

The packings of the molecules are shown in Figs. 2 and 3. The differences in the packings of the molecules appear in the shortest intermolecular Pt...Pt distances [4.569 (2) Å for (1) and 5.139 (2) Å for (2)] and the hydrogen bond contacts. Although the positions of the H atoms in the hydroxyl groups have not been determined, the short intermolecular O...O distance of 2.58 (2) Å in (1) indicates a strong hydrogen bond between the atoms, resulting in hydrogen bonded pairs of molecules. Owing to the centre of inversion between the O atoms, the O—H H atoms are most probably disordered. There are no other short interatomic contact distances in (1) and the pairs are held in the lattice with weak van der Waals interactions. In (2) the intermolecular O...O distance of 3.84 (2) Å is evidently too great for hydrogen bonding but hydrogen bonding does play an important role in stabilizing the crystal through a network involving N(1)...O [2.97 (2) Å], N(1)...Cl(1) [3.40 (1) Å], N(2)...Cl(2) [3.42 (2) Å] and O...Cl(1) [3.22 (1) Å].

Financial support from the Technology Development Centre, the Finnish Academy of Science and

the Emil Aaltonen Foundation is gratefully acknowledged.

#### References

- APPLETON, T. G. & HALL, J. R. (1972). *Inorg. Chem.* **11**, 112–117.  
 BROWN, B. E. & LOCK, C. J. L. (1987). *Acta Cryst.* **C43**, 12–14.  
 HALL, S. R. & STEWART, J. M. (1987). Editors. *XTAL2.2 User Manual*. Univ. of Western Australia, Australia, and Maryland, USA.  
 IBALL, J., MACDOUGALL, M. & SCRIMGEOUR, S. (1975). *Acta Cryst.* **B31**, 1672–1674.  
 LAITALAINEN, T., OKUNO, Y. & TOMOHIRO, T. (1987). *Fifth International Symposium on Platinum and other Metal Coordination Compounds in Cancer Chemotherapy*, 29 June – 2 July, 1987, Italy. No. 375 (poster).  
 MAHAL, G., VAN ELDICK, R., ROODT, A. & LEIPOLDT, J. G. (1987). *Inorg. Chim. Acta*, **132**, 165–166.  
 MÉGNAMISI-BÉLOMBÉ, M. & ENDRES, H. (1985). *Acta Cryst.* **C41**, 513–515.  
 OKSANEN, A., KIVEKÄS, R., LUMME, P., VALKONEN, J. & LAITALAINEN, T. (1989). *Acta Cryst.* **C45**, 1493–1495.  
 RAUDASHL-SIEBER, G., LIPPERT, B., BRITTON, J. F. & BEAUCHAMP, A. L. (1986). *Inorg. Chim. Acta*, **124**, 213–217.  
 SHELDRIK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.  
 SHIMURA, T., TOMOHIRO, T., LAITALAINEN, T., MORIYAMA, H., UEMURA, T. & OKUNO, Y. (1988). *Chem. Pharm. Bull.* **36**, 448–451.

*Acta Cryst.* (1991). **C47**, 722–725

## Synthesis and Structure of (CH<sub>3</sub>)<sub>2</sub>AsC(CF<sub>3</sub>)=C(CF<sub>3</sub>)As(CH<sub>3</sub>)<sub>2</sub>W(CO)<sub>2</sub>Br<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>

BY S. K. MANOCHA, L. M. MIHICHUK,\* R. J. BARTON AND B. E. ROBERTSON\*

*Department of Chemistry, University of Regina, Regina Saskatchewan, Canada S4S 0A2*

(Received 3 July 1990; accepted 14 September 1990)

**Abstract.** Dibromodicarbonyl[2,5-dimethyl-3,4-bis(trifluoromethyl)-2,5-diarsahexa-3-ene-As,As']-(triphenylphosphine)tungsten, (L-L)W(CO)<sub>2</sub>Br<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> [L-L = (CH<sub>3</sub>)<sub>2</sub>AsC(CF<sub>3</sub>)=C(CF<sub>3</sub>)As(CH<sub>3</sub>)<sub>2</sub>], C<sub>28</sub>H<sub>27</sub>As<sub>2</sub>Br<sub>2</sub>F<sub>6</sub>O<sub>2</sub>PW, *M<sub>r</sub>* = 1033.99, triclinic, *P* $\bar{1}$ , *a* = 9.381 (3), *b* = 12.662 (2), *c* = 14.276 (3) Å,  $\alpha$  = 79.17 (2),  $\beta$  = 82.38 (2),  $\gamma$  = 83.57 (2)°, *V* = 1644 (1) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 2.088 (1) Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)$  = 0.71069 Å,  $\mu$  = 85.50 cm<sup>-1</sup>, *F*(000) = 980, *T* = 223 (2) K. *R* value of 0.063 using 5206 independent reflections in range 3° ≤ 2θ ≤ 50° with *I*/σ(*I*) ≥ 2.0. The crystal structure shows the W atom to be seven-coordinate with a geometry most closely approximated by a capped trigonal prism with the capping group being a Br atom [(W—Br) = 2.648 (1) Å]. The capped face consists of one Br atom [(W—Br) = 2.675 (1) Å], an arsenic atom

[(W—As) = 2.609 (2) Å], a P atom [(W—P) = 2.548 (1) Å] and a carbonyl carbon atom [(W—C) = 1.95 (1) Å].

**Introduction.** There are few reported examples of stereochemically rigid seven-coordinate structures. As part of a series of studies of a seven-coordinate system involving tungsten and molybdenum and the ligand (L-L) where L-L = (CH<sub>3</sub>)<sub>2</sub>AsC(CF<sub>3</sub>)=C(CF<sub>3</sub>)As(CH<sub>3</sub>)<sub>2</sub> using X-ray crystallography and variable temperature NMR studies, we report here the synthesis, structure and the fluxional behaviour of the complex (L-L)W(CO)<sub>2</sub>Br<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>. Earlier work on a variety of seven-coordinate complexes of metal carbonyls has shown that they can be described by either a monocapped octahedral (MCO) geometry (Cotton, Falvello & Meadows, 1985; Mercer & Trotter, 1974) or a monocapped trigonal prismatic (MCTP) geometry (Drew & Wilkins, 1973;

\* To whom correspondence should be addressed.

Beauchamp, Belanger-Gariepy & Arali, 1985). Distortions from these idealized geometries are common in real systems. These studies are intended to explain the effects of steric and electronic interactions on the fluxional behaviour of such complexes.

**Experimental.** The ligand *cis*-2,3-bis(dimethylarsino)-1,1,1,4,4,4-hexafluorobut-2-ene, (*L-L*), was synthesized as previously reported (Crow, Cullen, Herring, Sams & Tapping, 1971). (*L-L*)W(CO)<sub>4</sub> was obtained by refluxing equimolar quantities of W(CO)<sub>6</sub> and (*L-L*) in mesitylene (which contained a small amount of tetrahydrofuran) at 433 K for 11 h under an argon atmosphere.

Slow oxidation of (*L-L*)W(CO)<sub>4</sub> by Br<sub>2</sub> in dichloromethane at 253 K yielded the seven-coordinate complex (*L-L*)W(CO)<sub>3</sub>Br<sub>2</sub> which, when reacted with triphenylphosphine in the same solvent under an argon atmosphere, gave (*L-L*)W(CO)<sub>2</sub>Br<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>. Orange-yellow crystals of the complex were obtained from a dichloromethane-hexane mixture under inert conditions using a Schlenk apparatus. The crystals appeared as large orthorhombic prisms with variable relative dimensions.

A crystal with approximate dimensions 0.37 × 0.45 × 0.55 mm was selected for the X-ray diffraction study and mounted on a glass fibre. Tungsten(II) seven-coordinate complexes have been reported to deteriorate at a rapid rate under X-ray radiation (Mihichuk, Pizzey, Robertson & Barton, 1986); thus the data were collected at 223 K, using a modified Enraf-Nonius nitrogen gas-flow low-temperature device. The crystal was coated with collodion to avoid any direct contact with moisture. Precession photographs were used to determine the space group and approximate lattice constants. Intensity data were collected on a Picker four-circle diffractometer with graphite-monochromated Mo *K*α radiation using the NRCC diffractometer control system. Three standard reflections were measured after every 47 reflections. A decay of 2% in the intensities of the standard reflections was observed during the data collection. *hkl*: *h*, 0 to 11; *k*, -14 to 15; *l*, -16 to 16. The intensities of 5793 independent reflections were measured in the range 3 ≤ 2θ ≤ 50°, of which 5206, with *I* ≥ 2σ(*I*), were considered to be observed. Though accurate dimensions for the crystal could not be obtained because of the collodion coating, approximate absorption corrections based on the Gaussian integration method were applied. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV) were applied.

The structure was solved using direct methods and refined by full-matrix least squares (on *F*) applied to the structure amplitudes, using anisotropic tempera-

ture factors for the non-H atoms. The H atoms were not located. Weights were assigned as  $w = 1/\sigma^2(F)$ , where  $\sigma(F)$  is based on counting statistics and the machine instability factor. The final refinement agreement factors were  $R = 0.063$  and  $wR = 0.086$ , where  $w = [\sigma(F_o)]^{-2}$  and the average and maximum shift/e.s.d. for structural parameters were 0.005 and 0.02, respectively, at the termination of the refinement. Pairs of residual electron-density peaks, ranging in height from +1.6 to +5.9 e Å<sup>-3</sup>, were found near each of the W, Br and As atoms. It is assumed that these peaks reflect the inaccuracy of the absorption corrections, which results from the fact that the faces of the crystal were not clearly visible. All calculations were carried out using the *XTAL* system of programs (Stewart & Hall, 1986).

**Discussion.** Table 1 lists the fractional coordinates of all non-H atoms and their equivalent isotropic thermal parameters. Selected bond distances and bond angles are listed in Table 2.\* The labelled diagram of the molecule is shown in Fig. 1.

The coordination sphere around the W atom includes the two arsenic atoms of the *L-L* ligand, two Br atoms, one P atom of the triphenylphosphine group and the C atoms of the two carbonyl groups. The coordination polyhedron is intermediate between the monocapped octahedron (*C*<sub>3v</sub>) and the quadrilaterally monocapped trigonal prism, MCTP (*C*<sub>2v</sub>). When the ligands are nonequivalent and the actual symmetry is lower than *C*<sub>3v</sub> or *C*<sub>2v</sub>, the assignment of a seven-coordinate structure to one of the above geometries may be ambiguous. Distortion from these idealized geometries is common in real systems. In order to define the polyhedron we have used the δ parameters of Porai-Koshits & Aslanov (1972). The δ angles for seven-coordinate polyhedra have been calculated by Muetterties & Guggenberger (1974).

On comparison of three particularly sensitive δ values (4.1, 7.1, 30.7°) with those which define the idealized monocapped octahedron (24.2, 24.2, 24.2°), and those which define the idealized monocapped trigonal prism (0, 0, 41.5°), we describe the present compound as approximating more closely to the geometry of the monocapped trigonal prism. The capping atom in an MCTP description is the Br(2) atom with the capped face consisting of the Br(1), As(1), C(2) and P atoms. The bidentate ligand *L-L* bridges an edge shared by an end triangular face and one of the two quadrilateral faces which is not

\* Lists of structure factors, anisotropic thermal parameters and additional bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53574 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic and thermal parameters ( $\text{\AA}^2 \times 10^2$ ) for the non-H atoms with *e.s.d.*'s in parentheses

$$U_{\text{eq}} = 1/3 \sum_{j=1}^3 U_j a_j^* a_j^* (\mathbf{a}, \mathbf{a}).$$

	x	y	z	$U_{\text{eq}}$
W	0.74077 (4)	0.45701 (3)	0.21895 (3)	2.28 (3)
As(1)	0.7647 (1)	0.65368 (9)	0.12634 (7)	2.89 (7)
As(2)	0.4841 (1)	0.55060 (9)	0.22657 (7)	2.71 (7)
Br(1)	0.6995 (1)	0.5402 (1)	0.38035 (7)	3.46 (8)
Br(2)	1.022 (1)	0.4474 (1)	0.22780 (8)	3.60 (8)
P	0.7911 (3)	0.2732 (2)	0.3234 (2)	2.7 (2)
C(1)	0.612 (1)	0.367 (1)	0.1796 (7)	3.2 (7)
C(2)	0.822 (1)	0.427 (1)	0.0923 (8)	3.4 (8)
C(3)	0.931 (1)	0.720 (1)	0.150 (1)	5 (1)
C(4)	0.768 (1)	0.680 (1)	-0.0128 (8)	4.3 (9)
C(5)	0.600 (1)	0.750 (1)	0.1693 (8)	3.6 (8)
C(6)	0.490 (1)	0.7084 (9)	0.2211 (8)	3.4 (8)
C(7)	0.341 (1)	0.496 (1)	0.3318 (8)	4.3 (9)
C(8)	0.377 (1)	0.560 (1)	0.1161 (8)	3.8 (8)
C(9)	0.612 (2)	0.873 (1)	0.140 (1)	6 (1)
C(10)	0.358 (1)	0.766 (1)	0.270 (1)	5 (1)
C(11)	0.907 (1)	0.1837 (9)	0.2514 (7)	3.3 (7)
C(12)	1.05 (1)	0.156 (1)	0.2689 (8)	4.1 (8)
C(13)	1.14 (2)	0.090 (1)	0.214 (1)	5 (1)
C(14)	1.08 (2)	0.050 (1)	0.141 (1)	6 (1)
C(15)	0.943 (2)	0.080 (1)	0.1210 (9)	5 (1)
C(16)	0.852 (1)	0.148 (1)	0.1773 (9)	4.5 (9)
C(17)	0.627 (1)	0.2058 (9)	0.3713 (7)	3.2 (7)
C(18)	0.529 (1)	0.260 (1)	0.4342 (9)	4.2 (9)
C(19)	0.399 (1)	0.219 (1)	0.473 (1)	4.6 (9)
C(20)	0.361 (1)	0.128 (1)	0.448 (1)	5 (1)
C(21)	0.358 (1)	0.411 (1)	0.7866 (9)	5.1 (9)
C(22)	0.450 (1)	0.345 (1)	0.7323 (8)	4.0 (8)
C(23)	0.874 (1)	0.2935 (9)	0.6288 (7)	3.3 (7)
C(24)	0.910 (1)	0.389 (1)	0.6524 (9)	4.2 (8)
C(25)	1.04 (2)	0.425 (1)	0.614 (1)	6 (1)
C(26)	1.13 (1)	0.372 (1)	0.553 (1)	5 (1)
C(27)	1.10 (1)	0.281 (1)	0.5273 (9)	4.7 (9)
C(28)	0.970 (1)	0.241 (1)	0.5657 (9)	4.3 (9)
F(1)	0.789 (1)	-0.3967 (7)	0.9343 (7)	7.4 (7)
F(2)	0.854 (1)	-0.4163 (8)	0.7905 (8)	8.9 (9)
F(3)	1.01 (1)	-0.4279 (8)	0.8865 (9)	10 (1)
F(4)	1.257 (9)	-0.264 (1)	0.7701 (8)	10 (1)
F(5)	1.12 (1)	-0.3628 (7)	0.7192 (8)	9.0 (9)
F(6)	1.17 (1)	-0.2116 (8)	0.6389 (6)	8.2 (8)
O(1)	0.9567 (9)	0.1865 (7)	0.8479 (7)	4.9 (7)
O(2)	0.6304 (9)	0.0953 (8)	0.9824 (5)	5.1 (7)

capped. This is in accordance with the earlier observation that strong  $\pi$  donors, such as the halides, prefer the apex of the capped face of the monocapped trigonal prism (Hoffmann, Beier, Muettterties & Rossi, 1977). Fig. 2 shows the torsional angles in the five-membered ring of the chelate ligand and their estimated standard deviations. The nature of the ring puckering was analysed according to the method of Cremer & Pople (1975). The relevant parameters are  $q = 0.51$ ,  $\varphi = -12.6^\circ$  indicating a highly puckered ring that more closely approximates the twist conformation than the envelope conformation. In the related complexes  $(L-L)\text{W}(\text{CO})_2\text{I}_2\text{P}(\text{OCH}_3)_3$  and  $(L-L)\text{W}(\text{CO})\text{Br}_2[\text{P}(\text{OCH}_3)_3]_2$  (Mihichuk, Giesinger, Robertson & Barton, 1987), the puckering parameters are  $q = 0.26$ ,  $\varphi = -10.1^\circ$  and  $q = 0.43$ ,  $\varphi = -13.2^\circ$  respectively. The higher puckering amplitude in the title compound can be correlated with the tendency of the molecule to adopt a conformation that keeps the Br atoms and the methyl groups at a maximum separation.

The significant shortening of the W—As bonds to 2.559 (1) and 2.609 (1)  $\text{\AA}$  from the predicted value of 2.73  $\text{\AA}$  (Cotton *et al.*, 1985) may be due to  $d\pi-d\pi$

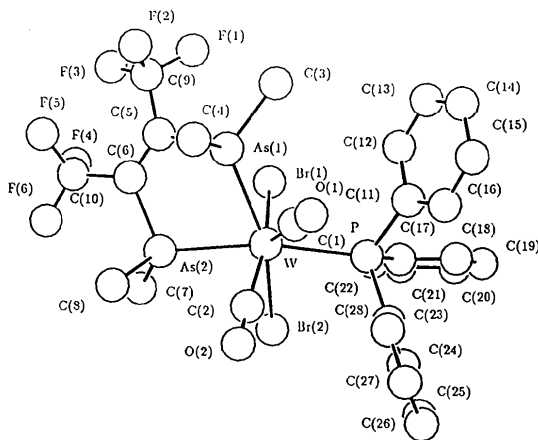


Fig. 1. Atomic labelling for the  $(\text{CH}_3)_2\text{AsC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{As}(\text{CH}_3)_2\text{W}(\text{CO})_2\text{Br}_2\text{P}(\text{C}_6\text{H}_5)_3$  molecule.

Table 2. Selected bond distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) with *e.s.d.*'s in parentheses

W—As(1)	2.609 (1)	As(2)—C(6)	1.99 (1)
W—As(2)	2.559 (1)	As(2)—C(7)	1.95 (1)
W—Br(1)	2.675 (1)	As(2)—C(8)	1.95 (1)
W—Br(2)	2.648 (1)	P—C(11)	1.84 (1)
W—P	2.548 (2)	P—C(17)	1.83 (1)
W—C(1)	1.95 (1)	P—C(23)	1.84 (1)
W—C(2)	1.95 (1)	C(5)—C(6)	1.28 (1)
As(1)—C(3)	1.95 (1)	C(1)—O(1)	1.13 (1)
As(1)—C(4)	1.95 (1)	C(2)—O(2)	1.16 (1)
As(1)—C(5)	1.96 (1)		
As(1)—W—As(2)	74.31 (4)	W—As(1)—C(3)	118.2 (4)
As(1)—Br(1)	87.03 (4)	W—As(1)—C(4)	116.0 (4)
As(1)—W—Br(2)	85.96 (4)	W—As(1)—C(5)	109.9 (3)
As(1)—W—P	162.67 (7)	C(3)—As(1)—C(4)	104.1 (6)
As(1)—W—C(1)	119.6 (3)	C(3)—As(1)—C(5)	104.2 (5)
As(1)—W—C(2)	80.0 (3)	C(4)—As(1)—C(5)	102.5 (5)
As(2)—W—Br(1)	73.98 (4)	W—As(2)—C(6)	110.4 (3)
As(2)—W—Br(2)	153.77 (5)	W—As(2)—C(7)	118.7 (3)
As(2)—W—P	119.64 (7)	W—As(2)—C(8)	118.4 (3)
As(2)—W—C(1)	70.6 (3)	C(6)—As(2)—C(7)	109.2 (5)
As(2)—W—C(2)	114.8 (3)	C(6)—As(2)—C(8)	96.6 (4)
Br(1)—W—Br(2)	88.14 (4)	C(7)—As(2)—C(8)	100.8 (4)
Br(1)—W—P	87.38 (7)	As(1)—C(5)—C(6)	119.22 (9)
Br(1)—W—C(1)	126.0 (3)	As(1)—C(5)—C(9)	117.1 (8)
Br(1)—W—C(2)	161.2 (3)	As(2)—C(6)—C(5)	115.2 (9)
Br(2)—W—C(1)	135.1 (3)	As(2)—C(6)—C(10)	115.8 (8)
Br(2)—W—C(2)	77.4 (3)	W—C(1)—O(1)	176.0 (9)
P—W—C(1)	76.6 (3)	W—C(2)—O(2)	177.1 (9)
P—W—C(2)	101.0 (3)	C(6)—C(5)—C(9)	123.3 (9)
C(1)—W—C(2)	72.4 (3)	C(5)—C(6)—C(10)	128.4 (9)

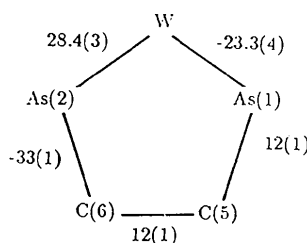


Fig. 2. Schematic diagram showing the torsional angles ( $^\circ$ ) in the five-membered ring of the chelate ligand and their estimated standard deviations in parentheses.

back donation from the W atom. The comparative shortness of the W—As(2) bond compared to the W—As(1) bond can be explained by consideration of their respective *trans* ligands. The Br(1) atom *trans* to the As(2) ligand is not as strong a  $d\pi$  acceptor as is the P atom which is *trans* to As(1), which results in a greater back donation to As(2) and a shortening of the W—As(2) bond length.

The room temperature  $^1\text{H}$  NMR spectrum in the arsenic methyl region is not consistent with the general geometry shown in Fig. 1. The solution  $^1\text{H}$  NMR (90 MHz) data shows four well resolved peaks at 190 (1) K, which indicates that the structure is static, consistent with the solid state results. However, at 219 (1) K the four peaks coalesce into one peak. The single resonance line becomes very sharp at 298 K indicative of a fast-exchange limiting spectrum. In the related complex (*L-L*)W(CO) $_2$ I $_2$ P(OCH $_3$ ) $_3$  (Mihichuk, Giesinger, Robertson & Barton, 1987), four peaks were observed at 216 K, which coalesce into two peaks at 221 K and then to one at 239 K. The reason that the title compound remains fluxional at comparatively lower temperature is not clear, but presumably involves the relative radius of the halogen atoms.

We thank the University of Regina for financial support to SM and LM and for the provision of computational facilities.

#### References

- BEAUCHAMP, A. L., BELANGER-GARIEPY, F. & ARAI, S. (1985). *Inorg. Chem.* **24**, 1860–1863.  
 COTTON, F. A., FALVELLO, L. R. & MEADOWS, J. H. (1985). *Inorg. Chem.* **24**, 514–517.  
 CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.  
 CROW, J. P., CULLEN, W. R., HERRING, F. G., SAMS, J. R. & TAPPING, R. L. (1971). *Inorg. Chem.* **10**, 1616–1623.  
 DREW, M. G. B. & WILKINS, J. D. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2664–2669.  
 HOFFMANN, R., BEIER, E. L., MUETTERTIES, E. L. & ROSSI, A. R. (1977). *Inorg. Chem.* **16**, 511–522.  
 MERCER, A. & TROTTER, J. (1974). *Can. J. Chem.* **52**, 3331–3336.  
 MIHICHUK, L. M., GIESINGER, C. L., ROBERTSON, B. E. & BARTON, R. J. (1987). *Can. J. Chem.* **65**, 2634–2638.  
 MIHICHUK, L. M., PIZZEY, M., ROBERTSON, B. E. & BARTON, R. J. (1986). *Can. J. Chem.* **64**, 991–995.  
 MUETTERTIES, E. L. & GUGGENBERGER, L. J. (1974). *J. Am. Chem. Soc.* **96**, 1748–1756.  
 PORAI-KOSHITS, M. A. & ASLANOV, L. A. (1972). *J. Struct. Chem.* **13**, 244–253.  
 STEWART, J. M. & HALL, S. R. (1986). *XTAL85*. Tech. Rep. TR-1675. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

*Acta Cryst.* (1991). **C47**, 725–728

## Structures of [*cis*-1,2-Bis(diphenylphosphino)ethylene]tetracarbonylmolybdenum(0) (1) and Bis[*cis*-1,2-bis(diphenylphosphino)ethylene]dicarbonylmolybdenum(0) (2)

BY CHUEN-HER UENG\* AND LI-CHING LEU

*Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan*

(Received 17 July 1990; accepted 17 September 1990)

**Abstract.** (1)  $\text{C}_{30}\text{H}_{22}\text{MoP}_2\text{O}_4$ ,  $M_r = 604.4$ , orthorhombic,  $Pbcn$ ,  $a = 15.884$  (5),  $b = 16.719$  (3),  $c = 20.807$  (4) Å,  $V = 5526$  (2) Å $^3$ ,  $Z = 8$ ,  $D_m = 1.5$  (1),  $D_x = 1.45$  Mg m $^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.7093$  Å,  $\mu = 0.30$  mm $^{-1}$ ,  $F(000) = 1224$ ,  $T = 298$  K, final  $R = 0.032$  for 2708 observed reflections. (2)  $\text{C}_{54}\text{H}_{44}\text{MoP}_4\text{O}_2$ ,  $M_r = 944.8$ , monoclinic,  $C2/c$ ,  $a = 21.644$  (4),  $b = 11.361$  (2),  $c = 18.708$  (5) Å,  $\beta = 99.02$  (2) $^\circ$ ,  $V = 4544$  (2) Å $^3$ ,  $Z = 4$ ,  $D_m = 1.4$  (1),  $D_x = 1.38$  Mg m $^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.7093$  Å,  $\mu = 0.46$  mm $^{-1}$ ,  $F(000) = 1944$ ,  $T = 298$  K, final  $R = 0.033$  for 3040 observed reflections. The two Mo—P lengths for compound (1) are almost the same, but the two Mo—P lengths in the same chelate ring for compound (2) are significantly different. The two

mutually *cis* CO groups in compound (1) have larger Mo—C distances than those in compound (2) owing to the presence of only two stronger  $\pi$ -acceptor CO ligands in the latter compound. The bite angle,  $\angle\text{P—Mo—P}$ , of compound (1) is slightly smaller than that of compound (2).

**Introduction.** The crystal structures of some bidentate phosphine derivatives of molybdenum(0) carbonyl, [bis(diphenylphosphino)methane]tetracarbonylmolybdenum(0),  $\text{Mo}(\text{CO})_4(\text{dppm})$  (Cheung, Lai & Mok, 1971), [1,2-bis(diphenylphosphino)ethane]tetracarbonylmolybdenum(0),  $\text{Mo}(\text{CO})_4(\text{dppe})$  (Bernal, Reisner, Dobson & Dobson, 1986), bis[1,3-bis-(diphenylphosphino)propane]dicarbonylmolybdenum(0),  $\text{Mo}(\text{CO})_2(\text{dppp})_2$  (Chow, Wang, Sheu & Peng, 1986), [1,3-bis(diphenylphosphino)pro-

\* To whom correspondence should be addressed.