989 mm⁻¹

T = 150.0 K

Block

0.30 × 0.25 × 0.15 mm

Pale yellow

Data collection

Rigaku AFC-7S diffractometer

ω/2θ scans

Absorption correction:

ψ scans (TEXSAN;

Molecular Structure

Corporation, 1992)

T_{min} = 0.868, *T_{max}* =

1.000

1735 measured reflections

1603 independent reflections

1413 observed reflections

[*I* ≥ 3σ(*I*)]

R_{int} = 0.023

θ_{max} = 25.00°

h = 0 → 8

k = 0 → 15

l = -11 → 10

3 standard reflections

monitored every 150

reflections

intensity decay: 0.61%

Refinement

Refinement on *F*

R = 0.0290

wR = 0.0363

S = 3.083

1413 reflections

106 parameters

H-atom parameters not

refined

w = 1/σ²(*F*)

(Δ/σ)_{max} = 0.006

Δρ_{max} = 0.64 e Å⁻³

Δρ_{min} = -1.18 e Å⁻³

(within 1 Å of Mo)

Atomic scattering factors

from *International Tables*

for X-ray Crystallography

(1974, Vol. IV)

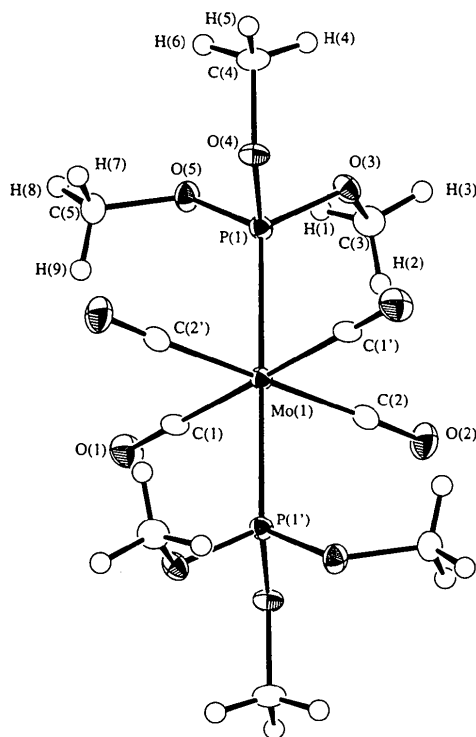


Fig. 1. View of the structure of *trans*-[Mo(CO)₄{P(OMe)₃}₂] showing the numbering scheme adopted. Displacement parameters are illustrated at the 40% probability level. The operation (-*x*, -*y*, -*z*) is indicated by a prime.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Mo	0	0	0	0.0149 (1)
P(1)	0.1242 (1)	0.08862 (6)	0.22614 (9)	0.0162 (2)
O(1)	0.1450 (4)	0.1682 (2)	-0.1878 (3)	0.0317 (7)

O(2)	0.4035 (4)	-0.1162 (2)	0.0196 (3)	0.0326 (7)
O(3)	0.3162 (3)	0.0490 (2)	0.3418 (2)	0.0211 (6)
O(4)	-0.0307 (3)	0.0856 (2)	0.3246 (2)	0.0200 (6)
O(5)	0.1896 (3)	0.2043 (2)	0.2274 (2)	0.0221 (6)
C(1)	0.0936 (5)	0.1080 (2)	-0.1198 (3)	0.0191 (8)
C(2)	0.2587 (5)	-0.0742 (2)	0.0148 (3)	0.0209 (9)
C(3)	0.5099 (5)	0.0590 (3)	0.3135 (4)	0.0256 (9)
C(4)	0.0116 (5)	0.1333 (3)	0.4665 (4)	0.0254 (9)
C(5)	0.0547 (5)	0.2776 (2)	0.1466 (4)	0.0277 (10)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Mo—P(1)	2.4256 (8)	O(1)—C(1)	1.145 (4)
Mo—C(1)	2.041 (3)	O(2)—C(2)	1.149 (4)
Mo—C(2)	2.037 (4)	O(3)—C(3)	1.451 (4)
P(1)—O(3)	1.606 (2)	O(4)—C(4)	1.458 (4)
P(1)—O(4)	1.595 (2)	O(5)—C(5)	1.445 (4)
P(1)—O(5)	1.611 (2)		
P(1)—Mo—C(1)	93.30 (9)	O(3)—P(1)—O(5)	97.0 (1)
P(1)—Mo—C(2)	93.12 (9)	O(4)—P(1)—O(5)	104.6 (1)
C(1)—Mo—C(2)	89.0 (1)	P(1)—O(3)—C(3)	120.3 (2)
Mo—P(1)—O(3)	120.52 (9)	P(1)—O(4)—C(4)	121.3 (2)
Mo—P(1)—O(4)	111.16 (9)	P(1)—O(5)—C(5)	119.9 (2)
Mo—P(1)—O(5)	121.02 (9)	Mo—C(1)—O(1)	179.6 (3)
O(3)—P(1)—O(4)	99.3 (1)	Mo—C(2)—O(2)	178.2 (3)

The diffractometer was equipped with an Oxford Systems low-temperature attachment (Cosier & Glazer, 1986). As there were no identifiable faces, the data were corrected for absorption using ψ scans. All non-H atoms were refined anisotropically. H atoms were included in fixed calculated positions assuming staggering across O—CH₃ bonds, with a C—H distance of 0.96 \AA . $U(\text{H})$ was set equal to $1.2U_{\text{eq}}(\text{C})$ and left unaltered during subsequent refinement.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

We thank the University of Southampton for support and the EPSRC for a grant to purchase the diffractometer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1224). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[Pt(PMe₃)₂(dppm)]Cl₂·2H₂O [dppm = Bis-(diphenylphosphino)methane]

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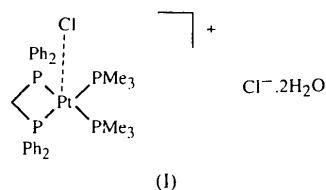
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Abstract

The crystal structure of [bis(diphenylphosphino)methane]bis(trimethylphosphine)platinum(II) chloride dihydrate, [Pt(C₃H₉P)₂(C₂₅H₂₂P₂)]Cl₂·2H₂O, contains [Pt(PMe₃)₂(dppm)]²⁺ cations with the Pt^{II} ion bound to a distorted square-planar arrangement of one chelating dppm ligand and two PMe₃ ligands [Pt—P(dppm) 2.317 (6), 2.352 (7) \AA ; Pt—P(PMe₃) 2.331 (7), 2.345 (7) \AA]. A weakly interacting Cl⁻ ion occupies an apical coordination site [Pt··Cl 3.175 (7) \AA] and a discrete Cl⁻ anion is present to balance the charges. Two H₂O molecules are also present in the asymmetric unit.

Comment

The title complex, (I), was prepared by the reaction of [Pt(dppm)₂]Cl₂ with PMe₃ in MeCN solution. The X-ray structure (Fig. 1) shows a slightly distorted square-planar arrangement of phosphorus donors from one chelating dppm ligand and two PMe₃ ligands around the Pt^{II} centre.



The Pt—P distances involving the dppm ligand (average 2.335 \AA) and the PMe₃ ligands (average 2.337 \AA) are slightly longer than the distances found in similar structures involving P₄ coordination around a Pt^{II} centre, e.g. [Pt{Ph₂PCH₂CH₂P(Ph)CH₂CH₂P(Ph)CH₂CH₂PPh₂}] (BPh₄)₂·3CH₂Cl₂ (average Pt—P 2.30 \AA ; Brüggeller, Nar & Messerschmidt, 1992) and [Pt(Ph₂PCH₂CH₂PPh₂)(Ph₂PNHPPPh₂)]Cl₂·CH₂Cl₂ (average Pt—P 2.31 \AA ; Bhattacharyya, Sheppard, Slawin, Williams & Woollins, 1993). The P(1)—Pt(1)—P(2) angle in the five-membered chelate ring is 70.3 (2) $^\circ$, similar to the values observed in other structurally characterized examples of complexes incorporating chelating