Crystal and Molecular Structure of Dibromotricarbonyl[1,2-bis(diphenylphosphino)ethane]molybdenum(II)–1-acetone

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Crystals of the title compound are monoclinic, space-group $P2_1/c$, with a = 10·330(11), b = 14·526(13), c = 22·120(16) Å, β = 99·76(13)°, Z = 4. The intensities of 1833 independent reflections above background were collected by counter methods and the structure has been refined by full-matrix least-squares methods to R 0·064. The molybdenum atom is seven-co-ordinate with a slightly distorted capped octahedral environment. A carbonyl group occupies the unique capping position [Mo–C 1·895(19) Å]. The capped face of the octahedron contains the other two carbonyl groups [Mo–C 1·958(20) and 1·935(22) Å] and a phosphorus from the bidentate ligand [Mo–P 2·500(4) Å]. The uncapped face contains two bromine atoms [2·658(2) and 2·665(3) Å] and the other phosphorus atom [2·618(5) Å], this bond Mo–P (*trans* to CO), being significantly longer (by 0·12 Å) than Mo–P (*trans* to Br).

DIBROMOTRICARBONYL[1,2-BIS(DIPHENYLPHOSPHINO)-ETHANE]MOLYBDENUM(II), $\mathrm{MoBr_2(CO)_3}$(diphos) (I; diphos = $\mathrm{Ph_2P{\cdot}[CH_2]_2{\cdot}PPh_2}$) whose molecular structure we report here, is one of a series of seven-co-ordinate complexes containing molybdenum- or tungsten-(II) which have been studied by X-ray diffraction. The crystal structures of $\mathrm{MoBr_2(CO)_2(AsPh_2{\cdot}CH_2{\cdot}AsPh_2)_2}$ (II) [1,2] and $\mathrm{WBr_2(CO)_3(AsPh_2{\cdot}CH_2{\cdot}AsPh_2)_2}$ (III) [1] have been determined and show the metal atom in a considerably distorted capped octahedral environment.

EXPERIMENTAL

Crystals of (I) were prepared as described previously.[3]

Crystal Data.—$\mathrm{C_{32}H_{30}O_4Br_2MoP_2}$, M = 796·2, Monoclinic, a = 10·330(11), b = 14·526(13), c = 22·120(16) Å, β = 99·76(13)°, D_c = 1·62, Z = 4, D_m = 1·59(3), U = 3271·3 Å^3, $F(000)$ = 1584. Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K_α) = 29·4 cm^{-1}. Space-group $P2_1/c$ from systematic absences: $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$.

A crystal with dimensions 0·20 × 0·05 × 0·20 mm was mounted with the b axis parallel to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions. It was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. A molybdenum tube was used with a zirconium filter at the receiving slit. The stationary-crystal–stationary-counter method was used with a 4° take-off angle and a counting time of 10 s. 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 change in intensity was detected. 3037 independent reflections were measured with 2θ < 40°. No absorption or extinction corrections were applied. The standard deviation σ(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. 1833 Reflections with $I > 2\sigma(I)$ were used in subsequent calculations.

Structure Determination.—The positions of the molybdenum and two bromine atoms were determined from a Patterson function and Fourier syntheses were then calculated to determine the positions of the remaining atoms. The structure was refined by full-matrix least squares. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections, independent of the value of F_o and sin θ/λ, was $\sqrt{w} = 1$ for $F_o < 70$ and $\sqrt{w} = 70/F_o$ for $F_o > 70$. Calculations were made on an ATLAS computer (at S.R.C. Chilton, Berkshire) with the programs described in ref. 4, together with some of our own programs on the Elliott 4130 at this university. Atomic scattering factors for molybdenum, bromine, phosphorus, oxygen, and carbon were taken from ref. 5, together with corrections for the real and imaginary part of the anomalous dispersion for molybdenum and bromine. The anisotropic temperature factor is defined as exp $-0{\cdot}25 \sum_i \sum_j h_ih_jb_ib_jB_{ij}$ (i, j = 1—3), where b_i is the i^{th} reciprocal cell dimension.

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[1] M. G. B. Drew, A. W. Johans, A. P. Wolters, and I. B. Tomkins, *Chem. Comm.*, 1971, 819.

[2] M. G. B. Drew, *J.C.S. Dalton*, 1972, 626.

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[4] 'X-Ray '67' system of programs, revised July, 1970, J. C. Baldwin, R. V. Chastain, D. F. High, F. A. Kundell, and J. M. Stewart, University of Maryland Technical Report, 67—58, 1967.

[5] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

The isotropic thermal parameter is $\exp(-B\sin^2\theta/\lambda^2)$. The molybdenum, bromine, and phosphorus atoms were refined anisotropically and the carbon and oxygen atoms isotropically. The 1833 observed reflections were refined to *R* 0·064. The 1204 zero reflections showed no large discrepancies. Difference Fourier syntheses showed no significant peaks and in the final cycle of refinement, all shifts were $<0{\cdot}040\sigma$. The final list of co-ordinates and thermal parameters, together with their standard deviations are given in Tables 1 and 2. Carbon ring atoms are written C(*Rn*), *R* being the ring number [(1)—(4)] and *n* the position of the atom (1—6). Atoms C-7–C-6(O-4)–C-8 make up the acetone molecule. Details of the co-ordination sphere of molybdenum are listed in Table 3 with dimensions for the remainder of the molecule in Table 4. The final observed and calculated structure factors for (I) are listed in Supplementary Publication SUP 2118 (7 pp., 1 microfiche).*

TABLE 1

Final positional and thermal parameters, with standard deviations in parentheses

Atom	*x*	*y*	*z*	$B/\text{Å}^2$
Mo	0·18417(15)	0·10603(11)	0·26714(7)	*a*
Br(1)	0·22242(22)	0·06722(15)	0·38628(9)	*a*
Br(2)	0·32597(22)	−0·04355(14)	0·25376(10)	*a*
P(1)	0·23923(43)	0·12365(33)	0·16196(21)	*a*
P(2)	0·39228(43)	0·21184(33)	0·28463(23)	*a*
C(1)	0·0242(20)	0·1376(13)	0·2159(9)	4·4(4)
O(1)	−0·0763(15)	0·1579(10)	0·1867(7)	6·2(3)
C(2)	0·1120(19)	0·2126(21)	0·3043(9)	4·7(4)
O(2)	0·0723(13)	0·2766(10)	0·3271(7)	6·1(3)
C(3)	0·0656(21)	0·0036(16)	0·2706(9)	5·5(5)
O(3)	−0·0092(17)	−0·0617(12)	0·2733(8)	8·0(3)
C(4)	0·4167(17)	0·1525(12)	0·1694(8)	3·4(4)
C(5)	0·4404(17)	0·2370(12)	0·2099(8)	3·9(4)
C(11)	0·1709(17)	0·2195(13)	0·1126(8)	3·8(4)
C(12)	0·1125(18)	0·2945(14)	0·1341(8)	4·3(4)
C(13)	0·0690(20)	0·3683(15)	0·0938(10)	5·3(5)
C(14)	0·0829(20)	0·3619(15)	0·0326(10)	5·3(5)
C(15)	0·1390(22)	0·2861(16)	0·0127(10)	6·0(5)
C(16)	0·1836(18)	0·2157(13)	0·0507(8)	4·2(4)
C(21)	0·2051(17)	0·0284(11)	0·1125(8)	3·5(4)
C(22)	0·0771(21)	−0·0105(16)	0·1010(10)	5·7(5)
C(23)	0·0456(23)	−0·0809(16)	0·0595(11)	6·4(5)
C(24)	0·1439(23)	−0·1228(17)	0·0318(11)	6·3(5)
C(25)	0·2625(23)	−0·0865(16)	0·0392(11)	6·3(5)
C(26)	0·3038(20)	−0·0152(15)	0·0832(10)	5·5(5)
C(31)	0·3720(17)	0·3229(12)	0·3201(8)	3·6(4)
C(32)	0·3317(17)	0·4008(13)	0·2854(8)	4·3(4)
C(33)	0·3047(21)	0·4834(16)	0·3165(10)	6·0(5)
C(34)	0·3162(22)	0·4823(16)	0·3778(11)	6·1(5)
C(35)	0·3547(23)	0·4063(17)	0·4138(11)	6·6(6)
C(36)	0·3875(20)	0·3248(14)	0·3844(10)	4·9(4)
C(41)	0·5483(18)	0·1685(13)	0·3265(8)	4·2(4)
C(42)	0·5587(22)	0·0815(15)	0·3518(10)	5·7(5)
C(43)	0·6881(26)	0·0461(18)	0·3803(12)	7·7(6)
C(44)	0·7920(26)	0·1066(19)	0·3845(12)	7·7(6)
C(45)	0·7827(24)	0·1968(17)	0·3617(11)	6·8(6)
C(46)	0·6531(20)	0·2303(14)	0·3333(9)	5·0(5)
O(4)	0·5324(17)	0·2154(13)	0·0409(8)	8·4(4)
C(6)	0·5867(26)	0·2900(20)	0·0506(12)	7·3(6)
C(7)	0·5151(41)	0·3748(29)	0·0338(19)	13·5(12)
C(8)	0·7172(42)	0·2989(30)	0·0843(19)	13·5(12)

[a] Anisotropic thermal parameters are given in Table 2.

DISCUSSION

The molybdenum atom in (I) is seven-co-ordinate with a slightly distorted capped octahedral environment, a carbonyl group occupying the unique capping position. The molecule is shown in Figure 1, together with the atomic numbering system. A different view of the co-ordination sphere of the central molybdenum atom is given in Figure 2. This projection is viewed down the

TABLE 2

Anisotropic thermal parameters, standard deviations in parentheses, for the heavy atoms

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	2·41(7)	2·48(8)	3·31(8)	−0·23(7)	0·53(8)	−0·00(7)
Br(1)	5·85(12)	4·96(13)	3·49(11)	0·06(12)	0·67(14)	0·01(12)
Br(2)	5·54(11)	3·43(14)	5·03(14)	1·41(12)	0·72(14)	0·26(13)
P(1)	0·26(2)	0·31(2)	0·36(2)	−0·01(2)	0·06(2)	0·00(2)
P(2)	0·21(2)	0·31(2)	0·44(3)	−0·01(2)	0·05(2)	0·01(2)

TABLE 3

Dimensions in the co-ordination sphere of molybdenum

(*a*) Bond distances

Mo–Br(1)	2·658(2)	Mo–C(1)	1·895(19)
Mo–Br(2)	2·665(3)	Mo–C(2)	1·958(20)
Mo–P(1)	2·500(4)	Mo–C(3)	1·935(22)
Mo–P(2)	2·618(5)		

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

	C(1)	C(2)	C(3)	P(1)	Br(1)	Br(2)	P(2)
C(1)		2·29	2·29	2·70	4·10	4·06	4·00
C(2)	72·8(8)		3·14	3·84	2·89	4·56	3·00
C(3)	73·5(8)	107·6(8)		3·67	2·93	2·86	4·50
P(1)	74·4(5)	118·2(5)	111·1(5)		5·06	3·19	3·17
Br(1)	127·8(5)	75·8(5)	77·7(5)	157·7(1)		3·66	3·73
Br(2)	124·8(6)	161·2(5)	75·0(6)	76·3(1)	86·8(1)		3·81
P(2)	123·9(6)	80·5(6)	162·6(6)	76·5(1)	89·9(1)	92·4(1)	

TABLE 4

Bond distances (Å) and angles (°)

(*a*) Atoms not in the phenyl rings

C(1)–O(1)	1·16(2)	Mo–C(1)–O(1)	177·0(15)
C(2)–O(2)	1·16(2)	Mo–C(2)–O(2)	178·2(16)
C(3)–O(3)	1·23(3)	Mo–C(3)–O(3)	179·4(17)
P(1)–C(4)	1·86(2)	Mo–P(1)–C(4)	108·5(5)
P(1)–C(11)	1·83(2)	Mo–P(1)–C(11)	120·4(5)
P(1)–C(21)	1·76(2)	Mo–P(1)–C(21)	116·4(5)
C(4)–C(5)	1·52(2)	C(4)–P(1)–C(11)	98·9(8)
P(2)–C(5)	1·84(2)	C(4)–P(1)–C(21)	108·8(8)
P(2)–C(31)	1·82(2)	C(11)–P(1)–C(21)	102·1(8)
P(2)–C(41)	1·83(2)	P(1)–C(4)–C(5)	107·1(11)
		C(4)–C(5)–P(2)	109·2(11)
O(4)–C(6)	1·22(3)	Mo–P(2)–C(5)	108·9(6)
C(6)–C(7)	1·45(5)	Mo–P(2)–C(31)	116·0(6)
C(6)–C(8)	1·43(5)	Mo–P(2)–C(41)	120·3(6)
O(4)–C(6)–C(7)	120·5(27)	C(5)–P(2)–C(31)	106·2(8)
O(4)–C(6)–C(8)	122·4(28)	C(5)–P(2)–C(41)	99·8(8)
C(7)–C(6)–C(8)	116·8(31)	C(31)–P(2)–C(41)	104·1(8)

(*b*) Dimensions in the phenyl rings

	Ring (1)	Ring (2)	Ring (3)	Ring (4)
C(1)–C(2)	1·37(3)	1·42(3)	1·39(2)	1·38(3)
C(2)–C(3)	1·42(3)	1·38(3)	1·43(2)	1·47(3)
C(3)–C(4)	1·39(3)	1·41(3)	1·34(3)	1·38(4)
C(4)–C(5)	1·36(3)	1·32(3)	1·38(3)	1·40(4)
C(5)–C(6)	1·36(3)	1·43(3)	1·42(3)	1·46(3)
C(6)–C(1)	1·41(2)	1·44(3)	1·40(2)	1·39(3)
P–C(1)–C(6)	117·0(13)	122·8(14)	116·8(13)	115·8(14)
P–C(1)–C(2)	123·1(12)	120·3(13)	121·9(12)	121·5(15)
C(2)–C(1)–C(6)	119·6(16)	116·9(16)	121·0(16)	122·7(18)
C(1)–C(2)–C(3)	119·7(15)	121·4(19)	118·7(15)	119·8(20)
C(2)–C(3)–C(4)	119·3(18)	120·3(21)	119·0(20)	116·5(23)
C(3)–C(4)–C(5)	119·4(19)	119·7(21)	124·1(21)	124·5(24)
C(4)–C(5)–C(6)	122·7(18)	122·6(20)	118·1(18)	117·9(22)
C(5)–C(6)–C(1)	118·8(17)	118·0(18)	119·0(18)	118·0(19)

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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. are sent as full size copies).

vector from the carbonyl group in the capping position to the metal atom and shows the atoms in the six octahedral positions. Figure 2 also shows the co-ordination sphere of the related molecule (II), in the equivalent projection.[1,2]

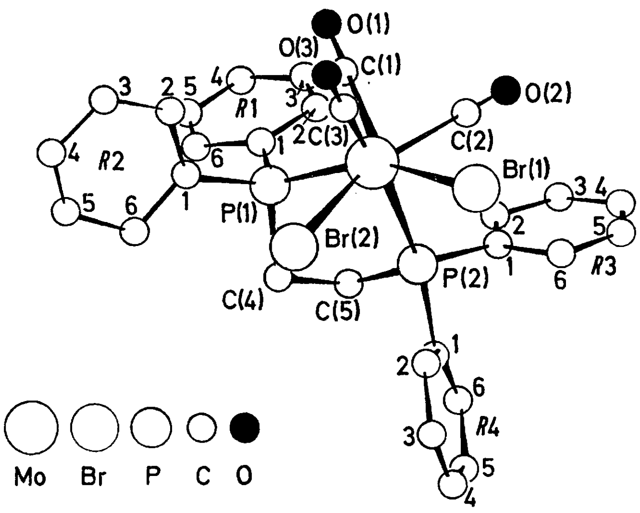

FIGURE 1 The molecule of (I) (acetone not shown)

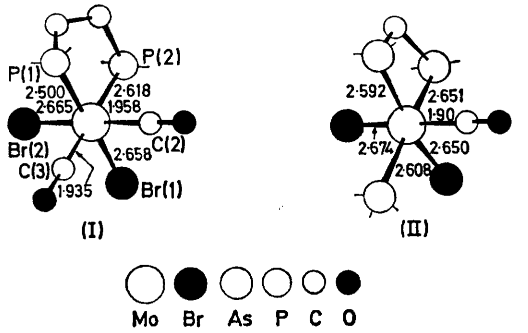

FIGURE 2 The co-ordination spheres of (I) and (II) with the capping carbonyl groups omitted

In (I), the face which is capped by the carbonyl group C(1)–O(1) contains the other two carbonyl groups C(2)–O(2) and C(3)–O(3) and one phosphorus atom P(1) from the chelating ligand. The uncapped face contains the two bromine atoms Br(1), Br(2) and the other phosphorus atom P(2). The usual features of the monocapped octahedral structure are found in (I). Thus the mean C(1)–Mo–A_c and C(1)–Mo–A_u angles [*] are 73·6 and 125·5° respectively. The mean A_c–Mo–A_c angle is 112·3°, considerably greater than the mean A_u–Mo–A_u angle which at 89·7° is equivalent to that found in an octahedron.

A feature of these capped octahedral structures (I)—(III) is that the unique capping atom has extremely close contacts with the three atoms in the capped face. Thus in (I), C(1) is 2·29, 2·29, and 2·70 Å from C(2), C(3), and P(1) respectively. These values can be compared with the minimum O · · · O contacts of 2·65 Å in the capped octahedral molecule [6] aquotris(1-phenyl-1,3-butanedionato)yttrium and of 2·46 Å in the pentagonal-bipyramidal molecule [7] tris(acetylacetonato)-chlorozirconium. In (I), although the C(1)–Mo–A_c angles are all similar, indicating that these three contacts are of similar import, the A_c–Mo–A_c angles do show some variations with C–Mo–C < C–Mo–P. In the uncapped face, the Br–Mo–Br angle is smaller than the two Br–Mo–P(2) angles; this can be contrasted with the uncapped face in (II) where the Br–Mo–Br angles are greater than the As–Mo–Br angles. It would appear that for ligand–ligand (L · · · L) repulsions, measured either by the L–Mo–L angle or by the L · · · L distance, $PPh_2 > Br > AsPh_2$. This order could, of course, be due to the particular orientations of the phenyl rings in the two structures and further data is desirable.

The angle subtended at the central molybdenum atom by the diphos ligand is 76·5(1)°, the bite, or P · · · P distance, being 3·17 Å. A similar value (75·3°) is found for the P–Mo–P angle in $(\pi\text{-}C_5H_5)Mo(CO)(diphos)Cl$.[8] The ligand is therefore well suited to fit along an edge in the capped octahedron, the angle being equivalent to those found subtended at the central molybdenum atom by pairs of atoms A_c, A_u, mutually *cis* [†] [the mean value of the six such angles in (I) being 77·0°]. The three angles subtended by atoms in mutually *trans*-positions are also very similar: 157·7(5), 161·2(5), and 162·6(6)°. Thus the environment of the molybdenum atom in (I) is closer to C_{3v} symmetry than in (II) where the bite of the $AsPh_2{\cdot}CH_2{\cdot}AsPh_2$ ligand, which is only 2·88 Å (As–Mo–As 66·7°), causes considerable distortion (see Figure 2).

The Mo^{II}–Br bond distances in (I) of 2·658(2) and 2·665(3) Å are equivalent to those found in (II) which are 2·650 and 2·674 Å. The two Mo–P distances in (I) are remarkably dissimilar; Mo–P(1) [2·500(4) Å] being 0·12 Å shorter than Mo–P(2) [2·617(5) Å]. The first of these two values is similar to Mo–P distances found in $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)(Ac)$ 2·473,[9] $(\pi\text{-}C_5H_5)_2Mo_2H(PMe_2)(CO)_4$, 2·42, 2·43,[10] and $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)I$ 2·481 Å.[8] As all these values are well below the 2·71 Å predicted from the sum of single-bond radii (Mo 1·61,[9] P 1·10 Å [11]), it has been postulated that the Mo–P bonds in these molecules have some double-bond character presumably through back donation ($d_\pi \rightarrow d_\pi$) from the metal. An increase in length for Mo–P bonds in positions *trans* to strong d_π accepting groups, such as carbonyls, is therefore to be expected. In (II), it was found

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[*] The symbols A_c and A_u denote atoms in the capped and uncapped faces respectively.

[†] The terms *cis* and *trans* are appropriate to describe only the A_c–Mo–A_u angles in a monocapped octahedron.

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

that the Mo–As_u bond was 0·05 Å longer than the Mo–As_c bond and this was explained [2] on the basis of some decrease in π bonding caused by the carbonyl in the capping position. In (I) therefore, atom P(2), being both *trans* to C(3) [P(2)–Mo–C(3) 162·6(6)°] and in the uncapped face [P(2)–Mo–C(1) 123·9(5)°], forms a weaker bond to molybdenum, with less π overlap, than atom P(1) which is *trans* to Br(1) and in the capped face.

A list of Mo–CO distances given in ref. 2 show a spread between 1·90 and 2·00 Å. In (II), the two distances are 1·92(4) and 1·90(4) Å. One would expect the distances in (I) to be slightly longer than these bonds because the competition for π donation from the metal is greater in (I) than in (II); (three carbonyl groups and two phosphorus atoms compared with two carbonyl groups and three arsenic atoms). However, although Mo–C(2) and Mo–C(3) are slightly longer than the Mo–C bonds in (II), the Mo–C(1) bond in the present structure is shorter than the other carbonyl bonds. If this difference is significant, it is of some interest as, although some amount of stereospecificity is well known for M–CO bonds in some structures [*i.e.* in $(MeC)Co_3(CO)_8(PPh_3)$, the Co–CO_{ax} and Co–C_{eq} bond lengths [12] are 1·79 and 1·74 Å respectively], such a disparity has not been observed in capped octahedral structures.

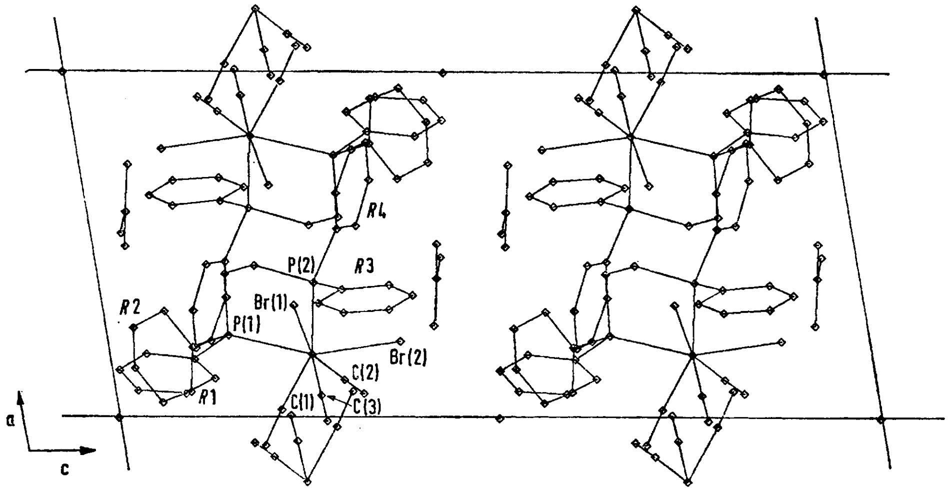

FIGURE 3 The unit cell of (I) in the *b* projection

The configuration of a ligand of the type diphos is adaptable to the steric forces in a molecule as the five-membered chelate ring can adopt any number of conformations and the benzene rings are free to rotate about the P–C(*R*1) bonds. In $(\pi\text{-}C_5H_5)MoCl(CO)$(diphos) [8] both carbon atoms are the same side of the Mo, P, P plane at distances of 0·45 and 1·03 Å, an arrangement that keeps the benzene rings away from the cyclopentadienyl ring. In (I), C(4) and C(5) are respectively 0·71 and —0·09 Å from the plane Mo, P, P (both bromine atoms are on the positive side of this plane). This conformation and the orientations of the phenyl rings appear to minimize intramolecular contacts between the benzene rings and the carbonyl groups (1) and (2). All intramolecular contacts <3·60 Å are given in Table 5. The capping carbonyl group C(1), O(1) has close contacts with ring (1), being 3·18 and 3·14 Å from C(11) and C(12) respectively. Any considerable rotation of the ring about the P(1)–C(11) axis would bring either C(12) or C(16) into close proximity to C(1) (Figure 1). Carbonyl (2) has close contacts with ring (3), C(2) being 3·09 Å from C(31). The orientation of the ring is such that O(2) is close to both C(32) and C(36). Carbonyl (3) has no close intramolecular contacts. The orientations of rings (2) and (4) are probably settled to a small extent by the proximity of Br(2) and to a large extent by intermolecular packing.

The steric strain in (I) caused by the CO ··· C(*Rn*) contacts is considerably greater than that found in (II),[2] in which the shortest such contact is 3·27 Å. This is due to the shortness of the Mo–P and P–C(*R*1) bonds in (I) as compared to the Mo–As and As–C(*R*1)

TABLE 5

Intra- and inter-molecular * distances (Å) <3·6 Å

C(1) ··· C(11)	3·18	C(8) ··· $O(1^{I})$	3·50
C(1) ··· C(12)	3·14	C(45) ··· $O(2^{I})$	3·41
C(1) ··· C(21)	3·56	O(4) ··· $C(25^{II})$	3·52
C(1) ··· C(22)	3·44	C(23) ··· $C(23^{III})$	3·54
C(2) ··· C(31)	3·10	C(45) ··· $C(24^{IV})$	3·52
C(2) ··· C(36)	3·49	C(13) ··· $C(43^{IV})$	3·58
O(1) ··· C(11)	3·38	C(33) ··· $O(1^{V})$	3·46
O(1) ··· C(12)	3·14	O(2) ··· $O(3^{V})$	3·22
O(2) ··· C(31)	3·20	C(12) ··· $O(3^{V})$	3·23
O(2) ··· C(32)	3·48	C(32) ··· $O(3^{V})$	3·41
O(2) ··· C(36)	3·36	C(33) ··· $O(3^{V})$	3·41
Br(2) ··· C(21)	3·33	C(13) ··· $O(3^{V})$	3·27
Br(2) ··· C(42)	3·47	C(35) ··· $O(4^{VI})$	3·56
		C(36) ··· $O(4^{VI})$	3·58

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

I $1 + x, y, z$
II $1 - x, -y, -z$
III $-x, -y, -z$
IV $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
V $-x, \frac{1}{2} + y, \frac{1}{2} - z$
VI $x, \frac{1}{2} - y, \frac{1}{2} + z$

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

bonds in (II). If such steric effects are of major importance, chelate rings formed using 1,2-bis(diphenylarsino)ethane would be more stable than the phosphorus chelate rings in molecules such as (I). There is no experimental data to this effect; indeed the opposite is true for four-membered chelate rings in that those formed with bis(diphenylarsino)methane in such compounds as (II) are less stable [13] than the phosphorus analogues; this disparity can be ascribed to steric effects in the ring, due to the fact that arsenic atoms are considerably larger than phosphorus atoms and one carbon atom is not sufficient to bridge easily between them in the chelate configuration.[13]

The P–C bond lengths in (I) are as expected, mean 1·82 Å. For both P(1) and P(2), the Mo–P–C(*R*1) angles are considerably larger (mean 118°) than the other Mo–P–C angles (109°) and the C–P–C angles (103°). An explanation for this effect has been given: [8] namely that the phosphorus orbital directed towards a metal atom has more *s* character than the orbitals directed towards the phenyl rings. The variation in Mo–P–C(*R*1) angles does not appear to follow any distinguishable pattern. The phenyl rings are planar, within experimental error, with the phosphorus atoms slightly displaced from the planes (deviations 0·07, 0·08, 0·20, and 0·14 Å). Such an effect has been noted in many structures (see ref. 8) and is presumably due to steric effects involving the phenyl rings.

The unit cell contains four acetone molecules in general positions. The packing diagram (in the *b* projection) is shown in Figure 3, with intermolecular contacts <3·60 Å in Table 5. The shortest such contacts are between the oxygen atoms of the carbonyl groups and some of the carbon atoms in the benzene rings. The acetone molecules, which appear to be essential for the preparation of suitable crystals, do not have many close contacts with (I) but appear to pack efficiently between the larger molecules. There are no contacts noticeably less than the sum of van der Waals radii.

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[13] R. Colton and C. J. Rix, *Austral. J. Chem.*, 1970, **23**, 441.