were not demonstrated by an infrared spectroscopic study (Dobos, Szabó & Zelei, 1975). The internal angle in the benzene ring at C(2), *i.e.* the atom where the Si(CH$_3$)$_3$ group is attached, is less than 120°, as found also in DMHSB (116·2°) and in α-naphthylphenylmethylsilane (118·4°) (Okaya & Ashida, 1966). The molecules are held together by van der Waals forces, the nearest intermolecular C···C distances ranging from 4·04 to 4·41 Å; the distances between molecules in the same layer are about 0·1 Å shorter on average than those between molecules lying in adjacent layers. A comparison of the results of our analysis with the (incomplete) results of Magdoff (1951) for *p*-di-t-butylbenzene suggests that the two structures are isomorphous.

The calculations were carried out on the ODRA-1304 computer at the Computing Centre of the Faculty of Sciences of the L. Eötvös University; the authors are indebted to the staff of the Computing Centre. We thank Dr Gy. Argay for the *ORTEP* stereo drawing.

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cis-Tetracarbonyl-1,4-*h*^{2}-1,2-bis(dimethylphosphino-1,2-dimethyl)diarsinemolybdenum(0)

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(*Received* 22 *February* 1975; *accepted* 26 *February* 1975)

Abstract. (CO)$_4$Mo(Me$_2$P–AsMe–AsMe–PMe$_2$), C$_{10}$H$_{18}$As$_2$P$_2$O$_4$Mo, orthorhombic, *Pbcn*, $a=8\cdot138$ (1), $b=15\cdot775$ (3), $c=14\cdot701$ (3) Å, $M=509\cdot98$, $Z=4$, $D_x=1\cdot79$ g cm^{-3}. The molecule possesses crystallographic C_2 symmetry with octahedral coordination of Mo by four carbonyl groups and the bidentate 1,2-bis-(dimethylphosphino-1,2-dimethyl)diarsine ligand. The Mo–C length of 2·453 (7) is significantly shorter than that of 2·489 (6) Å in the isomorphous derivative (CO)$_4$Mo(Me$_2$P–PMe–PMe–PMe$_2$). A very short As–As length of 2·343 (7) Å is observed.

Introduction. Cell dimensions were determined by a least-squares fit to settings for 15 reflexions ($\pm hkl$) on a Syntex $P2_1$ four-circle diffractometer (Mo $K\alpha$ 0·71069 Å). The intensities, from an elongated prismatic crystal sealed in a Lindemann-glass capillary and with approximate dimensions 0·55 × 0·22 × 0·16 mm, were collected on the diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Measurements were carried out in the ω-mode (range 1·4°) for $3\cdot0 \le 2\theta \le 50\cdot0°$ at scan speeds varying linearly between 2·55° min^{-1} (150 c.p.s. and below) and 9·77° min^{-1} (5000 c.p.s. and above). Scan and background time were equal. Two standard reflexions, monitored at regular intervals, displayed no significant variations due to crystal deterioration. Lorentz and polarization but no absorption [μ(Mo $K\alpha$)$=45\cdot3$ cm^{-1}] corrections were applied. After data reduction, 541 independent reflexions were obtained for which $I \ge 3\cdot0\sigma(I)$, where $\sigma(I)$ is based on the counting statistics.

The positions of the Mo, As and P atoms were located by direct methods, those of the remaining non-hydrogen atoms from subsequent difference syntheses. Positional parameters, and anisotropic temperature factors for Mo, As and P, were refined by full-matrix least-squares calculations. The final value of $R_G=[\sum w\Delta^2/\sum wF_o^2]^{1/2}$ was 0·130, with $R_w=\sum w^{1/2}\Delta/\sum w^{1/2}F_o$ of 0·100 and R 0·090. The weights applied were given by $w=k/[\sigma^2(F_o)+gF_o^2]$ where k and g refined to 2·5861 and 0·004577 respectively. An attempt to refine the carbonyl groups with anisotropic temperature factors did not produce a significant improvement in R_G and led to unrealistic component values for several of the atoms involved. A final difference map revealed possible locations for some, but not all, of the expected H atoms. However, in view of the relatively high value for R_G, which may in part be attributed to the high thermal motion, and the limited data, inclusion of these as fixed parameters in the least-squares refinement could not be justified. Other possible causes for the high value of R_G may be sought in the poor quality of the crystal used and the failure to apply an absorption correction. Complex neutral atom scattering factors (Cromer, 1965; Cromer & Waber, 1965) were employed for all atoms. The final coordinates and isotropic temperature factors are listed in Table 1, with the anisotropic temperature factors in Table 2. The full covariance matrix was implemented in the estimation of the bond lengths and selected angles (Tables 3 and 4). Fig. 1 gives the atomic numbering, Fig. 2 a projection of the structure perpendicular to [100].*

Table 1. *Atom positional parameters* ($\times 10^4$) *and isotropic temperature factors* ($Å^2 \times 10^3$)

	x	y	z	U
Mo	0	2388 (2)	2500	*
P(1)	700 (12)	3495 (6)	3606 (5)	*
As	84 (7)	4899 (2)	3296 (3)	*
C(1)	523 (37)	1547 (20)	3418 (22)	79 (10)
O(1)	937 (34)	1058 (17)	3962 (19)	127 (9)
C(2)	2269 (57)	2367 (28)	2048 (27)	115 (14)
O(2)	3632 (31)	2280 (17)	1762 (17)	116 (9)
C(3)	3033 (47)	3638 (23)	3907 (23)	113 (13)
C(4)	−210 (47)	3373 (25)	4730 (24)	116 (13)
C(5)	−2496 (57)	4691 (30)	3351 (26)	139 (17)

* Anisotropic temperature factor components are listed in Table 2.

Table 2. *Anisotropic temperature factors* ($Å^2 \times 10^3$)

The anisotropic temperature factor takes the form:

$$\exp\,[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^* + 2U_{13}lhc^*a^*+2U_{12}hka^*b^*)]\,.$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	72 (2)	47 (2)	67 (2)	0	−5 (3)	0
P(1)	104 (7)	64 (5)	56 (5)	15 (4)	−10 (5)	−8 (5)
As	210 (5)	58 (2)	147 (4)	32 (2)	−48 (4)	−1 (4)

Table 3. *Bond lengths* (Å)

Mo–P(1)	2·453 (7)	P(1)–As	2·316 (8)
As—As′	2·343 (7)	Mo–C(1)	1·94 (3)
Mo–C(2)	1·96 (4)	C(1)–O(1)	1·16 (3)
C(2)–O(2)	1·19 (3)	P(1)–C(3)	1·96 (3)
P(1)–C(4)	1·82 (3)	As—C(5)	2·13 (4)

Table 4. *Bond angles* (°)

P(1)–Mo–P(1)′	89·2 (3)	P(1)–Mo–C(1)	88·5 (8)
P(1)–Mo–C(2)	91·0 (11)	C(1)–Mo–C(2)	91·0 (12)
As—P(1)–Mo	120·0 (3)	C(3)–P(1)–Mo	117·2 (9)
C(4)–P(1)–Mo	115·6 (11)	C(3)–P(1)–As	98·2 (9)
C(4)–P(1)–As	101·0 (10)	C(3)–P(1)–C(4)	101·6 (12)
As′—As—P(1)	102·1 (2)	C(5)–As—P(1)	93·4 (10)
C(5)–As—As′	88·9 (8)	O(1)–C(1)–Mo	176 (2)
O(2)–C(2)–Mo	175 (2)		

Discussion. The synthesis of novel chelate complexes of the type *cis*-$Mo(CO)_4(PMe_2$–XMe–XMe–$PMe_2)$, [X = P (I), As (II)], involving the unknown tetraphosphine, Me_2P–PMe–PMe–PMe_2, or the 1,2-diphosphinodiarsine, Me_2P–AsMe–AsMe–PMe_2, has recently been reported (Stelzer & Unger, 1975). The crystal structure of (I) (Sheldrick, 1975), which was undertaken to confirm the nature of the chelate ring system, is noteworthy for the fact that the molecule displays two significantly different P–P lengths. A very short distance of 2·142 (12) for (P)P–P(P) contrasts with that of 2·200 (9) Å for (Mo)P–P(P), which falls within the range (2·18–2·22 Å) normally observed for the P–P bond (Cowley, 1965). Preliminary investigations on (II) indicated that it was isomorphous with (I), and, therefore, a crystal structure determination was carried out to throw more light on the nature of the bonding.

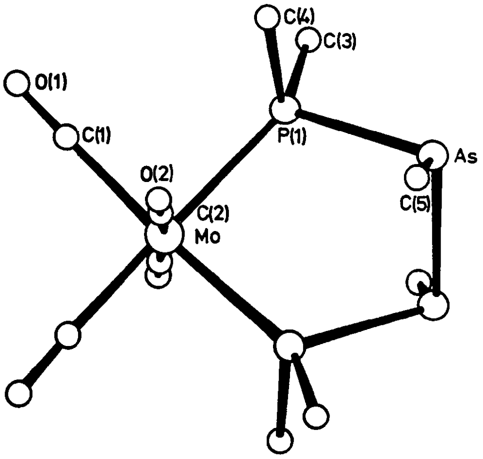

Fig. 1. Atom numbering in the molecule.

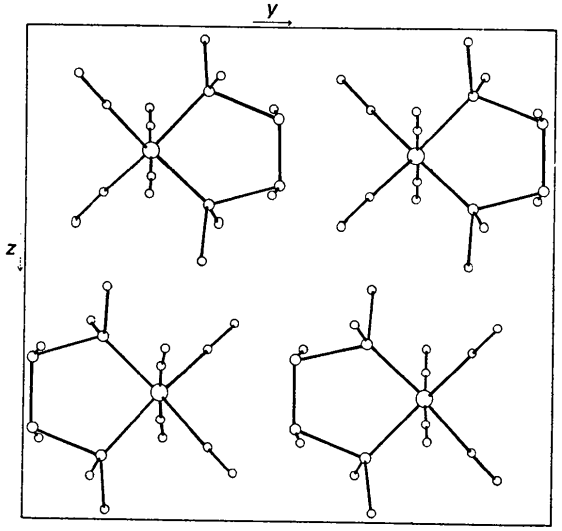

Fig. 2. Projection of the structure perpendicular to [100].

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30963 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The molecule of (II) possesses crystallographic C_2 symmetry with perfect (within the margin of significance) octahedral coordination of Mo by four carbonyl groups and the bidentate ligand Me_2P–AsMe–AsMe–PMe_2. The five-membered chelate ring is non-planar, the As–As bond being twisted out of the PMoP′ plane by 16·0°, which is similar to the 16·5° in (I). The As atom is 0·223 below the least-squares plane through the ring (unit weights), P 0·150 Å above. Angles of twist of between 3 and 23° have also been observed in the analogous $(CO)_4M(Me_2X–CF_2–CFR–XMe_2)$ (M = Mo or Cr, X = P or As, R = H or CF_3) (Cullen, Nowell, Roberts, Trotter & Ward, 1971). As in (I) no significant difference is observed between the Mo–C distances for the two carbonyl groups mutually *trans* to one another and the two *trans* to P. This behaviour contrasts with that observed in analogous Mo carbonyl complexes. Since the carbonyl group is a better π-acceptor than the PMe_2 group it would be expected that the Mo–C distance *trans* to P would be shorter than that *trans* to another carbonyl group. In $(CO)_4Mo(Ph_2P–CH_2–PPh_2)$, for instance, mean values of 1·93 and 2·04 Å respectively are observed for these bonds (Cheung, Lai & Mok, 1971). It is interesting that the Mo–C lengths of 1·94 (3) and 1·96 (4) Å in (II) are shorter, within the margin of the large associated standard deviations albeit not significantly, than those of 2·02 (2) and 2·05 (2) Å in (I). Likewise, the Mo–P length of 2·453 (7) is also shorter, in this case significantly, than that of 2·489 (6) Å in (I). Values between 2·476 and 2·537 Å for Mo–P have been found in other complexes. A comparison of these values with the sum of the covalent radii for Mo° and P (2·71 Å) suggests the presence of $(d \rightarrow d)$ π-bonding from Mo to P and indicates that this effect may be stronger in (II) than in (I), or in other reported complexes.

A very short As–As length of 2·343 (7) is found in (II), analogous to the short P–P distance in (I). This compares with values of 2·59 Å in α- and β-As_4S_4 (Porter & Sheldrick, 1972), 2·58 Å in $As_4S_6^{2-}$ (Porter & Sheldrick, 1971), 2·56 Å in As_4Se_4 (Porter & Sheldrick, 1973) and 2·45 Å in α-As_4S_3 (Whitfield, 1970). The presence of the short Mo–P and As–As bonds in the chelate ring suggests that some degree of π-delocalization takes place.

This work was carried out within the technology programme of the Bundesministerium für Forschung und Technologie (BRD). The calculations were carried out on the Institute PDP-10 computer with the program *SHELX* (G. M. Sheldrick) and ancilliary programs written by myself. I am indebted to Dr O. Stelzer and Dr E. Unger for the provision of crystals and to Frau A. Borkenstein for assistance during the structural determination and for the preparation of diagrams.

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