atom is three-coordinate. The I—Mo—I angles [87·46 (5) and 87·12 (5)°] and the I—Mo—O angles [82·2 (3)–85·6 (3)°] are significantly smaller than 90° and the angles between the normal of the cht plane and the Mo—I and Mo—O bonds [127·6 (5)–129·7 (5)°] are larger than expected for a tetrahedral arrangement of ligands around the Mo atom (109·47°).

The O atom of the H_4F ligand is pyramidally bonded as shown by the *ca* 20° angle formed by the Mo—O vector with the C—O—C plane. The dihedral angles of 165 and 157° between the planes C—O—C and C—C—C—C compare well with the 149·0 and 149·8° reported in coordinated H_4F (Brauer & Krüger, 1972, 1975).

The C—O bond lengths (mean 1·45 Å) are slightly longer than the 1·430 Å reported for H_4F in the gas phase by Geise, Adams & Bartell (1969), whereas the average C—C distance, 1·46 Å, is smaller (1·538 Å in the gas phase). Brauer & Krüger (1975) have explained these differences between coordinated H_4F and H_4F in the gas phase by a second-order hybridization.

It is of interest to compare (η^7-cht)$MoI_2.H_4F$ with the similar molecule (η^8-cot)$ZrCl_2.H_4F$ (cot = cyclooctatetraenyl) described by Brauer & Krüger (1975). Although the difference of 0·22 Å between the average metal—carbon distances [2·472 (15) Å in the Zr complex] reflects the difference in covalent radii between Zr and Mo, the metal—O bond lengths are comparable, and the difference between Mo—I and Zr—Cl bond lengths is equal to the difference between the covalent radii of I and of Cl. These features have been observed in numerous Mo and Zr 'sandwich' complexes and may be due to the difference in energy between the Zr and the Mo orbitals (Atwood, Hunter, Alt & Raush, 1976). The Zr *d* orbitals mainly involved in bonding with the cot ligand are too high in energy to be used as effectively as the Mo *d* orbitals with the cht ligand, but the Zr *s* and *p* orbitals, mainly used in the formation of the σ bonds with the O and Cl atoms, are only slightly higher in energy than the Mo *s* and *p* orbitals used in the formation of the bonds with O and I, thus explaining the similarities in pattern of σ-bond lengths.

References

Atwood, J. L., Hunter, W. E., Alt, H. & Raush, M. D. (1976). *J. Am. Chem. Soc.* **98**(2), 2454–2459.

Brauer, D. J. & Krüger, C. (1972). *J. Organomet. Chem.* **42**, 129–144.

Brauer, D. J. & Krüger, C. (1975). *Inorg. Chem.* **14**, 3053–3056.

Bush, M. A., Hardy, A. D. U., Manojlović-Muir, L. & Sim, G. A. (1971). *J. Chem. Soc. A*, pp. 1003–1009.

Carruthers, J. R. & Watkin, D. J. (1979). *CRYSTALS User Manual.* Oxford Univ. Computing Laboratory, Oxford.

Churchill, M. R. & O'Brien, T. A. (1969). *J. Chem. Soc. A*, pp. 1110–1115.

Geise, H. J., Adams, W. J. & Bartell, L. S. (1969). *Tetrahedron*, **25**, 3045–3052.

Gourdon, A. & Prout, K. (1981). *Acta Cryst.* B**37**, 1982–1985.

Green, M., Kirsch, H. P., Stone, F. G. A. & Welch, A. J. (1977). *J. Chem. Soc. Dalton Trans.* pp. 1755–1761.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Mallinson, P. R., Sim, G. A. & Woodhouse, D. I. (1980). *Acta Cryst.* B**36**, 450–452.

Rollett, J. S. (1965). In *Computing Methods in Crystallography.* Oxford: Pergamon Press.

Sim, G. A., Sime, J. G., Woodhouse, D. I. & Knox, G. R. (1979). *Acta Cryst.* B**35**, 2406–2409.

Ziegler, M. L., Sasse, H. E. & Nuber, B. (1975). *Z. Naturforsch. Teil B*, **30**, 22–29.

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Dibromodicarbonylbis(triphenylphosphine)tungsten(II)

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Abstract. $C_{38}H_{30}Br_2O_2P_2W$, triclinic, M_r = 923·85, a = 9·417 (11), b = 10·008 (9), c = 19·837 (9) Å, α = 89·7 (1), β = 112·8 (1), γ = 88·0 (1)°, U = 1721·9 Å^3, d_m = 1·77, d_c = 1·78 g cm^{-3}, $F(000)$ = 896, Z = 2, Mo $K\alpha$ radiation, λ = 0·7107 Å, μ = 61·3 cm^{-1}, space group $P\bar{1}$ from the successful structure solution. 3094 independent reflections have been refined to R = 0·079. The structure is made up of individual

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$WBr_2(CO)_2(PPh_3)_2$ moieties in which the W is six-coordinate but its geometry is neither octahedral nor trigonal-prismatic. This very unusual geometry, though also found in the isomorphous Mo compound, is thought to be caused by electronic effects [Kubacek & Hoffmann (1981). *J. Am. Chem. Soc.* **103**, 4320–4328].

Introduction. Some time ago we determined the structure of $MoBr_2(CO)_2(PPh_3)_2$ (Drew, Tomkins & Colton, 1970). Both the crystal structure and the molecular structure were unusual. In the crystal structure, the cell dimensions and the atomic coordinates were very close to the monoclinic space group *P*2/*c* with the Mo impaled on a twofold axis but, in fact, were definitely triclinic, with $F(hkl)$ similar but not identical to $F(h\bar{k}l)$ and α and γ deviating slightly from 90° [$\alpha = 90{\cdot}5\ (1)$, $\gamma = 92{\cdot}2\ (1)°$]. The molecular structure was curious in that the geometry around the metal atom conformed to neither octahedral nor trigonal-prismatic geometry. In addition, the data were of poor quality and the *R* value was only 0·15. At the time we were unable to offer an explanation for this odd structure.

However, Kubacek & Hoffmann (1981) have carried out a detailed theoretical analysis of molecular distortions in diamagnetic d^4 complexes of Mo^{II} and have shown that our structure was of lower energy than the corresponding octahedral geometry. We were therefore stimulated to look again at our structure and that of analogous compounds in the hope of obtaining better data and confirming these unusual features. Here we report the crystal and molecular structure of the isomorphous W analogue $WBr_2(CO)_2(PPh_3)_2$ (I).

Experimental. Some difficulty was experienced in synthesizing this complex reproducibly in a pure state by following literature procedures (Anker, Colton & Tomkins, 1967).

$$W(CO)_6 + Br_2 \longrightarrow WBr_2(CO)_4 \xrightarrow{2PPh_3}$$

$$WBr_2(CO)_3(PPh_3)_2 \underset{CO}{\overset{CH_2Cl_2}{\rightleftharpoons}} WBr_2(CO)_2(PPh_3)_2.$$

Spectroscopic examinations showed that traces of $(HPPh_3)\,[WBr_3(CO)_3(PPh_3)]$ were invariably formed at the second stage of the reaction and remained unchanged on heating in dichloromethane. Consequently a slightly modified method was employed which avoided the formation of this impurity. A stirred suspension of hexacarbonyltungsten (3·17 g, 9 mmol) in dry deoxygenated dichloromethane (50 cm^3) was treated at 195 K with bromine (0·47 g, 9 mmol). The mixture was allowed to warm slowly to room temperature as the solvent was removed *in vacuo*. The residue was dissolved in acetone (30 cm^3) and the filtered solution was added to a solution of triphenylphosphine (3·93 g, 15 mmol) dissolved in the minimum volume of acetone. On standing, yellow crystals of $WBr_2(CO)_3(PPh_3)_2$ separated out and were isolated in yields of 65–70% [ν(CO) (cm^{-1}) 2010 *m*, 1946 *s*, 1911 *m* (in CO-saturated CH_2Cl_2)].

A solution of $WBr_2(CO)_3(PPh_3)_2$ in dry, deoxygenated CH_2Cl_2 was heated under reflux in a nitrogen atmosphere for 4 h. The solution was evaporated to low bulk *in vacuo* yielding small deep-blue crystals of $WBr_2(CO)_2(PPh_3)_2$ [ν(CO) (cm^{-1}) 1958 *w*, 1873 *s* (Nujol)]. Crystals for the structure determination were grown from dichloromethane, but we were not able to find a single crystal. Most of those looked at showed several reciprocal lattices with slightly different orientations. We chose the crystal which had a predominant reciprocal lattice with little overlap with the other (much weaker) ones. This crystal was of approximate size 0·04 × 0·03 × 0·01 cm and was mounted along **c** in a Lindemann tube and intensities were measured on a Stoe STADI2 diffractometer equipped with a graphite monochromator. 5819 reflections with a 2θ maximum of 50° were measured by an ω scan with a scan speed of 0·0333° s^{-1} and a background count of 20 s. Of these, 3094 independent reflections with $I > 4\sigma(I)$ were used in subsequent calculations. An absorption correction was applied, but no correction was made for extinction.

The positions of the W atoms in (I) were obtained from the Patterson function and the positions of the remaining non-hydrogen atoms were obtained from Fourier maps. Atoms were refined anisotropically. H atoms were fixed in trigonal and tetrahedral positions at 0·95 Å from the C atoms and an overall thermal parameter for each ring was refined. The final *R* value was 0·079.* As is apparent from the cell dimensions and the positions of the atoms, a solution in which all atoms had coordinates $x, -y, z$ could not be ruled out. This alternative solution was refined to $R = 0{\cdot}080$ and was therefore discarded. As the published coordinates for the Mo complex (Drew *et al.*, 1970) conform to this discarded coordination set, it seems likely that their *y* coordinates ought to be reversed. At the time we were unable to distinguish between the two solutions.

Calculations were carried out using the *SHELX* 76 system (Sheldrick, 1976) at the University of Manchester Regional Computer Centre. Scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974).

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* We calculated the agreement factor between $F(hkl)$ and $F(h\bar{k}l)$ and it was 0·138. We then averaged $F(hkl)$ and $F(h\bar{k}l)$ to give 1942 independent reflections with $I > 4\sigma(I)$ and then refined the structure as monoclinic *P*2/*c*. The resulting *R* value was 0·086. (Conditions for refinement were comparable to those in the triclinic case; namely, all atoms anisotropic bar H which were isotropic.) The resulting dimensions were reasonable. These calculations show that there is very little difference between the present structure and a monoclinic one.

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3)

$\bar{U}$ values were calculated from the equation

$$\bar{U} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	*y*	*z*	*U*
W(1)	17 (1)	1933 (1)	2516 (1)	70 (1)
Br(1)	681 (4)	−20 (3)	1845 (2)	136 (5)
Br(2)	−557 (5)	19 (3)	3221 (2)	145 (5)
C(60)	1126 (28)	3006 (26)	2041 (14)	65 (32)
O(60)	1831 (22)	3564 (20)	1781 (11)	105 (27)
C(70)	−1082 (36)	3095 (28)	2928 (14)	79 (36)
O(70)	−1866 (23)	3724 (20)	3166 (10)	85 (26)
P(1)	2021 (8)	2979 (7)	3575 (3)	73 (8)
C(11)	3829 (32)	1975 (26)	3919 (15)	81 (34)
C(12)	4205 (39)	1173 (33)	3440 (20)	110 (48)
C(13)	5617 (42)	569 (32)	3694 (22)	119 (50)
C(14)	6642 (46)	618 (34)	4358 (26)	160 (63)
C(15)	6258 (42)	1388 (41)	4827 (22)	121 (57)
C(16)	4846 (38)	2005 (32)	4617 (17)	122 (45)
C(21)	1648 (30)	3274 (25)	4404 (14)	88 (32)
C(22)	2286 (36)	4366 (32)	4836 (16)	96 (40)
C(23)	2107 (44)	4507 (46)	5490 (20)	126 (57)
C(24)	1353 (43)	3645 (37)	5730 (17)	111 (48)
C(25)	758 (37)	2633 (33)	5321 (19)	142 (49)
C(26)	846 (35)	2440 (31)	4614 (16)	100 (42)
C(31)	2648 (28)	4540 (26)	3392 (15)	67 (33)
C(32)	3992 (35)	4712 (35)	3237 (22)	146 (53)
C(33)	4429 (50)	5946 (45)	3085 (22)	150 (69)
C(34)	3428 (63)	7011 (41)	2985 (28)	138 (81)
C(35)	2148 (53)	6878 (30)	3091 (23)	142 (60)
C(36)	1681 (40)	5696 (26)	3292 (16)	117 (43)
P(2)	−2015 (8)	3044 (7)	1429 (4)	70 (8)
C(41)	−1674 (30)	3243 (28)	568 (13)	73 (32)
C(42)	−1084 (43)	2151 (41)	341 (20)	165 (58)
C(43)	−875 (46)	2359 (53)	−330 (18)	184 (67)
C(44)	−1333 (41)	3376 (50)	−760 (16)	89 (53)
C(45)	−1776 (43)	4445 (39)	−462 (18)	105 (52)
C(46)	−2050 (34)	4449 (29)	183 (16)	94 (39)
C(51)	−2589 (32)	4698 (27)	1587 (14)	84 (34)
C(52)	−4124 (38)	5166 (37)	1427 (22)	127 (55)
C(53)	−4375 (52)	6447 (34)	1584 (25)	193 (70)
C(54)	−3264 (47)	7414 (33)	1791 (21)	117 (56)
C(55)	−1813 (37)	6934 (31)	1934 (19)	108 (45)
C(56)	−1457 (35)	5695 (22)	1788 (17)	104 (38)
C(61)	−3803 (33)	2162 (27)	1143 (14)	83 (35)
C(62)	−4791 (36)	2079 (37)	437 (17)	86 (46)
C(63)	−6197 (40)	1547 (41)	205 (18)	93 (51)
C(64)	−6558 (42)	973 (43)	764 (21)	117 (58)
C(65)	−5666 (37)	959 (36)	1430 (21)	106 (50)
C(66)	−4239 (35)	1529 (37)	1640 (16)	85 (46)

The weighting scheme was chosen to give similar values of $w\Delta^2$ over ranges of sin θ/λ and F_o. It was $w = 1/[\sigma^2(F) + 0{\cdot}002F^2]$ where $\sigma(F)$ was taken from counting statistics. The difference Fourier maps showed no significant peaks. Zero-weighted reflections showed no serious discrepancies. Atomic coordinates for (I) are given in Table 1 and dimensions in the coordination sphere in Table 2.*

Table 2. *Interatomic distances* (Å) *and angles* (°)

W(1)–Br(1)	2·564 (4)	W(1)–C(70)	1·92 (3)
W(1)–Br(2)	2·559 (4)	W(1)–P(1)	2·481 (6)
W(1)–C(6)	1·99 (3)	W(1)–P(2)	2·483 (6)
Br(1)–W(1)–Br(2)	81·93 (13)	C(60)–W(1)–P(1)	77·5 (7)
Br(1)–W(1)–C(60)	84·0 (8)	C(70)–W(1)–P(1)	74·4 (8)
Br(2)–W(1)–C(60)	159·6 (7)	Br(1)–W(1)–P(2)	97·19 (19)
Br(1)–W(1)–C(70)	161·6 (9)	Br(2)–W(1)–P(2)	122·20 (20)
Br(2)–W(1)–C(70)	87·0 (9)	C(60)–W(1)–P(2)	74·2 (6)
C(60)–W(1)–C(70)	110·1 (12)	C(70)–W(1)–P(2)	76·3 (7)
Br(1)–W(1)–P(1)	121·60 (19)	P(1)–W(1)–P(2)	128·48 (21)
Br(2)–W(1)–P(1)	97·49 (19)		

Discussion. The molecular structure is shown in Fig. 1, together with the atomic numbering scheme. The W atoms are six-coordinate, being bonded to two carbonyls [1·99 (3), 1·92 (3) Å], two Br atoms [2·564 (4), 2·559 (4) Å] and two P atoms [2·481 (6), 2·483 (6) Å]. The structure contains a pseudo twofold axis through the W atom which bisects the pairs of donor ligands. This axis is parallel to *y* and the coordinates of pairs of atoms related by it are *x*,*y*,*z* and $-x,-y,\tfrac{1}{2}-z$.

However, there were no problems of high correlation in the refinement. The geometry around the metal atom is curious. There are two angles close to 180°, *viz* Br(2)—W—C(60) 159·6 (7) and Br(1)—W—C(70) 161·6 (9)°, but the P(1)—W—P(2) angle is 128·5 (2)°. The dimensions are almost identical to those obtained in the Mo analogue.

Kubacek & Hoffmann (1981) have calculated theoretical distortions in $\text{Mo(CO)}_2L_2L'_2$ complexes for diamagnetic d^4 Mo^{II} and W^{II} complexes. They used extended Huckel calculations on the model compound $\text{Mo(CO)}_2\text{(PH}_3)_2\text{Cl}_2$ starting with an octahedral geometry, in which P atoms were mutually *trans* and which contained a *cis* equatorial plane of Cl and C atoms. They found two possible minima, within C_{2v} symmetry, in one of which the C—*M*—C angle increased substantially from 90°, Cl—*M*—Cl decreased from 90° and P—*M*—P decreased from 180°. This minimum fits in with the trends observed here and in the Mo analogue reported earlier but the magnitude of the distortion, of the P—*M*—P angle in particular, is

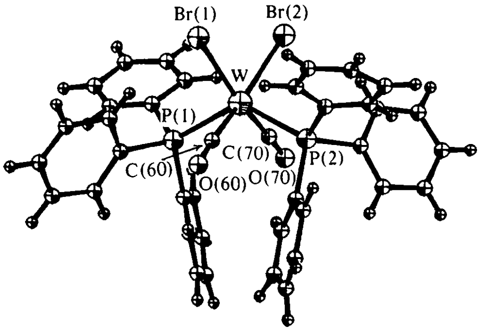

Fig. 1. A view of a molecule of (I) showing the atom numbering.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, phenyl-ring dimensions and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36668 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Least-squares planes in* (I)

Deviations of atoms from the planes are given in Å.

W* 0·00 (1), Br(1) −0·25 (1), Br(2) 0·25 (1), C(60) 0·27 (1), C(70) −0·26 (1)

Angles between phenyl rings (°): (1) and (2) 80·6 (1), (1) and (3) 89·5 (2), (2) and (3) 65·6 (1), (4) and (5) 78·2 (1), (4) and (6) 86·7 (1), (5) and (6) 88·5 (1).

* Atom not contributing to the plane.

calculated to be far smaller (within 20° of 180°) than that observed for the W (128·5°) and the Mo (127·8°) compounds.

In the present structure the equatorial plane is distorted in that the Br and C atoms are all *ca* 0·25 Å from the plane (Table 3). The angle between W,Br(1),Br(2) and W,C(60),C(70) is 18·1 (1)°. P(1) and P(2) are both bent away from the Br atoms and towards the carbonyls. All four P—W—C angles are in the range 74·2 (6) to 77·5 (7)°. However, the P atoms are not equidistant from the Br atoms. The relevant angles are P(1)—W—Br(1) 121·6 (2), P(2)—W—Br(2) 122·2 (2), and P(1)—W—Br(2) 97·5 (2), P(2)—W—Br(1) 97·2 (2)°. It is not at all clear why this should be so: one explanation is to be found in the orientation of the phenyl rings. The smallest Br—W—P—C torsion angles are concomitant with the larger Br—W—P angles. Thus Br(1)—W—P(1)—C(11) is −12·7 (1)° and Br(2)—W—P(2)—C(61) is −8·6 (1)°. Torsion angles involving the carbonyls and the phenyl rings show several angles of *ca* 30° but none as small as those quoted above.

Attempts to investigate the solution behaviour of this complex and to determine whether it was dynamic were unsuccessful because the low solubility of the compound precluded meaningful ^{13}C NMR measurements. However, we were able to confirm from intensity measurements in the carbonyl region (Beck, Melvikoff & Stahl, 1966) that the wide $M(CO)_2$ angle was maintained at 115 ± 5° in solution. In addition, the intense blue colouration of solutions of $WBr_2(CO)_2(PPh_3)_2$ was caused by a broad absorption band centred at 17 900 cm^{-1}. The corresponding tricarbonyl $WBr_2(CO)_3(PPh_3)_2$ was completely transparent in this region with no absorption maxima below 30 000 cm^{-1}.

We are currently investigating the structures, and chemical and physical properties of a range of related complexes in an attempt to define further the factors which determine the degree of deformation in the structures of this interesting class of molecules.

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References

ANKER, M. W., COLTON, R. & TOMKINS, I. B. (1967). *Aust. J. Chem.* **20**, 9–15.

BECK, W., MELVIKOFF, A. & STAHL, R. (1966). *Chem. Ber.* **99**, 3721–3725.

DREW, M. G. B., TOMKINS, I. B. & COLTON, R. (1970). *Aust. J. Chem.* **23**, 2517–2520.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

KUBACEK, P. & HOFFMANN, R. (1981). *J. Am. Chem. Soc.* **103**, 4320–4328.

SHELDRICK, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.

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Bis(oxamide oximato)palladium(II) Dihydrate

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Abstract. $Pd(C_2H_5N_4O_2)_2.2H_2O$, $C_4H_{10}N_8O_4Pd.2H_2O$, $M_r = 376·6$, monoclinic, $P2_1/c$, $a = 3·899$ (2), $b = 13·475$ (6), $c = 11·433$ (5) Å, $\beta = 95·65$ (4)°, $V = 597·8$ Å^3, $Z = 2$, $d_c = 2·09$ Mg m^{-3}. Final $R = 0·069$ for 1062 observed reflections. The centrosymmetric planar molecules form stacks along **a**, the normals to the planes being inclined at 26° to the stacking axis, resulting in an interplanar distance of 3·51 Å. The water bonds by hydrogen bridges to adjacent complexes of a stack, leading to a ladder-like structure.

Introduction. Our studies on the structural chemistry of complexes of oxamide oxime (diaminoglyoxime, $oaoH_2$) (Ephraim, 1889) with the metals of the Ni triad

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