

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$U_{eq} = (1/3) \sum_i \sum_j U^{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U _{eq}
Cu	0.41220 (2)	1/4	0.429551 (17)	0.03767 (14)
O1	0.48653 (13)	1/4	0.52604 (11)	0.0467 (5)
N1	0.53630 (15)	1/4	0.36423 (12)	0.0378 (5)
C1	0.58869 (17)	1/4	0.53476 (17)	0.0386 (6)
N2	0.27490 (16)	1/4	0.49067 (13)	0.0409 (5)
O2	0.33900 (14)	1/4	0.32988 (11)	0.0502 (5)
C2	0.6307 (2)	1/4	0.61258 (16)	0.0467 (6)
N3	0.08450 (19)	1/4	0.57191 (17)	0.0727 (11)
C3	0.7363 (2)	1/4	0.62682 (18)	0.0518 (7)
O3	0.35974 (18)	1/4	0.20051 (14)	0.1018 (12)
C4	0.8075 (2)	1/4	0.56476 (17)	0.0491 (7)
C5	0.77047 (19)	1/4	0.48833 (18)	0.0455 (6)
C6	0.66164 (18)	1/4	0.47180 (15)	0.0387 (5)
C7	0.63115 (19)	1/4	0.38929 (15)	0.0403 (6)
C8	0.5157 (2)	1/4	0.27742 (15)	0.0432 (6)
C9	0.3954 (2)	1/4	0.26703 (18)	0.0547 (8)
C10	0.56147 (17)	0.0633 (3)	0.23918 (12)	0.0556 (5)
C12	0.1833 (2)	1/4	0.45291 (18)	0.0515 (7)
C13	0.0894 (2)	1/4	0.4933 (2)	0.0665 (10)
C14	0.1756 (2)	1/4	0.60890 (19)	0.0687 (10)
C15	0.2706 (2)	1/4	0.56971 (16)	0.0524 (7)

Table 2. Selected geometric parameters (Å, °)

Cu—O1	1.8808 (18)	Cu—N1	1.925 (2)
Cu—O2	1.9204 (18)	Cu—N2	2.028 (2)
O1—Cu—O2	178.83 (7)	O1—Cu—N2	89.67 (8)
O1—Cu—N1	94.69 (8)	O2—Cu—N2	91.50 (8)
O2—Cu—N1	84.14 (8)	N1—Cu—N2	175.64 (9)

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *XCAD-4* (Harms, 1996). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996). Molecular graphics: *XP* (Siemens, 1996b). Software used to prepare material for publication: *SHELXL96* (Sheldrick, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1198). Services for accessing these data are described at the back of the journal.

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Tetracarbonylbis[(2-methoxyphenyl)diphenylphosphine-P]tungsten Dichloromethane 0.25-Solvate

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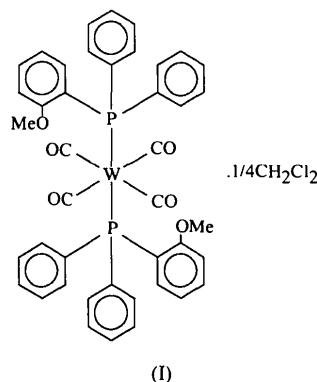
(Received 26 November 1996; accepted 22 April 1997)

Abstract

In the title complex, [W{P(C₆H₅)₂C₆H₄OCH₃-2}₂(CO)₄].1/4CH₂Cl₂, the W atom exhibits a slightly distorted octahedral coordination with the phosphine ligands in *trans* positions.

Comment

The title compound, (I), was prepared and its crystal structure examined as part of our continuing investigations on the coordination chemistry of functional phosphine ligands (Pietsch *et al.*, 1994; Pietsch, Dahlenburg, Wolski, Berke & Eremenko, 1995; Dahlenburg, Herbst & Kühnlein, 1997).



The structure consists of discrete molecules of the tungsten complex and dichloromethane solvate molecules lying on 4e positions with site symmetry

2. The W—P distances of 2.489 (2) Å observed for the two mutually *trans*-arranged phosphines are considerably shorter than those of 2.604 (3) [2.608 (3)] and 2.624 (3) Å [2.633 (3) Å] found for the *cis*-coordinated (2-methoxyphenyl)diphenylphosphine ligands in the two crystallographically independent cations of *mer,cis*-[W(CO)₂(NO){P(C₆H₅)₂C₆H₄OCH₃-2}₂NCCH₃][SbF₆] and thus confirm significant steric crowding between the bulky methoxy-substituted phosphines in the latter complex (Pietsch *et al.*, 1995).

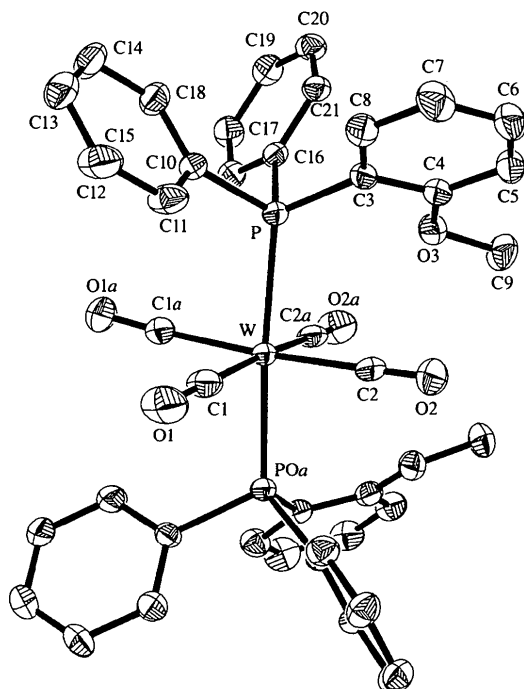


Fig. 1. Structure of the title complex with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.

Experimental

An equimolar mixture of [W(CO)₆] (3.61 g, 10.26 mmol) and [N(CH₂CH₃)₄]Cl was heated in diethylene glycol dimethyl ether (40 ml), under a blanket of nitrogen, at 393 K for 2 h. The yellow solution of [N(CH₂CH₃)₄][W(CO)₅Cl] so generated was filtered while hot and subsequently treated with P(C₆H₅)₂C₆H₄OCH₃-2 (3.30 g, 11.29 mmol). The mixture was stirred under reduced pressure at 323 K for 30 min and then diluted with diethyl ether (25 ml) and *n*-pentane (50 ml) to deposit a yellow precipitate, which was extracted with CH₂Cl₂. The extracts were filtered and layered with *n*-pentane, which afforded (I) as yellow prisms suitable for X-ray diffraction studies. IR (KBr): 1940 cm⁻¹ (CO); ¹H NMR (CD₂Cl₂): δ 3.66 (*s*, 6H, OCH₃); ¹³C NMR (CD₂Cl₂): δ 54.8 (*s*, OCH₃), 204.7 (*t*, *cis*-²J_{PC} = 6.6 Hz, CO); ³¹P NMR (CD₂Cl₂): δ 22.4 (*s* with ¹⁸³W satellites, ¹J_{WP} = 286.4 Hz).

Crystal data

[W(C₁₉H₁₇OP)₂(CO)₄]-
0.25CH₂Cl₂
M_r = 901.71
Monoclinic
C2/c
a = 25.524 (8) Å
b = 15.174 (5) Å
c = 10.978 (3) Å
β = 109.07 (3)°
V = 4019 (2) Å³
Z = 4
D_x = 1.490 Mg m⁻³
D_m not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 18
reflections

θ = 14–16°

μ = 3.032 mm⁻¹

T = 293 (2) K

Prism

0.60 × 0.50 × 0.50 mm

Yellow

Data collection

Siemens P4 diffractometer

ω scans

Absorption correction:

ψ scans (SHELXTL-Plus;

Sheldrick, 1990)

T_{min} = 0.14, T_{max} = 0.22

5641 measured reflections

4461 independent reflections

3878 reflections with

I > 2σ(I)

R_{int} = 0.017

θ_{max} = 27.28°

h = -32 → 18

k = 0 → 19

l = -13 → 14

3 standard reflections

every 100 reflections

intensity decay: none

Refinement

Refinement on F²

R[F² > 2σ(F²)] = 0.040

wR(F²) = 0.148

S = 1.165

4461 reflections

243 parameters

H atoms constrained

w = 1/[σ²(F_o²) + (0.0927P)²]

where P = (F_o² + 2F_c²)/3

(Δ/σ)_{max} = -0.035

Δρ_{max} = 1.269 e Å⁻³

Δρ_{min} = -0.838 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for
Crystallography (Vol. C)

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

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

	x	y	z	U _{eq}
W	0	0.26066 (2)	1/4	0.03459 (15)
P	-0.10270 (7)	0.25432 (9)	0.1520 (2)	0.0354 (3)
O1	0.0230 (3)	0.4161 (4)	0.0840 (7)	0.085 (2)
O2	0.0084 (3)	0.1150 (4)	0.0475 (6)	0.077 (2)
O3	-0.0907 (2)	0.0625 (3)	0.1493 (5)	0.0523 (12)
C1	0.0131 (3)	0.3578 (5)	0.1395 (8)	0.052 (2)
C2	0.0056 (3)	0.1671 (5)	0.1215 (8)	0.051 (2)
C3	-0.1312 (2)	0.1807 (4)	0.0145 (6)	0.0400 (13)
C4	-0.1199 (3)	0.0892 (5)	0.0266 (7)	0.0450 (15)
C5	-0.1391 (3)	0.0323 (5)	-0.0786 (8)	0.056 (2)
C6	-0.1703 (3)	0.0656 (6)	-0.1946 (8)	0.063 (2)
C7	-0.1833 (4)	0.1527 (6)	-0.2106 (7)	0.067 (2)
C8	-0.1637 (3)	0.2110 (5)	-0.1064 (7)	0.053 (2)
C9	-0.0734 (4)	-0.0265 (5)	0.1647 (9)	0.068 (2)
C10	-0.1369 (2)	0.3594 (4)	0.0879 (6)	0.0398 (13)
C11	-0.1160 (3)	0.4078 (5)	0.0071 (8)	0.058 (2)
C12	-0.1415 (4)	0.4876 (6)	-0.0438 (11)	0.078 (3)
C13	-0.1877 (3)	0.5184 (5)	-0.0175 (9)	0.070 (2)
C14	-0.2083 (3)	0.4697 (5)	0.0618 (9)	0.064 (2)
C15	-0.1832 (3)	0.3906 (5)	0.1142 (8)	0.053 (2)
C16	-0.1432 (3)	0.2214 (4)	0.2567 (6)	0.0393 (13)

C17	-0.1270 (3)	0.2469 (4)	0.3827 (8)	0.049 (2)
C18	-0.1589 (4)	0.2270 (5)	0.4605 (8)	0.056 (2)
C19	-0.2074 (3)	0.1807 (5)	0.4105 (8)	0.055 (2)
C20	-0.2240 (3)	0.1543 (5)	0.2866 (7)	0.051 (2)
C21	-0.1924 (3)	0.1743 (4)	0.2084 (7)	0.0448 (14)
C22†	0	0.6100 (12)	1/4	0.052 (9)
Cl†	0.0529 (4)	0.6777 (12)	0.2375 (11)	0.139 (7)

† Site occupancy = 0.25.

Table 2. Selected geometric parameters (Å, °)

W—C1	2.005 (7)	W—P	2.489 (2)
W—C2	2.039 (8)		
C1 ¹ —W—C1	85.4 (5)	C2—W—P	88.7 (2)
C1 ¹ —W—C2	173.5 (3)	C2 ¹ —W—P	88.3 (2)
C1—W—C2	91.7 (3)	C1 ¹ —W—P ¹	97.3 (2)
C1 ¹ —W—C2 ¹	91.7 (3)	C1—W—P ¹	86.0 (2)
C1—W—C2 ¹	173.5 (3)	C2—W—P ¹	88.3 (2)
C2—W—C2 ¹	91.8 (4)	C2 ¹ —W—P ¹	88.7 (2)
C1 ¹ —W—P	86.0 (2)	P—W—P ¹	175.57 (7)
C1—W—P	97.3 (2)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

All non-H atoms were located by direct methods and subsequent alternate cycles of difference Fourier synthesis and full-matrix least-squares refinement. The final structural model used anisotropic displacement parameters for the non-H atoms, except for the C atom of the solvent molecule. H atoms were included in geometrically idealized positions employing appropriate riding models with isotropic displacement parameters constrained to $1.5U_{eq}$ of their carrier atoms. Refinement of the site-occupation factor of the CH₂Cl₂ molecule indicated a 25% occupancy of the respective positions. The high degree of anisotropy observed for the Cl atom suggests unresolved disorder. The highest peaks in the final difference map were located near the W and Cl atoms.

Data collection: P3/V (Siemens, 1989). Cell refinement: P3/V. Data reduction: SHELXTL-Plus (Sheldrick, 1990). Program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL-Plus. Software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1228). Services for accessing these data are described at the back of the journal.

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Carbonylchloro[2-(diphenylphosphino)-thiophenolato-*P,S*]hydrido(triphenylphosphine-*P*)iridium(III)–Dichloromethane Solvate (4/1)

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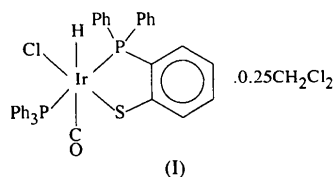
(Received 16 December 1996; accepted 4 April 1997)

Abstract

In the title complex, [IrH(Cl)(C₁₈H₁₄PS)(C₁₈H₁₅P)(CO)].·0.25CH₂Cl₂, the two P donors, the chloro and thiolato functions, and the carbonyl and hydride ligands are bonded in mutually *trans* positions. The five-membered chelate ring has an envelope conformation with the metal atom deviating from the plane defined by the P and S donors and the two bridging phenylene C atoms.

Comment

The title compound, (I), resulted from oxidative addition of hydrogen chloride to the iridium(I) complex [Ir(CO){P(C₆H₅)₃}{η²-P(C₆H₅)₂C₆H₄S-2}] (Dahlenburg, Herbst & Kühnlein, 1997). The present X-ray study was undertaken in order to confirm the stereochemistry of the product so obtained, since the hydride coordination *cis* or *trans* to S, Cl or CO could not be established unequivocally on the basis of IR and NMR data alone.



This structure determination proves that the hydride is bonded *trans* with respect to the CO, thiolato and chloro ligands, with the two P donors also occupying mutually *trans* sites in the pseudo-octahedral coordination sphere. The angle of 9.7 (4)° between the normals to the planes defined by P1, Ir and S, and P1, C2, C3 and S, indicates an envelope conformation of the five-membered chelate ring. As expected, the Ir—P bond within the metallacycle, 2.313 (2) Å, is slightly shorter than the distance between the central metal atom and the P(C₆H₅)₃ ligand, 2.357 (3) Å. Both Ir—P bond lengths are similar to those in related metallacyclic (triphenylphosphane)iridium(III) complexes, *e.g.* *mer*-[IrH(Br){P(C₆H₅)₃]₂{η²-P(C₆H₅)₂C₆H₄-2}] displaying