Crystal and Molecular Structure of [bis(diphenylarsino)methane]dibromodicarbonylmolybdenum(II)

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Crystals of the title compound are monoclinic, space-group $P2_1/c$, $Z = 4$, cell dimensions: $a = 11{\cdot}543(10)$, $b = 22{\cdot}121(17)$, $c = 19{\cdot}464(15)$ Å, and $\beta = 94{\cdot}31(11)°$. The structure was solved by Patterson and Fourier methods from diffractometer data and refined by a blocked full-matrix technique to R 0·085 for 2018 independent reflections. One of the arsine ligands is bi- and the other uni-dentate, so that the molybdenum atom is seven-co-ordinate. The environment of the metal atom is best described as distorted capped octahedral with a carbonyl group in the unique capping position [Mo–C 1·92(4) Å]. The capped face of the octahedron contains the other carbonyl group [Mo–C 1·90(4) Å] and two arsenic atoms from different arsine ligands [2·608(5) and 2·592(5) Å]. The uncapped face contains two bromine atoms [2·650(5) and 2·674(5) Å] and one arsenic atom [2·651(5) Å].

THE crystal structures of many seven-co-ordinate complexes have been determined but the majority of such compounds have been unrelated to each other. As the energy differences between the various ideal seven-co-ordinate geometries (pentagonal bipyramidal D_{5h}, capped trigonal prism C_{2v}, and capped octahedron C_{3v}) are quite small,[1] a comparison of the stereochemistry of related structures through X-ray analysis can be used to clarify the factors involved in the choice of geometry. Thus, a series of crystal-structure analyses of complexes containing the sexadentate ethylenediaminetetra-acetic acid ligand (H_4Y), namely $Mn(OH_2)Y$, $Rb[Fe(OH_2)Y],H_2O$, and $Li[Fe(OH_2)Y],2H_2O$, have shown a dependence of geometry on (*inter alia*) the electronic state of the metal.[2,3] A series of seven-co-ordinate complexes of molybdenum containing the terdentate cyclopentadiene

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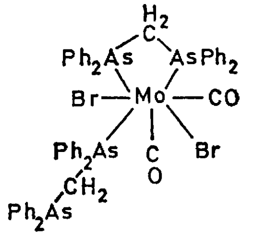
[1] E. L. Muetterties and C. N. Wright, *Quart. Rev.*, 1967, **21**, 109.

[2] S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, 1964, **3**, 27.

[3] M. D. Lind, M. J. Hamer, T. A. Hamer, and J. L. Hoard, *Inorg. Chem.*, 1964, **3**, 34.

ligand[4-8] exhibit very similar configurations, presumably because the ring is the dominant feature in the structures.

We have prepared crystals of a number of seven-co-ordinate complexes of the general formula $MX_2(CO)_nL_m$ (M = Mo or W; X = Cl, Br, or I) where L is a multidentate arsenic or phosphorus ligand. From an investigation of the structures of these molecules through *X*-ray diffraction, we hope to correlate changes in the co-ordination sphere of the metal atom with variations in ligand type. In this paper we report the crystal structure of [bis(diphenylarsino)methane]dibromodicarbonylmolybdenum(II), $MoBr_2(CO)_2(AsPh_2{\cdot}CH_2{\cdot}AsPh_2)_2$, (I), in which one of the arsine ligands is bi- and the other unidentate. A preliminary account of this work has appeared[9] in which the structure of (I) is compared to that of another molecule in this series, bis[bis(diphenylarsino)methane]dibromotricarbonyltungsten(II), (II) in which both arsine ligands are unidentate.



(I)

EXPERIMENTAL

Crystals of (I) were prepared as described previously.[10]

Crystal Data.—$C_{52}H_{44}As_4Br_2MoO_2$, $M = 1256{\cdot}4$, Monoclinic, $a = 11{\cdot}543(10)$, $b = 22{\cdot}121(17)$, $c = 19{\cdot}464(15)$ Å, $\beta = 94{\cdot}31(11)°$, $U = 4955{\cdot}9$ Å^3, $D_m = 1{\cdot}67(2)$, $Z = 4$, $D_c = 1{\cdot}683$, $F(000) = 2544$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 47·59 cm^{-1}. Space-group $P2_1/c$ from systematic absences: $h0l$, $l = 2n + 1$; and $0k0$, $k = 2n + 1$.

A crystal with dimensions 0·50 × 0·25 × 0·15 mm was mounted with the a^* axis parallel to the instrument of a General Electric XRD 5 diffractometer, equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Diffraction intensities and cell-dimensions were obtained by use of zirconium-filtered Mo-K_α radiation and the stationary-crystal–stationary-counter method with a 4° take-off angle and a counting time of 10 s. The intensities of 4560 independent reflections were measured with $2\theta < 40°$. Individual backgrounds were taken for those reflections whose counts were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background as a function of 2θ. Several standard reflections were measured repeatedly during the course of the experiment, but no significant changes in intensity were detected. No absorption or extinction correction was applied. The standard deviation $\sigma(I)$ of the reflections was taken to be $[I + 2E + (0{\cdot}03I)^2]^{\frac{1}{2}}$, where E is the estimated background of the reflection. 2018 reflections had $I > 2\sigma(I)$ and were used in the subsequent calculations.

Structure Determination.—Examination of the Patterson function showed the positions of five of the seven heavy atoms. The remaining atom positions were determined from successive Fourier maps. The structure was refined by a blocked full-matrix method. Five blocks were used; the first containing all atoms [molybdenum, arsenic, bromine (anisotropic), carbon, and oxygen (isotropic)] except those in the eight phenyl rings. These 48 carbon atoms were divided into four blocks of 12 atoms each. A weighting scheme was chosen such that average values of $w\Delta^2$ were obtained for groups of reflections independent of the value of F_o or $\sin\theta/\lambda$: this was $\sqrt{w} = 1$, for $F_o < 100$ and $\sqrt{w} = 100/F_o$ for $F_o > 100$. Calculations were made on the S.R.C. ATLAS computer and our Elliott 4130 with the programs described in ref. 11. Atomic scattering factors for molybdenum, arsenic, bromine, oxygen, and carbon were taken from ref. 12, as were the corrections for the real and imaginary part of the anomalous dispersion for molybdenum, bromine, and arsenic. The anisotropic thermal parameters were defined as exp $-2\pi^2 \sum_i\sum_j U_{ij}h_ih_j$, $(i, j = 1,2,3)$ and the isotropic thermal parameters as exp $[-8\pi^2U(\sin^2\theta/\lambda^2)]$. The final R was 0·085 and in the final cycle of refinement, all shifts were $< 0{\cdot}04\,\sigma$. The 2542 reflections given zero weight in the refinement showed no large discrepancies. A difference Fourier synthesis showed no significant peaks. The final list of positional co-ordinates and thermal parameters, together with standard deviations, is given in Tables 1 and 2. Phenyl ring carbon atoms are denoted by C(mn), m being the ring number [(1)—(8)] and n the position of the atom in the ring [(1)—(6)]. Details of the co-ordination sphere of molybdenum are given in Table 3. Table 4 lists the dimensions of the phenyl rings. The final observed and calculated structure factors for the structure are given in Supplementary Publication SUP 20289 (9 pp., 1 microfiche).*

DISCUSSION

The molybdenum atom in (I) is seven-co-ordinate with a distorted capped octahedral environment, a carbonyl group occupying the unique capping position. Figure 1(a) shows the co-ordination sphere of the metal atom with the unique position perpendicular to the plane of the paper. The atomic numbering system and the most important bond distances in the structure are also given. Figure 1(b) shows the co-ordination sphere of the related molecule (II) in the equivalent projection.[9] In (I), the

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

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TABLE 1

Final positional (×10^5, 10^4, or 10^3) and isotropic (×10^2) thermal parameters for (I), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	*U*
Mo	2401(3)	15296(14)	34244(16)	*a*
Br(1)	2723(4)	18330(20)	21357(21)	*a*
Br(2)	0558(4)	22636(17)	33983(21)	*a*
As(1)	0830(4)	08374(16)	27948(19)	*a*
As(2)	3560(4)	25381(17)	37460(20)	*a*
As(3)	2440(4)	17996(17)	47216(19)	*a*
As(4)	−0993(5)	06688(26)	14339(23)	*a*
C(1)	243(3)	0757(19)	3877(21)	6·8(12)
O(1)	246(2)	0301(13)	4174(14)	7·9(8)
C(2)	388(4)	1175(19)	3314(21)	7·1(13)
O(2)	471(3)	0960(13)	3221(15)	9·5(10)
C(3)	003(3)	1222(16)	1961(17)	4·8(10)
C(4)	291(3)	2689(16)	4664(18)	5·5(11)
C(11)	145(4)	008(2)	245(2)	6·3(11)
C(12)	255(4)	010(2)	221(2)	9·9(16)
C(13)	304(6)	−048(3)	201(4)	16·6(27)
C(14)	232(5)	−100(2)	201(2)	9·7(15)
C(15)	127(5)	−099(2)	216(3)	10·3(16)
C(16)	074(4)	−043(2)	243(2)	8·4(14)
C(21)	−038(3)	059(2)	330(2)	4·0(9)
C(22)	−137(3)	094(2)	325(2)	6·6(12)
C(23)	−233(4)	076(2)	364(2)	8·5(14)
C(24)	−230(4)	026(2)	411(2)	9·7(16)
C(25)	−121(4)	−009(2)	414(2)	7·6(13)
C(26)	−034(3)	010(2)	376(2)	5·3(10)
C(31)	−237(6)	113(3)	136(3)	14·1(23)
C(32)	−227(7)	191(4)	136(4)	18·4(30)
C(33)	−333(8)	229(4)	139(4)	19·1(31)
C(34)	−442(8)	191(4)	143(4)	20·9(33)
C(35)	−440(6)	130(3)	138(3)	14·4(22)
C(36)	−331(7)	107(3)	151(3)	13·8(23)
C(41)	−026(4)	089(2)	059(2)	8·2(13)
C(42)	−071(5)	125(2)	009(3)	10·8(17)
C(43)	−023(6)	139(3)	−054(3)	14·6(32)
C(44)	081(5)	112(2)	−058(3)	11·2(18)
C(45)	148(5)	069(3)	−014(3)	14·3(22)
C(46)	072(5)	056(2)	051(3)	11·6(18)
C(51)	519(3)	253(2)	384(2)	6·8(12)
C(52)	586(4)	244(2)	336(2)	6·4(11)
C(53)	706(4)	240(2)	342(2)	8·8(15)
C(54)	759(4)	241(2)	400(3)	8·7(15)
C(55)	709(5)	247(2)	457(3)	11·2(17)
C(56)	575(4)	257(2)	457(3)	10·2(16)
C(61)	333(4)	330(4)	331(2)	9·7(15)
C(62)	245(4)	336(2)	274(2)	7·4(12)
C(63)	223(5)	396(2)	244(3)	11·3(18)
C(64)	295(4)	445(2)	273(2)	8·7(14)
C(65)	371(5)	438(3)	322(3)	11·7(18)
C(66)	405(4)	379(2)	360(3)	11·1(17)
C(71)	114(3)	179(2)	520(2)	4·8(9)
C(72)	109(4)	215(2)	583(2)	8·9(14)
C(73)	009(4)	207(2)	622(3)	9·9(16)
C(74)	−086(4)	166(2)	604(2)	8·6(14)
C(75)	−076(4)	138(2)	545(2)	7·3(12)
C(76)	015(3)	144(2)	507(2)	6·0(11)
C(81)	369(3)	145(2)	532(2)	5·1(10)
C(82)	451(4)	110(2)	507(3)	9·7(16)
C(83)	551(5)	089(2)	551(3)	11·2(17)
C(84)	549(4)	101(2)	621(3)	9·4(15)
C(85)	460(5)	132(3)	648(3)	14·0(22)
C(86)	375(4)	158(2)	598(3)	11·5(18)

[a] Anisotropic thermal parameters given in Table 2.

TABLE 2

Anisotropic thermal parameters (×10^2) for the heavy atoms in (I)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	4·8(3)	2·4(3)	3·3(3)	0·9(2)	−0·8(2)	−0·0(2)
Br(1)	9·6(4)	6·9(4)	5·3(3)	1·2(3)	−0·0(2)	0·8(2)
Br(2)	6·5(4)	4·5(3)	6·4(3)	1·5(2)	−0·7(2)	−0·1(2)
As(1)	6·8(4)	3·0(3)	3·9(3)	0·9(2)	−1·2(2)	−0·0(2)
As(2)	6·1(4)	3·5(3)	4·9(3)	0·2(3)	−0·4(2)	0·3(2)
As(3)	6·4(4)	3·6(3)	4·2(3)	0·8(2)	−0·8(2)	0·1(2)
As(4)	9·1(4)	12·0(5)	4·4(4)	−3·7(3)	−2·2(3)	1·8(3)

TABLE 3

Dimensions in the co-ordination sphere of molybdenum in (I)

(*a*) Bond distances (Å)

Mo–C(1)	1·92(4)	Mo–As(3)	2·592(5)
Mo–C(2)	1·90(4)	Mo–Br(1)	2·650(5)
Mo–As(1)	2·608(5)	Mo–Br(2)	2·674(5)
Mo–As(2)	2·651(5)		

(*b*) Distances (Å) between atoms in the co-ordination sphere and angles (°) subtended at the metal atom.

	C(1)	C(2)	As(1)	As(3)	Br(1)	Br(2)	As(2)
C(1)		2·26	2·70	2·83	4·19	4·07	4·19
C(2)	72(2)		3·67	3·59	2·95	4·54	3·16
As(1)	71(1)	108(1)		4·58	3·42	3·39	5·16
As(3)	76(1)	105(1)	123·6(2)		5·07	3·40	2·88
Br(1)	131(1)	79(1)	81·1(2)	150·5(2)		3·76	3·57
Br(2)	122(1)	165(1)	79·9(2)	80·4(2)	89·8(2)		3·53
As(2)	130(1)	86(1)	157·7(2)	66·7(2)	84·6(2)	83·1(2)	

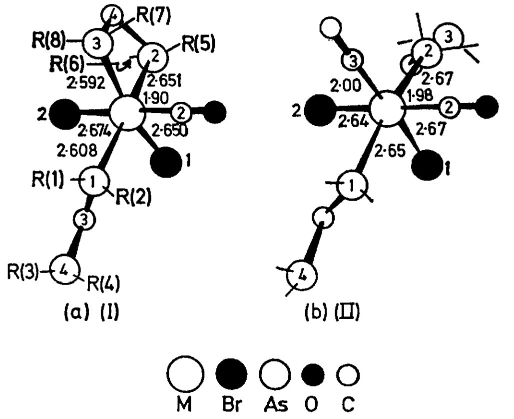

FIGURE 1 Projections of the co-ordination spheres of (I) and (II) viewed down the vector from the carbonyl group in the capping position (omitted from the diagram) to the metal atom (R = ring)

face which is capped by the carbonyl group C(1)–O(1) contains the second carbonyl group C(2)–O(2) and two arsenic atoms As(1) and As(3) from different ligands. The uncapped face contains the two bromine atoms, Br(1) and Br(2), and the arsenic atom As(2).* The angles subtended at the central molybdenum atom by the unique carbon atom C(1) and atoms in the capped face and uncapped face average to 73 and 128° respectively. These angles agree well with those found in other capped octahedral structures [*i.e.* 74 and 131° in aquo-

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* The most convenient method for describing the configuration of a seven-co-ordinate molecule is in terms of distortion from one of the ideal symmetries. However, a large number of molecules that do not have the pentagonal bipyramidal symmetry can be adequately described in terms of either a distorted capped octahedron or a distorted trigonal prism.[1] For example, (I) can also be considered as a capped trigonal prism with Br(1) as the capping atom and atoms, As(1), As(2), C(2), and Br(2) constituting the capped quadrilateral face. Although we believe the capped octahedron to be the most adequate description of (I), we recognize that such a distinction between C_{2v} and C_{3v} symmetry is, for the present molecule, primarily a matter of convenience.

tris(diphenylpropanedionato)holmium[13]]. In (I), the angles subtended at the central atom by two atoms in the capped face are much larger than those from the uncapped face (mean values 112 and 86° respectively). In the capped octahedral molecule, aquotris(1-phenyl-1,3-butanedionato)yttrium(III),[14] mean angles are 113 and 83° respectively. In these two complexes of the form $ML_3(H_2O)$,[13,14] the water molecule occupies the capping position and six oxygen atoms from the bidentate ligands occupy the octahedral positions, thus maintaining approximate C_{3v} symmetry. In these structures non-bonded (O · · · O) contacts between neighbouring atoms in the co-ordination sphere are of the order of 2·7 Å. In (I), the size of the ligands vary considerably and hence so do the contacts in the co-ordination sphere, giving distortions from C_{3v} symmetry. For example, of the angles subtended at the molybdenum atom by pairs of atoms in the capped face, the As(1)–Mo–As(3) angle is considerably larger (123·6°) than the two C(2)–Mo–As angles which are 108 and 105°. The geometry of this face is affected by the phenyl rings bonded to the arsenic atoms, as several intramolecular contacts <3·50 Å occur between the two carbonyl groups and the atoms in these phenyl rings. In the uncapped face, the Br–Mo–Br angle is 89·8°, significantly larger than the Br–Mo–As(2) angles of 83·1 and 84·6°. The relative importance of the three different ligands in ligand–ligand non-bonded repulsion would therefore appear to be Br > $AsPh_2$ > CO. This is consistent with the arrangement of atoms in the capped octahedron, a carbonyl group occupying the capping position, which is the most sterically crowded of all seven positions, while two arsenic atoms and one carbonyl group occupy the capped face as its nearest neighbours.

TABLE 4

Molecular geometry in (I)

(*a*) Dimensions of atoms not in the phenyl rings

(i) Distances (Å)

C(1)–O(1)	1·16(5)	As(3)–C(4)	2·05(4)	As(2)–C(51)	1·87(4)	As(4)–C(31)	1·89(4)
C(2)–O(2)	1·10(5)	As(4)–C(3)	1·94(3)	As(2)–C(61)	1·90(5)	As(4)–C(41)	1·92(5)
As(1)–C(3)	2·00(3)	As(1)–C(11)	1·96(4)	As(3)–C(71)	1·82(4)		
As(2)–C(4)	2·02(4)	As(1)–C(21)	1·85(3)	As(3)–C(81)	1·95(3)		

(ii) Angles (°)

C(3)–As(4)–C(31)	100(2)	Mo–As(1)–C(3)	113(1)	Mo–As(2)–C(4)	98(1)	Mo–As(3)–C(4)	99(1)
C(3)–As(4)–C(41)	90(2)	Mo–As(1)–C(11)	114(1)	Mo–As(2)–C(51)	120(1)	Mo–As(3)–C(71)	123(1)
C(31)–As(4)–C(41)	103(2)	Mo–As(1)–C(21)	117(1)	Mo–As(2)–C(61)	126(1)	Mo–As(3)–C(81)	117(1)
As(1)–C(3)–As(4)	113(2)	C(3)–As(1)–C(11)	105(1)	C(4)–As(2)–C(51)	111(2)	C(4)–As(3)–C(71)	105(1)
As(2)–C(4)–As(3)	90(1)	C(3)–As(1)–C(21)	104(1)	C(4)–As(2)–C(61)	102(2)	C(4)–As(3)–C(81)	103(1)
Mo–C(1)–O(1)	177(3)	C(11)–As(1)–C(21)	104(2)	C(51)–As(2)–C(61)	99(2)	C(71)–As(3)–C(81)	107(1)
Mo–C(2)–O(2)	177(3)						

(*b*) Dimensions in the phenyl rings

Ring	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
C(1)–C(2)	1·39(7)	1·37(5)	1·71(11)	1·37(7)	1·27(6)	1·44(6)	1·45(6)	1·34(6)
C(2)–C(3)	1·47(9)	1·45(6)	1·51(12)	1·41(9)	1·38(6)	1·46(7)	1·44(6)	1·46(7)
C(3)–C(4)	1·42(9)	1·45(7)	1·52(13)	1·35(9)	1·25(6)	1·46(7)	1·45(6)	1·38(8)
C(4)–C(5)	1·26(8)	1·46(7)	1·36(12)	1·45(8)	1·30(7)	1·26(7)	1·32(6)	1·38(8)
C(5)–C(6)	1·50(7)	1·35(6)	1·36(10)	1·63(9)	1·56(8)	1·53(7)	1·33(6)	1·45(8)
C(6)–C(1)	1·40(6)	1·41(5)	1·16(11)	1·37(7)	1·54(6)	1·46(7)	1·40(5)	1·30(7)
As–C(1)–C(2)	117(3)	117(3)	119(5)	127(4)	126(3)	120(3)	121(3)	121(3)
As–C(1)–C(6)	118(3)	125(3)	136(6)	114(4)	116(3)	115(3)	127(3)	119(3)
C(2)–C(1)–C(6)	124(4)	118(3)	101(6)	118(5)	117(4)	125(4)	112(3)	120(4)
C(1)–C(2)–C(3)	116(5)	119(4)	121(6)	129(5)	127(4)	119(4)	118(4)	122(4)
C(2)–C(3)–C(4)	118(6)	123(4)	111(7)	111(5)	120(5)	116(4)	124(4)	116(5)
C(3)–C(4)–C(5)	125(5)	114(4)	123(7)	134(6)	124(5)	122(5)	114(4)	123(5)
C(4)–C(5)–C(6)	121(5)	121(4)	112(7)	106(5)	121(5)	128(5)	124(4)	115(5)
C(5)–C(6)–C(1)	115(4)	125(3)	141(7)	121(5)	110(4)	109(4)	128(4)	124(5)

These distortions from three-fold symmetry also occur in (II), in which all seven ligands are unidentate. However, in (I), one of the arsine ligands is a chelate, forming a highly strained four-membered ring, which causes additional distortions in the co-ordination sphere. The four-membered ring is non-planar, the carbon atom C(4) being 0·60 Å from the plane of the other three atoms, Mo, As(2), and As(3). In the ring, the As(2) · · · As(3) distance is 2·88 Å, compared to As(1) · · · As(4) of 3·28 Å in the unidentate ligand. The As(2)–Mo–As(3) angle is 66·7(15°), about 15° less than equivalent angles in (I), and less than the equivalent angle in (II), C(3)–W–As(2), which is 77·8(13)°. Although the As(1)–M–As(2) angles are equivalent in (I) and (II) at 157·6°, the As(3)–Mo–Br(1) angle in (I) is significantly less (150·5°) than the C(3)–W–Br(1) angle (158·6°) in (II). This suggests that the distortion of the co-ordination sphere of (I), imposed by the four-membered ring, is focused on the position of As(3) rather than that of As(2) (see Figure 1). In that four-membered ring, values of the other angles are considerably lower than in the unidentate arsine ligand. Thus the As(2)–C(4)–As(3) angle

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[13] A. Zalkin, D. H. Templeton, and D. G. Karraker, *Inorg. Chem.*, 1969, **8**, 2680.

[14] F. A. Cotton and P. Legzdins, *Inorg. Chem.*, 1968, **7**, 1777.

is 90° and the Mo–As–C(4) angles are 98°, as against 113 and 113° respectively in the unidentate ligand.*

The relative positions of the atoms in the co-ordination sphere of molybdenum has been explained on the basis of ligand–ligand repulsions. However other factors are involved. Both (I) and (II) are prepared from $MBr_2(CO)_4$ in which the two bromine atoms are mutually *cis* [15] and this configuration is maintained in both compounds. The carbonyl groups are strong π acceptors and as such prefer positions mutually *cis*, where competition for the metal d_π electrons in $d_\pi \rightarrow \pi_\pi^*$ overlap is avoided. Thus in (I), (II), and in $(C_{10}H_8N_2)(CO)_3ClMo(SnMeCl_2)$ [16] and $(C_4H_{10}S_2)(CO)_3ClW(SnMeCl_2)$,[17] in which the metal atoms have capped octahedral environments, no pair of carbonyl groups is mutually *trans*.

The two M–CO bond distances in (I) are equivalent at 1·92(4) and 1·90(4) Å. These values can be compared to other Mo^{II}–CO distances: 1·99, $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$; [4] 2·00, $(\pi\text{-}C_5H_5)Mo(CO)_3(C_3F_7)$; [5] 1·93, 1·98, $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3{\cdot}COMe)$; [6] 1·98, $(\pi\text{-}C_5H_5)Mo(CO)_3(PPh_3)I$; [7] 1·94, $(\pi\text{-}C_5H_5)Mo(CO)(PPh_2{\cdot}[CH_2]_2{\cdot}PPh_2)Cl$; [7] and 1·89, 1·93, and 1·96, $MoBr_2(CO)_3(PPh_2{\cdot}[CH_2]_2{\cdot}PPh_2)$.[18] That the bonds in (I) are shorter than the majority of these bonds may not be significant in view of their standard deviations (which may be underestimated by the blocking of the matrix), but there are good reasons for short Mo–C bonds in (I). The halogens (I > Br > Cl) tend to increase the electron density at the metal and hence the number of electrons available for back-donation.[19] As bis(diphenylarsino)methane is not a particularly good π-bonding ligand, such donation will be concentrated on the two carbonyl groups. M–CO distances in the same molecule are often stereospecific [*i.e.* in $(MeC)Co_3(CO)_8PPh_3$,[20] the Co–C(ax) and Co–C(eq) distances are 1·79 and 1·74 Å respectively]. In the present structure, no such trend is observed. The Mo–C–O angles [177(3)°] and the C–O distances [1·16(5) and 1·10(5) Å] are normal.

The Mo–As(2) bond length [2·651(5) Å] is longer than the other two Mo–As bonds [2·608(5) and 2·592(5) Å]. The mean Mo–As distance (2·62 Å) is thus considerably less than the value predicted from the sum of single bond radii (2·82 Å, taking r_{Mo} 1·61,[6] and r_{As} 1·21 Å [21]). Mo^{II}–P distances are also shorter than the sum of ionic radii (2·71 Å [6,21]) in similar compounds: *e.g.*, 2·473,[6] 2·42 and 2·43,[8] and 2·481 Å.[7] It can be concluded that both Mo–P and Mo–As bonds have some double-bond character presumably through back-donation ($d_\pi \rightarrow d_\pi$) from the metal. Indeed, it is noticeable that in (I) and (II) the arsenic atoms do not occupy positions *trans* to the strongly π-accepting carbonyl groups. In (II), the two arsenic atoms are mutually *trans* and the two bromine atoms are *trans* to carbonyl. When phosphorus is *trans* to carbonyl, as in the capped octahedral molecule $MoBr_2(CO)_3(PPh_2{\cdot}[CH_2]_2{\cdot}PPh_2)$,[18] a weakening of the Mo–P bond is observed, Mo–P(*trans* to CO) being 2·62 Å and (*trans* to Br) 2·50 Å. Such an effect is even found in $(\pi\text{-}C_5H_5)Mo(CO)(PPh_2{\cdot}[CH_2]_2{\cdot}PPh_2)Cl$,[7] where Mo–P(*trans* to CO) is 0·055 Å longer than MoP(*trans* to Cl) despite the fact that the description '*trans* to' is an oversimplification, the P–Mo–CO angle being 113·7°. However, in the present molecule, a similar effect is found as As(2), which forms the longest Mo–As bond, is in the uncapped octahedral face and is therefore more nearly in the *trans*-position to a carbonyl group than either of the other two arsenic atoms [As(2)–Mo–C(1) 130°]. The shortest of the three Mo–As bonds [Mo–As(3)] is *trans* to bromine. The Mo–Br bond can be assumed to be of predominantly σ character with the possibility of some donation from the halogen. In any case, the amount of back donation Mo → As would not be any the less for the arsenic atom being *trans* to bromine.

From the Mo^{II}–P bond lengths we have listed and the Mo^{II}–As bond lengths in (I), it would appear that the relative bond orders are similar, assuming a difference of 0·11 Å in the covalent radii of phosphorus and arsenic.[21] This is somewhat surprising as phosphorus is considered to be a better σ donor and π acceptor than arsenic. Indeed in a discussion of the reaction: [9,10]

$$\underset{\text{(I)}}{M(CO)_2L_2X_2} + CO \rightleftharpoons \underset{\text{(II)}}{M(CO)_3L_2X_2}$$
$$[L = (Ph_2As)_2CH_2]$$

it was postulated that one of the Mo–As bonds in (I) would have to be particularly weak for the reaction to occur, particularly as carbon monoxide is not a reactive ligand under the conditions used. From our analysis of (I), this does not appear to be the case, for although Mo–As(2) is the weakest such bond, it still has an appreciable amount of double-bond character. The corresponding bis(diphenylphosphino)methane complexes [analogous to (I)] do not take up carbon monoxide [22] similarly. This was thought to be due to the difference in strength of the Mo–P and Mo–As bonds rather than to any difference in steric strain in the four-membered ring, but is not confirmed by our analysis of (I).

The mean As–C bond lengths in the four-membered rings (2·03 Å) are greater than those of the bridging As–C bonds in the unidentate ligand (1·97 ± 0·03 Å).

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* The structure of $Mo(CO)_4(PPh_2{\cdot}CH_2{\cdot}PPh_2)$ has been reported (K. K. Cheung, T. F. Lai, and K. S. Mok, *J. Chem. Soc.* (*A*), 1971, 1644). In this octahedral structure, the four-membered ring is planar, angles being P–Mo–P 67·3, Mo–P–C 96·9 (mean), and P–C–P 95·6°. Presumably, the non-planarity of the arsine chelate ring in (I) is due to increased steric strain. It has been shown that this chelate ring is less stable than the corresponding phosphorus ring in reaction with either excess of ligand or with carbon monoxide (R. Colton and C. J. Rix, *Austral. J. Chem.*, 1971, **23**, 441).

[15] R. Colton and I. B. Tomkins, *Austral. J. Chem.*, 1966, **19**, 1143.

[16] M. Elder and D. Hall, *Inorg. Chem.*, 1969, **8**, 1268.

[17] M. Elder and D. Hall, *Inorg. Chem.*, 1969, **8**, 1273.

[18] M. G. B. Drew, unpublished work.

[19] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1282.

[20] M. D. Brice, B. R. Penfold, W. T. Robinson, and S. R. Taylor, *Inorg. Chem.*, 1970, **9**, 363.

[21] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, 3rd edn., Ithaca, New York, 1960.

[22] M. W. Anker, R. Colton, and I. B. Tomkins, *Austral. J. Chem.*, 1968, **21**, 1143.

The mean As–C(*m*1) bond length (1·89 Å) is less than these As–C(bridge) lengths. Of the eight benzene rings, the majority have acceptable dimensions and temperature factors. Rings (3) and (4), which are bonded to As(4), the only arsenic atom not bonded to the central molybdenum atom, have the highest temperature factors and the widest spread of dimensions. In all, no dimension differs from the expected value by $>3\sigma$. Table 5 lists inter- and intermolecular contacts $<3\cdot5$ Å, those between phenyl rings on the same arsenic atom being omitted. The intermolecular contacts between carbon atoms in the phenyl rings play the major role in the packing of the molecules in the unit cell. These contact distances are close to the sum of van der Waals radii. The *a* projection of the unit cell is shown in Figure 2.

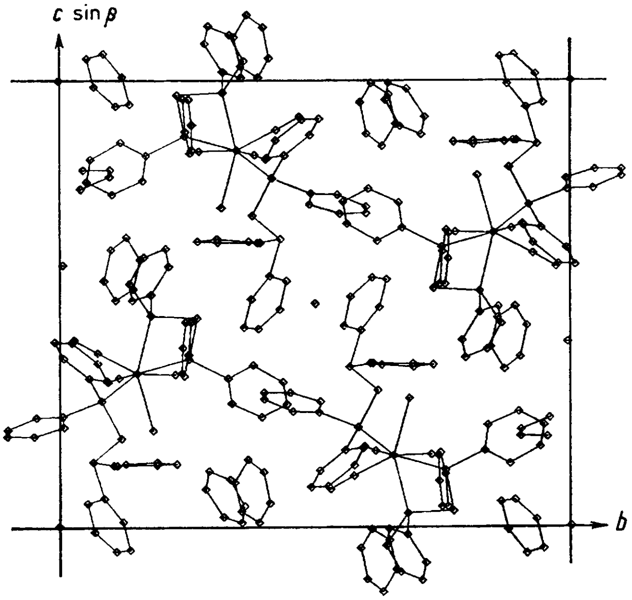

FIGURE 2 The *a* projection of the unit cell of (I)

TABLE 5

Inter- and intra-molecular contacts ($<3\cdot5$ Å) between atoms in (I)

C(3) · · · Br(1)	3·38	C(2) · · · C(12)	3·48
C(1) · · · C(11)	3·27	C(2) · · · C(82)	3·45
C(1) · · · C(21)	3·37	C(2) · · · C(51)	3·47
C(1) · · · C(81)	3·43	O(2) · · · C(23$^{\mathrm{I}}$)	3·48
C(1) · · · C(82)	3·30	C(44) · · · C(15$^{\mathrm{II}}$)	3·39
O(1) · · · C(26)	3·29	C(46) · · · C(46$^{\mathrm{II}}$)	3·50
O(1) · · · C(82)	3·35	C(85) · · · C(63$^{\mathrm{III}}$)	3·48

Roman numerals as superscripts refer to an atom in the following equivalent positions relative to the reference molecule at x, y, z (Table 1):

(I) $1 + x, y, z$
(II) $-x, -y, -z$
(III) $x, \frac{1}{2} - y, \frac{1}{2} + z$

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