

Fig. 2. ORTEP view of the molecule in the monoclinic modification.

molybdenum centre. Amongst the phenyl rings of the other P ligands the P atoms deviate from the mean plane of the rings by as much as 0.316 (5) Å.

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## Structure of *mer*-Tricarbonyl(triethylphosphine)[vinylidenebis(diphenylphosphine)]tungsten(0)

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**Abstract.**  $[\text{W}(\text{CO})_3\{(\text{C}_2\text{H}_5)_3\text{P}\}\text{CH}_2\text{C}\{(\text{C}_6\text{H}_5)_2\text{P}\}_2]$ ,  $M_r = 782.49$ , monoclinic,  $P2_1/c$ ,  $a = 12.813$  (2),  $b = 12.339$  (2),  $c = 21.980$  (3) Å,  $\beta = 103.39$  (1)°,  $U = 3380.5$  (8) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.536$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 3.417$  mm<sup>-1</sup>,  $F(000) = 1560$ , room temperature,  $R = 0.0345$ , 3762 unique reflections with  $I > 2.0\sigma(I)$ . The title compound is an octahedrally coordinated mononuclear tungsten(0) complex with three carbonyls arranged in a *mer* configuration, a triethylphosphine and a chelating vinylidenebis(diphenylphosphine). Important bond lengths are W–P(1) 2.500 (4), W–P(2) 2.438 (4), W–P(3) 2.458 (4),  $\langle \text{W–C} \rangle$  1.99 (1), P(1)–C(131) 1.827 (9), P(2)–C(131) 1.835 (9) and C(131)–C(132) 1.32 (1) Å.

**Introduction.** There are an abundance of complexes containing bis(diphenylphosphino)methane as a mono-

### References

- ALYEA, E. C., FERGUSON, G. & SOMOGYVARI, A. (1983). *Organometallics*, **2**, 668–674.
- AUBURN, P. R., MACKENZIE, P. B. & BOSNICH, B. (1985). *J. Am. Chem. Soc.* **107**, 2033–2046.
- FORDER, R. A. & PROUT, K. (1974). *Acta Cryst.* **B30**, 2778–2780.
- FRENZ, B. A. (1981). *Enraf–Nonius Structure Determination Package*. College Station, Texas, USA.
- FRIZZELL, J. J., LUCK, R., MORRIS, R. H. & PENG, S. (1985). *J. Organomet. Chem.* **284**, 243–255.
- HOSSAIN, M. B. & VAN DER HELM, D. (1978). *Inorg. Chem.* **17**, 2893–2900.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- IVERSON, D. J., HUNTER, G., BLOUNT, J. F., DAMEWOOD, J. R. & MISLOW, K. (1981). *J. Am. Chem. Soc.* **103**, 6073–6083.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- KOSHLAND, D. E., MYERS, S. E. & CHESICK, J. P. (1977). *Acta Cryst.* **B33**, 2013–2019.
- LUCK, R., MORRIS, R. H. & SAWYER, J. F. (1984a). *Organometallics*, **3**, 247–255.
- LUCK, R., MORRIS, R. H. & SAWYER, J. F. (1984b). *Organometallics*, **3**, 1009–1014.
- MASON, R., THOMAS, K. M. & HEATH, G. A. (1975). *J. Organomet. Chem.* **90**, 195–202.
- SELLA, A. (1986). MSc Thesis, Univ. of Toronto, Canada.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

dentate, chelating or bridging ligand (Puddephatt, 1983). Complexes of functionalized variations of this ligand such as vinylidenebis(diphenylphosphine) (vdpp) (Colquhoun & McFarlane, 1982), however, are less common. Complexes of vdpp with transition metals (such as Cr, Mo, W or Pt) are of interest because complex formation increases the activity of the vinylidene group, which readily undergoes Michael-type additions, even at very low temperatures (Cooper, Hassan, Shaw & Thornton-Pett, 1985). In view of this, it is surprising to find that few such complexes have been structurally characterized: examples are confined to a bridged digold complex (Schmidbaur, Herr, Muller & Riede, 1985), a bridged osmium triangle and a mononuclear iron species (Clucas, Dawson, Dolby, Harding, Pearson & Smith, 1986). We present here the structure of a mononuclear tungsten complex.

**Experimental.** A pale red block-shaped crystal (0.25 × 0.4 × 0.65 mm) was obtained from a solution in dichloromethane–methanol. All measurements made on a Nicolet P3/F diffractometer; lattice parameters from 25 reflections, centred (35.0 < 2θ < 40.0°), graphite-monochromated Mo Kα radiation, ω–2θ scans, ω scan widths 2° + α-doublet splitting, scan speeds 2.0–29.3° min<sup>-1</sup> subject to a fast pre-scan. Complete data set (h 0→13, k 0→13, l -24→24; 2θ < 45°) measured over 152 exposure hours with no significant decay of a standard reflection (measured every 50 reflections); 4334 unique data, 3762 with I > 2.0σ(I) considered observed and used in structure solution and refinement. Structure solution by Patterson synthesis (for W atom) and difference Fourier methods; empirical absorption correction (Walker & Stuart, 1983); full-matrix least-squares refinement on F with anisotropic thermal parameters for all non-hydrogen atoms (331 parameters), no H atoms located. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Refinement converged to R = 0.0345, wR = 0.0344, w<sup>-1</sup> = σ<sup>2</sup>(F<sub>o</sub>) + 0.0002(F<sub>o</sub>)<sup>2</sup>, S = 2.336, difference synthesis showed max. density of 0.63 e Å<sup>-3</sup> (min. -0.59 e Å<sup>-3</sup>); max. Δ/σ = 0.56 in U<sub>22</sub> of C(215). All calculations performed on an Amdahl 5850 computer. Programs SHELX76 (Sheldrick, 1976) and ORTEPII (Johnson, 1976).

**Discussion.** Final fractional coordinates and equivalent isotropic thermal parameters are listed in Table 1.\* The molecular structure and its numbering scheme are shown in Fig. 1 while selected bond lengths and angles are listed in Table 2. The W atom is octahedrally coordinated with two apical carbonyl groups and an equatorial plane defined by the vdpp chelate with a triethylphosphine *trans* to one P atom and a carbonyl *trans* to the other. The W–C distances do not vary significantly at 1.96 (1), 1.99 (1) and 2.01 (1) Å and are comparable to those in other tungsten(O) carbonyl complexes (Blagg, Hutton, Shaw & Thornton-Pett, 1985); the two W–P(vdpp) distances are significantly different [2.438 (4) (*trans* to P) and 2.500 (4) Å (*trans* to C)] and reflect the differing *trans* influence of phosphines relative to carbonyls. Because of the bite restriction of the vdpp chelate the equatorial valence angles at the W atom are not equal [ranging from 68.5 (2) to 98.3 (3)°] although the W atom remains in the equatorial plane (sum of angles = 360.3°).

In common with the digold and iron complexes mentioned previously, there is no structural evidence for

\* Lists of structure factors and anisotropic thermal parameters and a full list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44302 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atom coordinates (× 10<sup>4</sup>) and equivalent isotropic temperature factors (Å<sup>2</sup> × 10<sup>3</sup>)

$$U_{eq} = \frac{1}{3} \sum_{i,j} U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U <sub>eq</sub>
W	2278-1 (2)	1747-7 (2)	1616-3 (1)	38-1 (2)
P(1)	2584 (2)	3520 (1)	1134 (1)	43 (1)
P(2)	4171 (1)	2245 (2)	1877 (1)	40 (1)
P(3)	342 (2)	1595 (2)	1161 (1)	63 (1)
C(111)	2663 (4)	3766 (4)	325 (2)	52 (2)
C(112)	2947 (4)	4786 (4)	143 (2)	84 (2)
C(113)	3008 (4)	4967 (4)	-474 (2)	99 (2)
C(114)	2784 (4)	4127 (4)	-910 (2)	100 (2)
C(115)	2500 (4)	3106 (4)	-728 (2)	85 (2)
C(116)	2440 (4)	2926 (4)	-110 (2)	64 (2)
C(121)	1882 (3)	4709 (3)	1316 (2)	59 (2)
C(122)	1008 (3)	5116 (3)	874 (2)	77 (2)
C(123)	374 (3)	5933 (3)	1040 (2)	103 (3)
C(124)	615 (3)	6343 (3)	1648 (2)	106 (3)
C(125)	1488 (3)	5935 (3)	2090 (2)	99 (3)
C(126)	2122 (3)	5118 (3)	1924 (2)	77 (2)
C(131)	3974 (6)	3636 (6)	1589 (3)	48 (2)
C(132)	4585 (8)	4500 (7)	1723 (5)	86 (3)
C(211)	5073 (4)	1606 (4)	1447 (2)	51 (2)
C(212)	5485 (4)	584 (4)	1641 (2)	103 (3)
C(213)	6116 (4)	37 (4)	1302 (2)	112 (3)
C(214)	6335 (4)	511 (4)	769 (2)	110 (3)
C(215)	5923 (4)	1533 (4)	575 (2)	142 (3)
C(216)	5292 (4)	2080 (4)	914 (2)	116 (3)
C(221)	5013 (3)	2356 (3)	2670 (1)	44 (2)
C(222)	4534 (3)	2212 (3)	3173 (1)	56 (2)
C(223)	5131 (3)	2369 (3)	3783 (1)	68 (2)
C(224)	6207 (3)	2671 (3)	3891 (1)	69 (2)
C(225)	6687 (3)	2815 (3)	3387 (1)	72 (2)
C(226)	6090 (3)	2657 (3)	2777 (1)	61 (2)
C(31)	-101 (7)	2263 (9)	370 (4)	88 (3)
C(32)	-1310 (9)	2238 (10)	73 (5)	116 (3)
C(33)	-609 (8)	2119 (10)	1584 (5)	109 (3)
C(34)	-630 (10)	3331 (10)	1648 (6)	132 (3)
C(35)	-155 (8)	215 (10)	928 (6)	119 (3)
C(36)	-92 (10)	-537 (11)	1461 (7)	155 (3)
O(1)	2440 (6)	486 (6)	2168 (3)	54 (2)
O(2)	2578 (5)	-229 (5)	2530 (3)	76 (2)
O(3)	1928 (6)	2529 (6)	2334 (3)	54 (2)
C(1)	1714 (5)	2904 (5)	2778 (3)	83 (2)
C(2)	2490 (6)	757 (6)	928 (3)	57 (2)
O(3)	2595 (6)	161 (5)	552 (3)	93 (2)

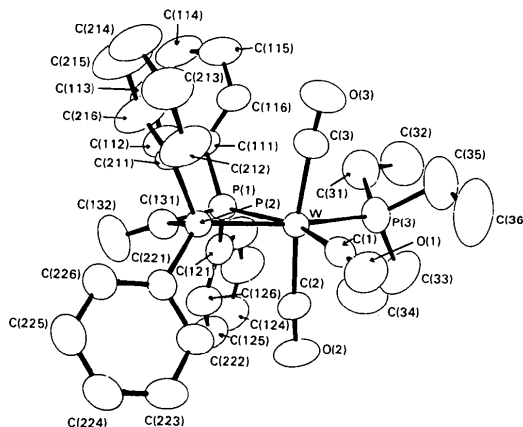


Fig. 1. The molecular structure of the title compound illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level.

C=C bond activation of the vdpp ligand since the C=C distance [1.32 (1) Å] in this complex is not significantly different from that of 1.327 (6) Å observed in the free ligand (Schmidbaur, Herr & Riede, 1984). As in the mononuclear iron complex, however,

Table 2. Selected interatomic bond distances (Å) and angles (°) with estimated standard deviations in parentheses

W P(1)	2.500 (4)	W-C(1)	1.96 (1)
W P(2)	2.438 (4)	W-C(2)	1.987 (9)
W P(3)	2.458 (4)	W-C(3)	2.01 (1)
P(1)-C(131)	1.835 (9)	P(2)-C(131)	1.827 (9)
<P-C(phenyl)>	1.827 (6)	<P(3)-C(ethyl)>	1.85 (1)
<C-O>	1.160 (9)		
P(1)-W P(2)	68.5 (2)	P(2)-W-P(3)	166.0 (1)
P(2)-W-C(1)	95.6 (3)	P(3)-W-C(1)	98.3 (3)
C(2)-W-C(3)	170.6 (3)	P(1)-C(131)-P(2)	98.8 (4)
P(1)-C(131)-C(132)	129.6 (7)	P(2)-C(131)-C(132)	131.1 (6)
W-C(2)-O(2)	174.3 (6)	W-C(3)-O(3)	177.1 (7)
W-C(1)-O(1)	175.5 (6)		

the angle P(1)-C(131)-P(2) is considerably reduced from 119.0 (3) to 98.8 (4)°, although the carbon atom retains its planar  $sp^2$  configuration since the angles about it sum to 359.5°. The vinylidene group is bent significantly out of the equatorial plane [the angle between the planes defined by W, P(1), P(2) and P(1), P(2), C(131), C(132) is 20°], which contrasts with the two bridged species, which are essentially planar, and is much greater than the corresponding angle of 10° in the mononuclear iron complex. This may well reflect the increase in steric crowding around the central metal atom brought about by the presence of the triethylphosphine ligand. Steric effects are also apparent on the two apical carbonyl groups which are bent slightly

away from the vdpp chelate leading to a C(2)-W-C(3) angle of 170.6 (3)°.

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#### References

- BLAGG, A., HUTTON, A. T., SHAW, B. L. & THORNTON-PETT, M. (1985). *Inorg. Chim. Acta*, **100**, L33-L36.
- CLUCAS, J. A., DAWSON, R. H., DOLBY, P. A., HARDING, M. M., PEARSON, K. & SMITH, A. K. (1986). *J. Organomet. Chem.* **311**, 153-162.
- COLQUHOUN, I. J. & MCFARLANE, W. (1982). *J. Chem. Soc. Dalton Trans.* pp. 1915-1921.
- COOPER, G. R., HASSAN, F., SHAW, B. L. & THORNTON-PETT, M. (1985). *J. Chem. Soc. Chem. Commun.* pp. 614-616.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- PUDDEPHATT, R. J. (1983). *Chem. Soc. Rev.* **12**, 99-127.
- SCHMIDBAUR, H., HERR, R., MULLER, G. & RIEDE, J. (1985). *Organometallics*, **4**, 1208-1213.
- SCHMIDBAUR, H., HERR, R. & RIEDE, J. (1984). *Chem. Ber.* **117**, 2322-2327.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for X-ray structure determination. Univ. of Cambridge, England.
- WALKER, N. & STUART, D. (1983). *Acta Cryst. A* **39**, 158-166.

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## Structure of Bis(tetraphenylphosphonium) Tris[chlorocopper(I)]oxotrithiotungstate(VI)\*

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**Abstract.**  $[P(C_6H_5)_4]_2[WOS_3(CuCl)_3]$ ,  $M_r = 1271.8$ , triclinic,  $P\bar{1}$ ,  $a = 9.896$  (1),  $b = 11.665$  (1),  $c = 23.559$  (2) Å,  $\alpha = 78.794$  (7),  $\beta = 78.421$  (7),  $\gamma = 70.741$  (4)°,  $V = 2490.9$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.695$  Mg m<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $\mu = 4.00$  mm<sup>-1</sup>,  $F(000) = 1252$ ,  $T = 293$  K,  $R = 0.0340$  for 5649 unique reflections with  $F > 4\sigma(F)$ . The W, three Cu and three S atoms of the anion are arranged on seven vertices of a trigonally distorted cube; the eighth vertex, opposite W, is unoccupied. The W atom

is tetrahedrally coordinated by one terminal O atom and by three S atoms, each of which also bonds to two Cu atoms. The Cu coordination is trigonal planar, by two bridging S and one terminal Cl. Mean bond distances are W-O = 1.711 (4), W-S = 2.268 (5), Cu-S = 2.257 (7), Cu-Cl = 2.155 (5), W...Cu = 2.658 (7) Å.

**Introduction.** The tetrathiomolybdate(VI) anion  $[MoS_4]^{2-}$  and related species have been widely used in transition-metal coordination chemistry, often as bidentate ligands to a later transition metal (Müller, Diemann, Jostes & Bögge, 1981). Particular attention

\*IUPAC name: bis(tetraphenylphosphonium) oxo[1,2,3-trichloro-1,2,2,3,3,1-tri- $\mu$ -thio-tricuprato(I)-S<sup>1</sup>,S<sup>2</sup>,S<sup>3</sup>]tungstate(2-).