$wR = 0.0348$
$S = 0.82$
3221 reflections
469 parameters
Only coordinates of H atoms refined

$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Mo	0.04243 (3)	0.50954 (2)	0.76046 (2)	2.540 (8)
Br(1)	0.19767 (5)	0.44411 (3)	0.86280 (3)	3.71 (1)
Br(2)	−0.11811 (6)	0.56335 (2)	0.64844 (3)	3.99 (1)
Br(3)	0.04615 (6)	0.60681 (3)	0.85065 (3)	3.88 (1)
Br(4)	0.26687 (6)	0.54136 (3)	0.69257 (3)	3.90 (1)
N(1)	0.0201 (4)	0.4258 (2)	0.6838 (2)	2.98 (8)
N(2)	−0.1489 (4)	0.4798 (2)	0.8198 (2)	2.95 (8)
C(11)	0.0486 (6)	0.4274 (3)	0.6062 (3)	3.5 (1)
C(12)	0.0406 (6)	0.3752 (3)	0.5583 (3)	4.3 (1)
C(13)	−0.0010 (6)	0.3198 (3)	0.5898 (3)	4.5 (1)
C(14)	−0.0321 (6)	0.3174 (3)	0.6687 (3)	4.2 (1)
C(15)	−0.0191 (6)	0.3712 (2)	0.7134 (3)	3.7 (1)
C(21)	−0.2750 (5)	0.4673 (2)	0.7772 (3)	3.5 (1)
C(22)	−0.3969 (6)	0.4543 (3)	0.8130 (4)	4.4 (1)
C(23)	−0.3927 (6)	0.4514 (2)	0.8956 (4)	4.0 (1)
C(24)	−0.2657 (6)	0.4624 (3)	0.9402 (3)	3.9 (1)
C(25)	−0.1481 (5)	0.4773 (2)	0.9000 (3)	3.3 (1)
P	0.4239 (1)	0.76538 (6)	0.04856 (8)	2.67 (3)
C(30)	0.2455 (5)	0.7492 (2)	0.0740 (3)	2.8 (1)
C(31)	0.1871 (5)	0.7890 (2)	0.1289 (2)	3.4 (1)
C(32)	0.0499 (6)	0.7782 (3)	0.1496 (3)	4.1 (1)
C(33)	−0.0254 (3)	0.7287 (3)	0.1183 (3)	4.2 (1)
C(34)	0.0329 (6)	0.6893 (3)	0.0663 (3)	3.9 (1)
C(35)	0.1684 (5)	0.6989 (2)	0.0435 (3)	3.1 (1)
C(40)	0.5368 (5)	0.7629 (2)	0.1406 (3)	3.0 (1)
C(41)	0.6254 (5)	0.8113 (3)	0.1643 (3)	3.5 (1)
C(42)	0.7090 (6)	0.8065 (3)	0.2365 (3)	4.8 (1)
C(43)	0.7040 (6)	0.7553 (3)	0.2824 (4)	5.4 (2)
C(44)	0.6181 (9)	0.7064 (3)	0.2587 (4)	6.8 (2)
C(45)	0.5317 (8)	0.7103 (3)	0.1876 (3)	5.2 (1)
C(50)	0.4346 (5)	0.8395 (2)	0.0003 (3)	2.8 (1)
C(51)	0.5575 (6)	0.8533 (3)	−0.0365 (3)	4.2 (1)
C(52)	0.5691 (6)	0.9099 (3)	−0.0739 (3)	4.6 (1)
C(53)	0.4602 (6)	0.9513 (2)	−0.0765 (3)	3.9 (1)
C(54)	0.3392 (6)	0.9377 (3)	−0.0395 (3)	4.0 (1)
C(55)	0.3261 (5)	0.8822 (2)	−0.0013 (3)	3.4 (1)
C(60)	0.4761 (5)	0.7079 (2)	−0.0204 (3)	3.1 (1)
C(61)	0.5944 (6)	0.6706 (3)	−0.0022 (3)	4.2 (1)
C(62)	0.6274 (8)	0.6257 (3)	−0.0565 (4)	5.7 (2)
C(63)	0.5454 (8)	0.6176 (3)	−0.1264 (4)	5.9 (2)
C(64)	0.4288 (6)	0.6539 (3)	−0.1453 (3)	4.8 (1)
C(65)	0.3966 (6)	0.6998 (3)	−0.0924 (3)	4.1 (1)

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

Mo—Br(1)	2.5781 (7)	Mo—N(2)	2.224 (4)
Mo—Br(2)	2.5831 (7)	P—C(30)	1.803 (5)
Mo—Br(3)	2.5825 (7)	P—C(40)	1.796 (5)
Mo—Br(4)	2.5761 (7)	P—C(50)	1.799 (5)
Mo—N(1)	2.215 (4)	P—C(60)	1.789 (5)
Br(1)—Mo—N(1)	87.5 (1)	Br(4)—Mo—N(1)	90.4 (1)
Br(1)—Mo—N(2)	89.2 (1)	Br(1)—Mo—Br(2)	173.33 (2)
Br(1)—Mo—Br(3)	94.62 (2)	N(1)—Mo—Br(3)	175.3 (1)
Br(1)—Mo—Br(4)	89.66 (2)	N(2)—Mo—Br(4)	178.6 (1)
Br(2)—Mo—N(1)	85.8 (1)	C(30)—P—C(40)	107.0 (2)
Br(2)—Mo—N(2)	90.1 (1)	C(30)—P—C(50)	111.4 (2)
Br(2)—Mo—Br(3)	91.96 (2)	C(30)—P—C(60)	109.2 (2)
Br(2)—Mo—Br(4)	90.96 (2)	C(40)—P—C(50)	111.0 (2)
N(1)—Mo—N(2)	88.8 (1)	C(40)—P—C(60)	110.7 (2)
N(2)—Mo—Br(3)	87.0 (1)	C(50)—P—C(60)	107.6 (2)
Br(3)—Mo—Br(4)	93.82 (2)		

The displacement parameters of the H atoms were fixed at 1.3 times those of the C atoms to which they were connected. The *SDP* (Enraf–Nonius, 1985) and *NRCVAX* programs (Gabe, Le Page, Charland, Lee & White, 1989) were used for computing and graphics.

We are indebted to the Ministry of Research of the Republic of Slovenia and University of Ljubljana for supporting this work.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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{2,2-Bis[(diphenylphosphino)methyl]-1-phenylthiopropane-*P*,*P′*,*S*}tricarbonyltungsten(0)

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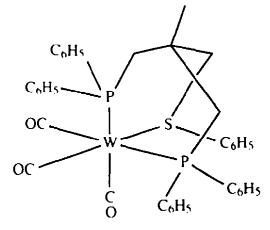
Abstract

The title complex, $[W(CO)_3(C_{35}H_{34}P_2S)]$, has an octahedral coordination geometry about the W atom, which is surrounded by three carbonyl ligands in a facial arrangement, two P atoms and one S atom.

Comment

Studies of metal complexes containing 'hybrid' donor ligands continue to be an interesting area in coordination chemistry, since the different donor atoms are able to modify the properties of the complexes. A tungsten carbonyl complex, (I), containing a tripodal sulfide–phosphine ligand, 2,2-bis[(diphenylphosphino)methyl]-1-phenylthiopropane (P_2S) has been prepared and its crystal structure determined.



(I)

The W atom displays a slightly distorted octahedral coordination geometry with the three carbonyl ligands in a facial arrangement. The three carbonyl stretching frequencies (1935, 1850 and 1831 cm^{-1}) support the *cis* relationship between them (Braterman, 1975). All bond distances lie within the normal range, as shown in Table 2. The W—S bond distance of 2.552 (2) Å is similar to those reported for (2,3-dihydrothiophene)-W($Ph_2PCH_2CH_2PPh_2$)(CO)$_3$ [2.573 (5) Å (Glavee, Daniels & Angelici, 1989)] and (CO)$_4$W(^{t}Bu-SCH$_2$CH$_2$S^{t}Bu) [2.565 (4) and 2.559 (5) Å (Reisner, Bernal & Dobson, 1978)]. The length of the metal to carbon bond *trans* to the S atom is shorter than those *trans* to the P atoms by about 0.05 Å; this is due to the *trans* influence of the donor atoms (Pidcock, Richards & Venanzi, 1966). The angles between any two of the donor atoms of the tripodal ligand and the metal center [P1—W—P2 83.95 (5), P1—W—S3 86.43 (5), P2—W—S3 80.74 (5)°] are less than the normal 90° because of the constraints imposed by the tripodal frame. All angles between C and any donor of the tripodal system [*i.e.* C(*n*)—W—P(*m*) or C(*n*)—W—S3; *n* = 6, 7 or 8, *m* = 1 or 2] are larger than 90° as a result of the steric interaction between the carbonyl ligands and the substituents of the donor atoms of the P_2S ligand (Table 2). Analysis of the dihedral angles around the chelate rings of the complex reveals that each of the rings has four positive and two negative values (Table 2). This indicates that all the rings are in twist-boat conformations, as expected.

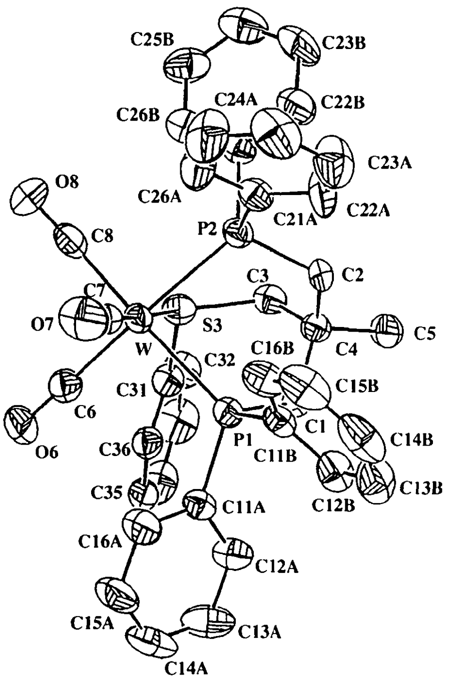


Fig. 1. An *ORTEP* (Johnson, 1965) drawing of the title complex. Displacement ellipsoids are shown at the 50% probability level. H atoms have been omitted for clarity.

Experimental

The title complex was prepared by the reaction of the tripodal ligand P_2S (Liu, Wang, Cheng & Peng, 1989; Wang, Cheng, Lee, Peng & Liu, 1993) and (η^6-cycloheptatriene)tricarbonyltungsten(0) in refluxing methylcyclohexane. The crude reaction mixture was purified by chromatography on silica gel with hexane/ethyl acetate as an eluant. Crystals suitable for X-ray analysis were obtained by recrystallization from hexane/ethyl acetate.

Crystal data

[W(CO)$_3$($C_{35}H_{34}P_2S$)]
M_r = 816.55
Orthorhombic
Pbca
a = 12.176 (4) Å
b = 20.336 (3) Å
c = 27.728 (7) Å
V = 6866 (3) Å^3
Z = 8
D_x = 1.58 Mg m^{-3}

Mo *Kα* radiation
λ = 0.7107 Å
Cell parameters from 24 reflections
θ = 12.1–13.5°
μ = 3.62 mm^{-1}
T = 298 K
Chunk
0.50 × 0.20 × 0.20 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min}$ = 0.77, $T_{\max}$ = 1.00
4456 measured reflections
4456 independent reflections

3199 observed reflections [$I > 2\sigma(I)$]
$\theta_{\max}$ = 22.5°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 29$
3 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F
$R = 0.024$
$wR = 0.017$
$S = 1.50$
3199 reflections
407 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.072$

$\Delta\rho_{\max} = 0.57$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ e Å^{-3}
Extinction correction: secondary
Extinction coefficient: $1.21\,(4) \times 10^{-4}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	$B_{\rm eq}$
W	0.03837 (2)	0.19096 (1)	0.10498 (1)	2.70 (1)
P1	0.2191 (1)	0.15136 (7)	0.07188 (5)	2.81 (7)
P2	0.1480 (1)	0.21287 (7)	0.18009 (5)	2.91 (7)
S3	0.1058 (1)	0.30685 (8)	0.08570 (5)	3.28 (7)
C1	0.3251 (4)	0.2161 (2)	0.0746 (2)	2.8 (3)
C2	0.2957 (4)	0.2260 (2)	0.1666 (2)	2.9 (3)
C3	0.2444 (4)	0.3218 (2)	0.1105 (2)	3.2 (3)
C4	0.3214 (4)	0.2630 (3)	0.1186 (2)	3.0 (3)
C5	0.4370 (4)	0.2926 (3)	0.1245 (2)	4.1 (3)
C6	−0.0386 (5)	0.1777 (3)	0.0432 (2)	3.6 (3)
O6	−0.0862 (3)	0.1694 (2)	0.0074 (1)	5.1 (2)
C7	−0.0133 (4)	0.1050 (3)	0.1234 (2)	3.6 (3)
O7	−0.0494 (4)	0.0531 (2)	0.1340 (2)	5.6 (2)
C8	−0.1006 (5)	0.2240 (3)	0.1320 (2)	3.7 (3)
O8	−0.1844 (3)	0.2392 (2)	0.1484 (2)	5.8 (2)
C11*A*	0.2215 (3)	0.1231 (2)	0.0087 (2)	3.1 (3)
C12*A*	0.2998 (5)	0.1430 (3)	−0.0249 (2)	4.3 (3)
C13*A*	0.2951 (8)	0.1186 (3)	−0.0715 (2)	5.7 (4)
C14*A*	0.2143 (6)	0.0753 (3)	−0.0842 (2)	5.7 (4)
C15*A*	0.1366 (6)	0.0561 (3)	−0.0514 (2)	5.7 (4)
C16*A*	0.1413 (5)	0.0793 (3)	−0.0052 (2)	4.3 (3)
C11*B*	0.2896 (4)	0.0811 (2)	0.1000 (2)	3.2 (3)
C12*B*	0.3936 (5)	0.0627 (3)	0.0837 (2)	4.2 (3)
C13*B*	0.4462 (5)	0.0091 (3)	0.1043 (2)	5.4 (3)
C14*B*	0.3976 (6)	−0.0262 (3)	0.1405 (2)	5.5 (4)
C15*B*	0.2951 (8)	−0.0088 (3)	0.1565 (2)	5.3 (4)
C16*B*	0.2405 (5)	0.0450 (3)	0.1365 (2)	4.1 (3)
C21*A*	0.1488 (4)	0.1491 (3)	0.2272 (2)	3.1 (3)
C22*A*	0.2424 (5)	0.1267 (3)	0.2494 (2)	4.6 (3)
C23*A*	0.2366 (6)	0.0782 (3)	0.2844 (2)	5.7 (4)
C24*A*	0.1385 (6)	0.0529 (3)	0.2968 (2)	5.8 (4)
C25*A*	0.0449 (6)	0.0741 (3)	0.2748 (2)	6.3 (4)
C26*A*	0.0497 (5)	0.1218 (3)	0.2397 (2)	4.8 (3)
C21*B*	0.1143 (4)	0.2850 (3)	0.2181 (2)	3.3 (3)
C22*B*	0.1814 (5)	0.3020 (3)	0.2566 (2)	5.4 (4)
C23*B*	0.1592 (6)	0.3557 (3)	0.2858 (2)	6.9 (4)
C24*B*	0.0670 (6)	0.3927 (3)	0.2774 (2)	5.5 (4)
C25*B*	−0.0019 (5)	0.3762 (3)	0.2405 (2)	5.1 (4)
C26*B*	0.0230 (5)	0.3233 (3)	0.2113 (2)	4.3 (3)
C31	0.1290 (4)	0.3293 (3)	0.0237 (2)	3.3 (3)
C32	0.1517 (5)	0.3945 (3)	0.0145 (2)	4.6 (3)
C33	0.1755 (5)	0.4142 (3)	−0.0320 (2)	5.4 (4)
C34	0.1744 (5)	0.3689 (3)	−0.0692 (2)	5.6 (4)
C35	0.1493 (4)	0.3053 (3)	−0.0602 (2)	4.4 (3)
C36	0.1262 (4)	0.2842 (3)	−0.0133 (2)	3.5 (3)

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

W—P1	2.516 (2)	P1—C1	1.845 (5)
W—P2	2.514 (2)	C1—C4	1.549 (7)
W—S3	2.552 (2)	P2—C2	1.856 (5)
W—C6	1.972 (5)	C2—C4	1.560 (7)
W—C7	1.927 (5)	S3—C3	1.846 (5)
W—C8	1.969 (5)	C3—C4	1.536 (7)
P1—W—P2	83.95 (5)	P2—W—C8	94.6 (2)
P1—W—S3	86.43 (5)	S3—W—C6	95.6 (2)
P1—W—C6	93.2 (2)	S3—W—C7	176.7 (2)
P1—W—C7	95.3 (2)	S3—W—C8	92.4 (2)
P1—W—C8	178.3 (2)	C6—W—C7	87.2 (2)
P2—W—S3	80.74 (5)	C6—W—C8	88.2 (2)
P2—W—C6	175.4 (2)	C7—W—C8	85.9 (2)
P2—W—C7	96.6 (2)		

Ring W—P1—C1—C4—C2—P2	
W—P1—C1—C4	35.4 (2)
P1—C1—C4—C2	41.2 (3)
C1—C4—C2—P2	−85.3 (4)
C4—C2—P2—W	35.8 (2)
C2—P2—W—P1	25.2 (2)
P2—W—P1—C1	−57.7 (2)
Ring W—P2—C2—C4—C3—S3	
W—P2—C2—C4	35.8 (2)
P2—C2—C4—C3	42.5 (3)
C2—C4—C3—S3	−80.9 (4)
C4—C3—S3—W	26.0 (2)
C3—S3—W—P2	33.7 (2)
S3—W—P2—C2	−62.2 (2)
Ring W—P1—C1—C4—C3—S3	
W—P1—C1—C4	35.4 (2)
P1—C1—C4—C3	−86.4 (4)
C1—C4—C3—S3	46.9 (3)
C4—C3—S3—W	26.0 (2)
C3—S3—W—P1	−50.7 (2)
S3—W—P1—C1	23.3 (2)

The structure was solved by the heavy-atom method using the *NRCSDP* VAX package (Gabe & Lee, 1981) with 79 atoms and 407 parameters. The H atoms were located in a difference Fourier map after isotropic refinement and then fixed in an idealized geometry.

The authors acknowledge the financial support of this work by the National Science Council (Republic of China).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HR1013). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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