Stereochemistry of Seven-co-ordination: Crystal Structures of *rac*- and *meso*-Tricarbonyldi-iodo[*o*-phenylenebis(methylphenylarsine)]-molybdenum(II)

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The crystal structures of the title compounds (I) [*rac*-*o*-$C_6H_4(AsMePh)_2Mo(CO)_3I_2$],$CHCl_3$, and (II) [*meso*-*o*-$C_6H_4(AsMePh)_2Mo(CO)_3I_2$], have been determined from diffractometer data by the heavy-atom method and refined by least squares to R 0·08 [(I), 2809 reflections] and 0·11 [(II) 2371 reflections]. Crystals of both compounds are triclinic, space group $P\bar{1}$, with $Z = 2$ in unit cells of dimensions: (I), $a = 14{\cdot}985(5)$, $b = 12{\cdot}337(3)$, $c = 9{\cdot}654(1)$ Å, $\alpha = 110{\cdot}78(2)$, $\beta = 101{\cdot}90(2)$, $\gamma = 104{\cdot}74(2)°$; (II), $a = 15{\cdot}828(6)$, $b = 10{\cdot}505(1)$, $c = 9{\cdot}733(1)$ Å, $\alpha = 120{\cdot}604(8)$, $\beta = 98{\cdot}99(2)$, $\gamma = 97{\cdot}69(2)°$. Both complexes are comprised of discrete molecules with seven-co-ordinate molybdenum atoms, being of the type [M(bidentate)(unidentate)$_5$]. A theoretical description of this system has been developed in terms of repulsion theory, yielding four different possible stereochemical types of which examples are found for three among these and previously determined structures of this type.

MANY metal carbonyls and their derivatives act as bases and form addition complexes with a wide variety of Lewis acids.[1,2] The action of halogens on the complexes [LMo(CO)$_4$], where L is a suitable bidentate ligand, *e.g.* *o*-phenylenebis(dimethylarsine) or 1,2-bis(diphenylphosphino)ethane, produces the seven-co-ordinate molybdenum(II) derivatives [LMo(CO)$_3$X$_2$] (X = Br or I).[3,4] In connection with our studies on the stereochemistry of asymmetric tertiary arsines and their metal complexes,[5,6] we have determined the crystal structures of the title compounds formed by the oxidative-elimination reaction (1), the *rac*-derivative being a chloroform solvate.

$$[(rac/meso\text{-diars})Mo(CO)_4] + I_2 \xrightarrow{CHCl_3} [(rac/meso\text{-diars})Mo(CO)_3I_2] + CO \quad (1)$$

As these two complexes provide two of the few known examples of the [M(bidentate)(monodentate)$_5$] seven-co-ordinate stereochemistry, they have provided an opportunity to develop and apply the repulsion theory described previously[7] to this type of co-ordination geometry. Crystals of (I) and (II) were prepared as described previously.[6]

EXPERIMENTAL

For absorption correction purposes, crystals used for data collection were considered as (I) a sphere (0·15 mm diameter) and (II) a prism (0·07 × 0·19 × 0·19) respectively. Cell dimensions of each were obtained by a least-squares fit of the angular parameters of 15 reflections centred in the counter aperture of a Syntex $P\bar{1}$ diffractometer; for each crystal a unique data set was collected in the range $2\theta < 100°$ (Cu-K_α radiation, Ni-filtered, $\lambda = 1{\cdot}5418$ Å) by conventional 2θ—θ scan yielding for (I), 3135 independent reflections of which 2809 with $I > \sigma(I)$ were considered 'observed,' and for (II) 2682, of which 2371 with $I > 3\sigma(I)$ were considered observed and used in the solution and refinement.

Crystal Data.—(*a*) (I). $C_{24}H_{21}As_2Cl_3I_2MoO_3$, $M = 963{\cdot}4$, Triclinic, $a = 14{\cdot}985(5)$, $b = 12{\cdot}337(3)$, $c = 9{\cdot}654(1)$ Å, $\alpha = 110{\cdot}78(2)$, $\beta = 101{\cdot}90(2)$, $\gamma = 104{\cdot}74(2)°$, $U = 1524{\cdot}5(6)$ Å^3, $D_m = 2{\cdot}03(3)$, $Z = 2$, $D_c = 2{\cdot}10$ g cm^{-3}, $F(000) = 908$, $\mu(\text{Cu-}K_\alpha) = 252$ cm^{-1}. Space group $P\bar{1}$ (C_i^1, No. 2).

(*b*) (II). $C_{23}H_{20}As_2I_2MoO_3$, $M = 844{\cdot}0$, Triclinic, $a = 15{\cdot}828(6)$, $b = 10{\cdot}505(1)$, $c = 9{\cdot}733(1)$ Å, $\alpha = 120{\cdot}604(8)$, $\beta = 98{\cdot}99(2)$, $\gamma = 97{\cdot}69(2)°$, $U = 1331{\cdot}6(6)$ Å^3, $D_m = 2{\cdot}03(2)$, $Z = 2$, $D_c = 2{\cdot}10$ g cm^{-3}, $F(000) = 792$, $\mu(\text{Cu-}K_\alpha) = 260$ cm^{-1}. Space group $P\bar{1}$.

Both structures were solved by the heavy-atom method and refined by 9 × 9 block-diagonal least-squares, the parameters of the $MoI_2As_2C_3$ molecular core being refined as a single block to approximate to a full-matrix procedure; anisotropic thermal parameters used were of the form $[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2hka^*b^* + 2hla^*c^* + 2klb^*c^*)]$. Non-methyl hydrogen atoms were estimated geometrically (assuming C–H 0·95 Å) and included in the final calculation of R; in the final refinement cycle no parameter shift exceeded $0{\cdot}2\sigma$; for (I) R was 0·080 and R' 0·093; for (II), R 0·11 and R' 0·13 $[R' = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$. Unit weights were used for (I); for (II) $w = (\sigma^2|F_o| + n \times 10^{-4}|F_o|^2)^{-1}$, n being 16. Neutral atom scattering factors were used,[8] those for I, Mo, As and Cl being corrected for anomalous dispersion effects ($\Delta f'$, $\Delta f''$).[9] No correction was applied for extinction, although an 'over-perfect' crystalline specimen is believed to be the origin of the high R value for (II).

Computation was carried out on the CDC 6200 machine at this University using the local version of the '*X*-Ray '72' programme system.[10] Structure factors are given in Supplementary Publication No. SUP 21201 (20 pp., 1 microfiche).† Final co-ordinates and thermal parameters are listed in Table 1, distances and angles in Table 2, and details

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† For details, see Notice to Authors No. 7 in *J.C.S. Dalton*, Index issue, 1973.

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TABLE 1

Final non-hydrogen atomic fractional co-ordinates (C and O $\times 10^3$, others $\times 10^4$) and thermal parameters ($\times 10^3$ Å^2), with least squares estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(*a*) For molecule of (I)									
Mo	2976(1)	4998(2)	3122(2)	48(2)	41(17)	50(2)	5(1)	12(1)	24(1)
I(1)	2785(2)	6955(2)	5596(2)	123(2)	66(2)	58(2)	26(1)	30(1)	18(1)
I(2)	950(1)	3616(2)	2280(2)	54(2)	57(2)	70(2)	9(1)	29(1)	30(1)
C(1)	426(2)	641(2)	389(4)	69(20)	56(18)	88(22)	−6(15)	−22(17)	35(17)
O(1)	497(1)	718(2)	429(3)	64(14)	90(16)	169(24)	−31(12)	−22(15)	75(17)
C(2)	392(2)	426(2)	307(4)	117(26)	54(18)	86(22)	23(17)	66(20)	34(16)
O(2)	459(1)	384(2)	312(3)	77(14)	90(15)	105(16)	38(12)	13(12)	43(13)
C(3)	302(2)	443(3)	485(4)	54(18)	88(22)	88(2)	17(6)	16(16)	46(19)
O(3)	307(2)	413(2)	586(3)	110(18)	146(21)	101(17)	22(16)	33(14)	97(17)
As(1)	2356(2)	6054(2)	1322(3)	54(2)	38(2)	53(2)	13(1)	24(1)	23(1)
As(2)	2620(2)	3415(2)	262(3)	45(2)	38(2)	57(2)	11(1)	21(1)	22(1)
C(5)	171(2)	485(2)	−83(3)	55(15)	48(14)	68(17)	17(12)	44(14)	39(13)
C(6)	116(2)	510(2)	−195(3)	61(17)	56(16)	66(18)	20(14)	15(14)	36(14)
C(7)	67(2)	420(3)	−342(3)	81(20)	78(19)	64(18)	34(16)	39(16)	45(16)
C(8)	72(2)	302(3)	−387(3)	75(19)	75(19)	46(16)	38(16)	16(14)	28(15)
C(9)	124(2)	276(2)	−278(3)	62(17)	49(15)	46(15)	11(13)	23(13)	16(13)
C(10)	176(2)	367(2)	−127(3)	44(14)	53(15)	64(16)	14(12)	31(13)	39(13)
C(11)	336(2)	741(2)	127(3)	66(18)	20(12)	94(21)	−11(12)	34(16)	27(14)
C(12)	367(2)	719(2)	−5(3)	73(18)	53(16)	56(16)	16(14)	38(14)	25(14)
C(13)	444(2)	819(3)	11(4)	58(18)	76(19)	101(23)	16(65)	42(16)	61(18)
C(14)	483(2)	926(2)	135(3)	56(17)	47(16)	97(22)	−21(13)	26(16)	36(16)
C(15)	452(2)	945(2)	263(3)	74(20)	58(18)	62(18)	16(15)	9(15)	12(15)
C(16)	375(2)	850(2)	259(3)	60(18)	36(15)	102(22)	−3(13)	33(16)	35(15)
C(17)	140(2)	678(2)	178(4)	105(24)	57(18)	89(22)	30(17)	58(19)	36(17)
C(21)	221(2)	165(2)	−38(3)	77(19)	32(14)	79(19)	18(13)	37(16)	21(14)
C(22)	284(2)	105(2)	−34(3)	50(17)	67(18)	113(23)	34(15)	39(16)	54(18)
C(23)	253(2)	−27(3)	−88(5)	75(21)	73(21)	178(35)	44(18)	42(22)	86(24)
C(24)	155(2)	−90(2)	−129(4)	87(22)	41(16)	122(26)	22(15)	56(20)	40(17)
C(25)	89(2)	−30(2)	−129(4)	51(17)	38(15)	126(27)	−4(13)	29(17)	28(17)
C(26)	117(2)	96(2)	−82(3)	48(15)	47(15)	76(18)	10(12)	20(14)	28(14)
C(27)	378(17)	367(3)	−48(3)	41(15)	83(19)	100(22)	24(14)	51(15)	56(18)
C(4)	221(3)	85(6)	453(6)	69(27)	318(71)	160(44)	−45(35)	−3(27)	140(48)
Cl(1)	3049(9)	680(10)	5720(10)	142(9)	146(9)	109(8)	58(8)	31(7)	40(7)
Cl(2)	1034(8)	−260(10)	4150(20)	96(8)	113(9)	294(18)	−6(6)	91(10)	−6(10)
Cl(3)	2371(17)	−840(20)	2920(20)	349(26)	324(25)	196(16)	117(21)	116(17)	194(18)
(*b*) For molecule of (II)									
Mo	2444(1)	1923(2)	649(2)	55(2)	44(2)	45(2)	21(1)	23(1)	27(1)
I(1)	2813(1)	4470(2)	302(2)	103(2)	69(2)	88(2)	35(1)	47(1)	59(1)
I(2)	4263(1)	1877(2)	718(2)	60(2)	71(2)	70(2)	25(1)	33(1)	42(1)
C(1)	143(2)	283(2)	109(3)	98(20)	35(13)	69(17)	22(13)	37(15)	30(13)
O(1)	80(1)	329(2)	126(2)	80(12)	63(11)	87(13)	35(10)	29(10)	32(10)
C(2)	139(2)	28(3)	−39(3)	73(17)	74(18)	47(14)	29(14)	17(13)	34(13)
O(2)	72(1)	−68(2)	−106(2)	67(10)	54(10)	63(10)	4(8)	7(8)	26(9)
C(3)	234(2)	87(3)	−182(3)	52(15)	84(19)	43(14)	12(13)	13(12)	17(13)
O(3)	228(1)	35(3)	−317(2)	124(17)	119(17)	44(11)	8(14)	27(11)	37(11)
As(1)	3043(2)	3854(3)	3889(3)	57(2)	45(2)	48(2)	17(1)	23(1)	26(1)
As(2)	2684(2)	156(3)	1726(3)	58(2)	46(2)	59(2)	22(1)	24(1)	31(1)
C(5)	356(1)	288(3)	491(3)	57(14)	60(14)	44(13)	17(12)	30(11)	32(11)
C(6)	405(2)	363(3)	651(3)	82(18)	67(17)	66(17)	14(14)	42(14)	39(14)
C(7)	444(2)	293(4)	725(3)	76(18)	121(24)	67(17)	29(17)	27(15)	66(18)
C(8)	430(2)	132(3)	622(3)	83(19)	102(22)	70(18)	29(17)	18(15)	60(17)
C(9)	386(2)	60(3)	467(3)	79(18)	97(20)	96(20)	49(16)	48(16)	82(18)
C(10)	345(1)	135(2)	401(2)	46(13)	49(13)	36(12)	6(10)	4(10)	20(11)
C(11)	221(1)	476(2)	513(3)	56(14)	25(11)	61(14)	23(10)	26(11)	15(10)
C(12)	193(2)	425(2)	615(3)	68(16)	38(13)	58(15)	9(11)	33(13)	13(12)
C(13)	133(2)	490(3)	697(3)	57(15)	75(18)	79(18)	22(14)	40(14)	39(15)
C(14)	95(2)	595(3)	677(4)	55(17)	64(18)	139(29)	24(15)	59(18)	−12(18)
C(15)	124(2)	641(3)	578(3)	85(19)	79(19)	77(18)	51(16)	52(16)	38(16)
C(16)	188(2)	580(3)	502(3)	80(18)	43(14)	62(16)	25(13)	20(14)	17(12)
C(17)	394(2)	567(3)	459(3)	92(20)	52(15)	85(19)	19(14)	45(16)	40(14)
C(21)	164(2)	−73(2)	210(3)	72(15)	37(12)	41(13)	7(11)	6(11)	25(11)
C(22)	109(1)	17(2)	281(3)	57(14)	41(13)	72(16)	27(11)	33(12)	34(12)
C(23)	35(2)	−40(3)	322(3)	72(88)	106(22)	63(17)	24(16)	22(14)	55(17)
C(24)	26(2)	−188(3)	278(4)	114(25)	88(22)	102(24)	−27(19)	22(2)	70(20)
C(25)	78(2)	−280(3)	205(4)	109(24)	61(18)	122(26)	8(17)	58(21)	52(18)
C(26)	146(2)	−225(3)	175(3)	74(17)	62(16)	88(19)	22(14)	27(15)	51(15)
C(27)	317(2)	−154(3)	44(7)	65(16)	67(17)	92(20)	34(14)	35(15)	45(16)

of planes in Table 3. Views of the molecules are shown in Figures 1 and 2, showing 50% thermal ellipsoids.

DISCUSSION

Both crystal lattices are comprised of discrete molecules, the central molybdenum atom being seven-co-ordinated by the bidentate diarsine ligand and five unidentate ligands, two iodide ions and three carbonyl groups; in addition the lattice of (I) contains chloroform solvent molecules which, unlike some other chloroform solvates, appear to show no significant interaction *via* the hydrogen atom to any adjacent entity. The interatomic distances and angles within the chloroform are normal, albeit with somewhat high standard deviations, probably a consequence of its high thermal motion. There is little unusual in the metal–ligand distances: there are precedents of similar magnitude for Mo^{II} in systems with high co-ordination numbers (*i.e.* >6) for Mo–I, 2·85—2·88 (refs. 11 and 12) and Mo–As 2·60—2·66 Å.[13] In both structures in spite of the relatively low accuracy of the light atom geometry, it is clear that Mo–C(2) is appreciably shorter than Mo–C(1) and Mo–C(3) (1·87, 1·92, *cf.* 1·97—2·03 Å).

The stereochemistry of metal complexes containing bidentate ligands is often significantly different from that of complexes containing only unidentate ligands, but can likewise be predicted by the minimisation of the total repulsion energy between the individual donor atoms (or alternatively between the valence-shell electron pairs), but omitting the repulsion between the two ends of each bidentate ligand, which are assumed to form rigid chelate rings.

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses. Values for (II) follow those for (I)

(*a*) Distances

Mo–I(1)	2·856(3), 2·859(4)
Mo–I(2)	2·854(3), 2,877(3)
Mo–C(1)	2·02(3), 1·97(3)
C(1)–O(1)	1·12(3), 1·16(4)
Mo–C(2)	1·87(4), 1·92(2)
C(2)–O(2)	1·24(4), 1·19(3)
Mo–C(3)	2·02(4), 2·03(2)
C(3)–O(3)	1·16(5), 1·12(3)
Mo–As(1)	2·663(4), 2·645(3)
Mo–As(2)	2·603(3), 2·595(4)
As(1)–C(17)	1·92(4), 1·94(3)
As(1)–C(11)	1·98(3), 1·94(2)
As(1)–C(5)	1·92(2), 1·92(3)
C(11)–C(12)	1·40(4), 1·45(4)
C(12)–C(13)	1·39(4), 1·37(4)
C(13)–C(14)	1·31(3), 1·41(5)
C(14)–C(15)	1·37(5), 1·38(6)
C(15)–C(16)	1·40(4), 1·38(4)
C(11)–C(16)	1·36(3), 1·32(4)
C(5)–C(6)	1·40(4), 1·36(3)
C(6)–C(7)	1·35(3), 1·40(4)
C(7)–C(8)	1·38(4), 1·42(4)
C(8)–C(9)	1·36(4), 1·30(4)
C(9)–C(10)	1·39(3), 1·40(5)
C(5)–C(10)	1·40(4), 1·35(3)
As(2)–C(10)	1·92(3), 1·97(2)
As(2)–C(27)	2·00(3), 1·93(3)
As(2)–C(21)	1·93(2), 1·96(3)
C(21)–C(22)	1·34(5), 1·37(3)
C(22)–C(23)	1·43(4), 1·44(5)
C(23)–C(24)	1·36(4), 1·36(5)
C(24)–C(25)	1·36(4), 1·35(5)
C(25)–C(26)	1·37(4), 1·29(5)
C(21)–C(26)	1·45(4), 1·43(4)
C(4)–Cl(1)	1·63(6)
C(4)–Cl(2)	1·81(5)
C(4)–Cl(3)	1·61(7)

TABLE 2 (*Continued*)

(*b*) Angles

I(1)–Mo–I(2)	89·0(1), 86·2(1)
I(1)–Mo–As(1)	85·1(1), 88·2(1)
I(1)–Mo–As(2)	157·6(1), 158·6(1)
I(1)–Mo–C(1)	76·6(9), 75·3(9)
I(1)–Mo–C(2)	131·7(8), 128·5(9)
I(1)–Mo–C(3)	75·7(9), 78·0(9)
I(2)–Mo–As(1)	84·7(1), 85·1(1)
I(2)–Mo–As(2)	79·41(8), 77·7(1)
I(2)–Mo–C(1)	162·7(9), 157·0(7)
I(2)–Mo–C(2)	122·8(8), 130·8(9)
I(2)–Mo–C(3)	80·2(7), 81·0(7)
As(1)–Mo–As(2)	74·8(1), 76·6(1)
As(1)–Mo–C(1)	84(1), 80·9(7)
As(1)–Mo–C(2)	129(1), 123·7(9)
As(1)–Mo–C(3)	156(1), 161·0(8)
As(2)–Mo–C(1)	111(1), 116(1)
As(2)–Mo–C(2)	70·2(8), 73(1)
As(2)–Mo–C(3)	120·3(8), 112(1)
C(1)–Mo–C(2)	74(1), 72(1)
C(1)–Mo–C(3)	105(1), 108(1)
C(2)–Mo–C(3)	76(2), 75(1)
Mo–C(1)–O(1)	179(3), 176(2)
Mo–C(2)–O(2)	176(2), 176(3)
Mo–C(3)–O(3)	178(2), 177(3)
Mo–As(1)–C(5)	111·3(9), 110·8(6)
Mo–As(1)–C(11)	116·5(9), 118·0(6)
Mo–As(1)–C(17)	117(1), 115(1)
Mo–As(2)–C(10)	112·6(7), 110·6(8)
Mo–As(2)–C(21)	122·4(9), 115·7(8)
Mo–As(2)–C(27)	113·7(6), 117(1)
C(5)–As(1)–C(11)	105(1), 104(1)
C(5)–As(1)–C(17)	103(1), 106(1)
C(11)–As(1)–C(17)	102(1), 101(1)
C(10)–As(2)–C(21)	106(1), 99(1)
C(10)–As(2)–C(27)	98(1), 107(1)
C(21)–As(2)–C(27)	100(1), 105(1)
As(1)–C(5)–C(6)	123(2), 124(2)
As(1)–C(5)–C(10)	119(2), 120(2)
C(5)–C(6)–C(7)	120(3), 125(2)
C(6)–C(7)–C(8)	122(3), 116(2)
C(7)–C(8)–C(9)	119(2), 120(4)
C(8)–C(9)–C(10)	121(3), 122(3)
C(9)–C(10)–C(5)	120(2), 121(2)
As(2)–C(10)–C(5)	117(1), 119(2)
As(2)–C(10)–C(9)	123(2), 120(2)
As(1)–C(11)–C(12)	119(1), 119(2)
As(1)–C(11)–C(16)	116(2), 121(2)
C(11)–C(12)–C(13)	114(2), 116(3)
C(12)–C(13)–C(14)	124(3), 123(3)
C(13)–C(14)–C(15)	121(3), 118(3)
C(14)–C(15)–C(16)	120(2), 119(3)
C(15)–C(16)–C(11)	117(3), 124(3)
As(2)–C(21)–C(22)	122(2), 119(2)
As(2)–C(21)–C(26)	118(2), 122(2)
C(21)–C(22)–C(23)	123(2), 121(3)
C(22)–C(23)–C(24)	117(3), 124(1)
C(23)–C(24)–C(25)	121(3), 127(4)
C(24)–C(25)–C(26)	123(2), 119(3)
C(25)–C(26)–C(21)	117(3), 121(3)
Cl(1)–C(4)–Cl(2)	109(4)
Cl(1)–C(4)–Cl(3)	117(3)
Cl(2)–C(4)–Cl(3)	111(2)

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[11] M. A. Bush, A. D. U. Hardy, Lj. Manojlovic-Muir, and G. A. Sim, *J. Chem. Soc.* (*A*), 1971, 1003.

[12] D. F. Lewis and S. J. Lippard, *Inorg. Chem.*, 1972, **11**, 621.

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

TABLE 3

(A) Least-squares planes in the form $pX + qY + rZ = s$, where X, Y, Z are orthogonal co-ordinates in Å, so that X is parallel to a, and Z is in the ac plane. Deviations (Å) from the plane are given in square brackets; values for (II) follow those for (I)

Plane (i): C(5)—(10)

	10^4p	10^4q	10^4r	s	σ/Å
(I)	8563	2797	−4343	3·926	0·01
(II)	8954	1402	−4226	3·051	0·02

[C(5) 0·00, 0·00; C(6) 0·00, 0·00; C(7) 0·00, 0·00; C(8) 0·01, −0·02; C(9) −0·01, 0·02; C(10) 0·00, −0·01; As(1) −0·13, 0·06; As(2) 0·17, −0·15; C(11) 1·54, −1·58; C(17) −1·43, 1·38; C(21) −0·46, −2·04; C(27) 2·15, −2·46; Mo −0·64, 0·51]

Plane (ii): C(11)—(16)

	10^4p	10^4q	10^4r	s	σ/Å
(I)	7325	−3370	5915	−2·428	0·01
(II)	4946	7368	4610	5·128	0·02

[C(11) 0·00, −0·01; C(12) 0·00, −0·01; C(13) 0·00, 0·01; C(14) 0·00, −0·01; C(15) 0·00, 0·00; C(16) 0·00, 0·02; As(1) 0·14, −0·10; C(5) −0·38, 0·37; C(17) −1·38, 1·44; Mo 2·50, −2·37]

Plane (iii): C(21)—(26)

	10^4p	10^4q	10^4r	s	σ/Å
(I)	−1660	1459	9753	−1·363	0·02
(II)	3762	3247	8678	2·799	0·01

[C(21) −0·02, 0·00; C(22) 0·03, −0·01; C(23) −0·02, 0·01; C(24) 0·01, 0·00; C(25) 0·00, −0·01; C(26) 0·01, 0·02; As(2) −0·04, 0·10; C(10) −1·35, 2·02; C(27) 1·11, −0·17; Mo 2·15, −1·33]

Plane (iv): Mo, As(1), As(2)

	10^4p	10^4q	10^4r	s	σ/Å
(I)	8888	4374	−1369	4·320	
(II)	9833	850	−1607	3·657	

[I(1) −0·50, 0·75; I(2) −2·80, 2·81; C(1) 1·85, −1·69; C(2), 1·08, −1·36; C(3) −0·62, 0·56; C(5) −0·50, 0·46; C(10) −0·62, 0·53; C(11) 1·71, −1·65; C(17) −1·22, 1·23; C(21) −0·83, −1·76; C(27) 1·83, 1·11]

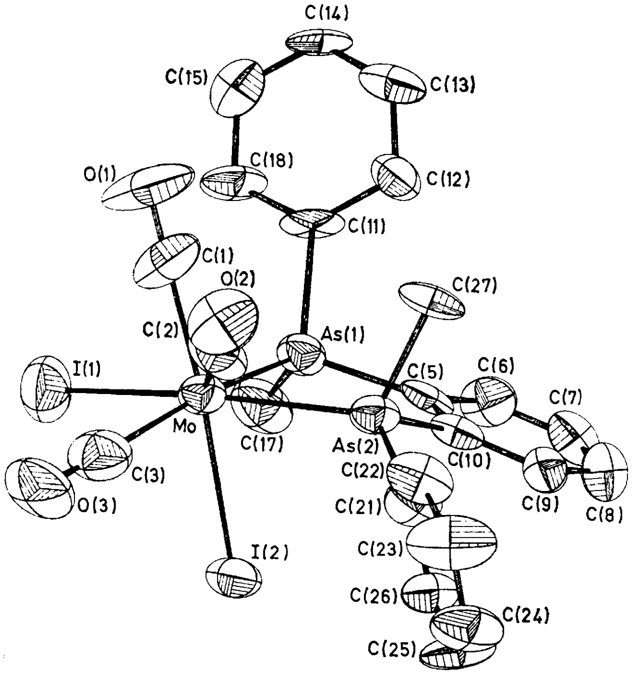

FIGURE 1 The molecule of (I), $[Mo(CO)_3I_2(rac\text{-}o\text{-}C_6H_4(AsMePh)_2)],CHCl_3$

The procedure is the same as that used in previous calculations.[7] The bidentate ligand AB and the five unidentate ligands C, D, E, F, and G lie on the surface of a sphere of unit radius, the positions of which are given by the spherical co-ordinates ϕ_i and θ_i. The axes are defined by placing the bidentate AB symmetrically across the ' North Pole ' at $\phi = 0$, with the ' longitudes ' given by $\theta_A = 0°$, $\theta_B = 180°$. The co-ordinates of the i^{th} atoms are given by ϕ_i, defined as the angle between the M–i bond and the axis passing through the metal atom and the midpoint of AB, and by θ_i, defined as the angle between the MAB plane and the plane incorporating M,i, and the midpoint of AB (Figure 3).

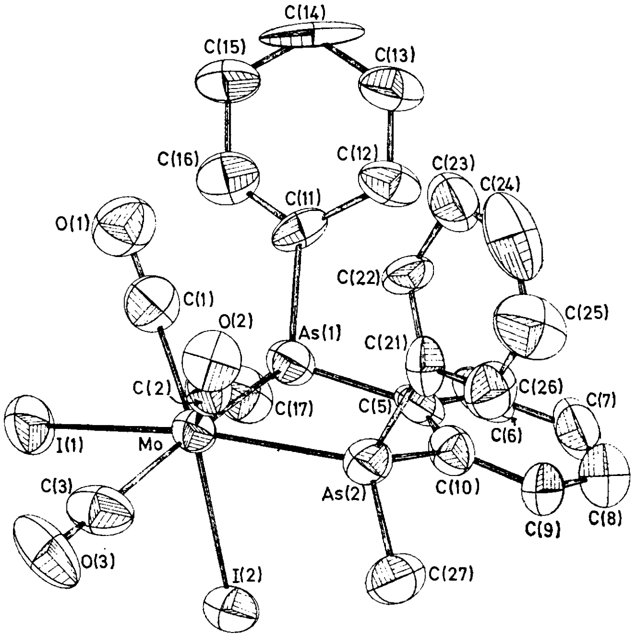

FIGURE 2 The molecule of (II), $[Mo(CO)_3I_2\{meso\text{-}o\text{-}C_6H_4(AsMePh)_2\}]$

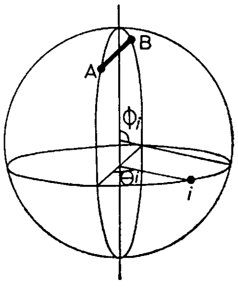

FIGURE 3 Axes used to define the stereochemistry of $[M(bidentate)(unidentate)_5]^{x\pm}$

The ' normalised bite ' of the bidentate ligand is defined by $b = AB/MA = AB/MB$.

At small values of the normalised bite, $b \leqslant 1·1$, two separate minima were found on the potential-energy surface, whereas at larger bites, $b \geqslant 1·2$, four separate minima are found.

The angular parameters for these minima are listed in

Table 4, and will be discussed in turn. Because of the large number of independent variables, calculations were only carried out in angular increments of 1°, and generally for only one type of assumed repulsive law, namely $n = 6$.

(*a*) $b = 0{\cdot}7$—$1{\cdot}1$.—The two minima occurring on the potential energy surface are of comparable energy. Both stereochemistries have C_{2v} symmetry, with one of the unidentate ligands at the 'South Pole,' $\phi = 180°$.

In stereochemistry A, the bidentate AB is projected between the remaining four monodentate ligands, forming the capped trigonal prism shown (Figure 4). In stereochemistry B, the bidentate AB is projected towards two of the remaining four unidentate ligands, forming the pentagonal bipyramid (Figure 5).

TABLE 4

Calculated angular co-ordinates, and repulsion coefficients X, for $[\mathrm{M(bidentate)(unidentate)_5}]^{x\pm}$

	ϕ_A	ϕ_C	θ_C	ϕ_D	θ_D	ϕ_E	θ_E	ϕ_F	θ_F	ϕ_G	θ_G	X
(*a*) $n = 6$												
(i) Minimum A												
b												
0·7	20·5	97	46	97	134	97	226	97	314	180		2·285
0·8	23·6	97	47	98	134	98	226	97	313	180		2·374
0·9 [a]	26·7	95	63	101	149	95	243	101	329	180		2·476
1·0	30·0	98	52	100	137	98	232	100	317	180		2·596
1·1	33·4	100	48	100	132	100	228	100	312	180		2·735
1·2	36·9	99	51	102	133	102	227	99	309	177	0	2·896
1·3	40·5	88	66	114	138	114	222	88	294	151	0	3·035
(ii) Minimum B												
0·7	20·5	100	0	93	90	100	180	93	270	180		2·280
0·8	23·6	102	0	92	90	102	180	92	270	180		2·369
0·9	26·7	103	0	92	90	103	180	92	270	180		2·474
1·0	30·0	105	0	91	90	105	180	91	270	180		2·600
1·1	33·4	107	0	90	90	107	180	90	270	180		2·751
1·2 [b]	36·9	(108)	(0)	(90)	(90)	(108)	(180)	(90)	(270)	(180)		(2·936)
1·3	40·5	110	0	89	90	110	180	89	270	180		3·163
1·4	44·4	112	0	88	90	112	180	88	270	180		3·450
(iii) Minimum C												
1·2	36·9	111	350	82	90	111	190	89	270	161	90	2·906
1·3	40·5	117	343	76	90	117	197	82	270	151	90	3·023
1·4	44·4	122	337	72	90	122	203	76	270	146	90	3·098
(iv) Minimum D												
1·2	36·9	100	52	100	128	132	208	132	332	77	270	2·933
1·3	40·5	101	53	101	128	133	209	132	332	76	270	3·024
1·4	44·4	103	53	103	128	132	211	132	330	74	270	3·130
(*b*) $n = 1$												
(i) Minimum A												
1·2	36·9	89	63	111	139	109	225	91	301	136	3	13·625
(ii) Minimum B												
1·2 [b]	36·9	(108)	(0)	(90)	(90)	(108)	(180)	(90)	(270)	(180)	(—)	(13·620)
(iii) Minimum C												
1·2	36·9	109	356	87	90	109	184	91	270	172	90	13·620
(*c*) $n = 12$												
(i) Minimum A												
1·2	36·9	96	57	106	137	106	223	96	303	170	0	0·646
(ii) Minimum B												
1·2 [b]	36·9	(108)	(0)	(90)	(90)	(108)	(180)	(90)	(270)	(180)	(—)	(0·772)
(iii) Minimum C												
1·2	36·9	113	345	78	90	113	195	82	270	155	90	0·663
(iv) Minimum D												
1·2	36·9	98	61	104	139	154	226	114	339	80	264	0·656

[a] This stereochemistry is intermediate between A and B, and occurs when the relative energies of these two stereochemistries cross over. [b] This stereochemistry does not occur as a minimum for this particular normalised bite; the values in parentheses were obtained by artificially imposing C_{2v} symmetry.

(*b*) $b = 1{\cdot}2$—$1{\cdot}4$.—The four minima now occurring on the potential-energy surface are again of comparable energy.

Minimum A is distorted as the growth of the bidentate ligand pushes the unique unidentate ligand off the 'South Pole.' The distortion is towards the direction of forming a pentagonal bipyramid with the bidentate spanning one of the edges linking an axial and equatorial site (Figure 6). However, this idealised pentagonal bipyramid is never reached, since this minimum on the potential-energy surface disappears before the normalised bite reaches $b = 2^{\frac{1}{2}}$ which would fit perfectly on this polyhedral edge. This illustrates the inadequacy of arguments concerning the relative stability of different stereochemistries based merely on the fitting of chelates of various bites onto appropriate edges of different coordination polyhedra.

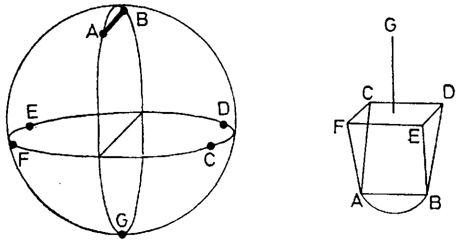

FIGURE 4 Stereochemistry A (b = 0·7—1·1)

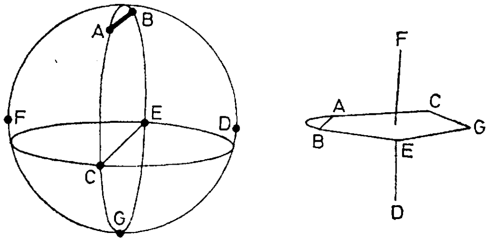

FIGURE 5 Stereochemistry B (b = 0·7—1·1)

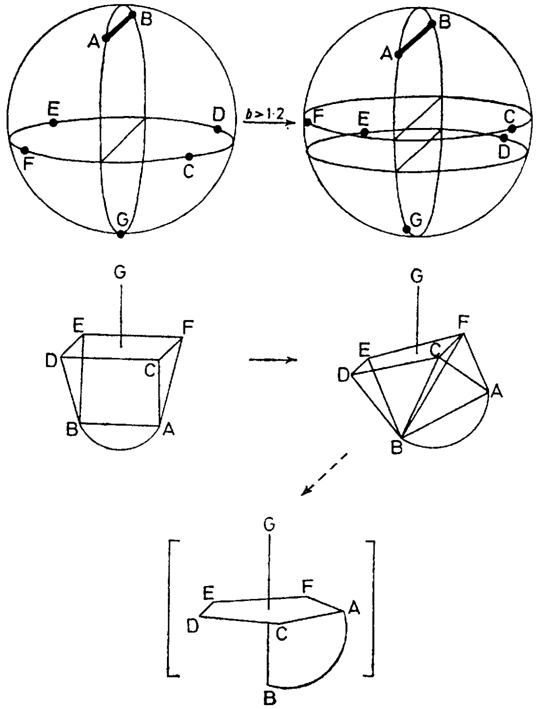

FIGURE 6 Distortion of stereochemistry A as the normalised bite b is increased

As the normalised bite of the bidentate ligand increases minimum B splits into two separate minima, minimum B as before, and minimum C. In the intermediate region of b = 1·2, minimum B does not exist as a separate entity, but a broad trough spreads over both minimum B and minimum C. (The normalised bite corresponding to a planar pentagonal bipyramid is given by $b = 2$ arsin 36° = 1·18.)

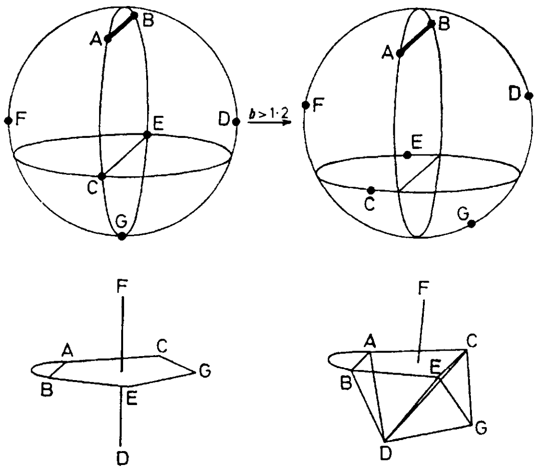

FIGURE 7 Transformation of stereochemistry B into C as normalised bite b is increased

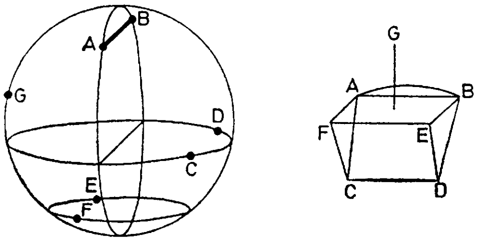

FIGURE 8 Stereochemistry D (b = 1·2—1·4)

TABLE 5

Stereochemistry of compounds of the type $[M(bidentate)(unidentate)_5]^{x\pm}$

	No.	b	Stereo-chemistry
$[NH_4]_3[Mo(O_2)OF_4]F$ [a]	(VIII)	0·71	B
$K_2[Mo(O_2)OF_4],H_2O$ [b]	(IX)	0·74	B
$[Ta(bipy)Cl_2Me_3]$ [c]	(X)	1·12	C
$[Mo(Ph_2As{\cdot}CH_2{\cdot}AsPh_2)Br_2(CO)_2$-$(Ph_2As{\cdot}CH_2{\cdot}AsPh_2)]$ [d]	(III)	1·14	D
$[W\{C_6H_4(AsMe_2)_2\}OCl_4]$ [e]	(XI)	1·18	B
$[Mo(bipy)(HgCl)Cl(CO)_3]$ [f]	(IV)	1·18	D
$[W(bipy)(GeBr_3)Br(CO)_3]$ [g]	(V)	1·2	D
[Mo{*rac*-*o*-$C_6H_4(AsMePh)_2\}I_2(CO)_3]$,-$CHCl_3$ [h]	(I)	1·21	D
[Mo{*meso*-*o*-$C_6H_4(AsMePh)_2\}I_2(CO)_3]$ [h]	(II)	1·24	D
$[Mo(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)Br_2(CO)_3]$,-$Me_2CO$ [i]	(VI	1·24	D
[W{*o*-$C_6H_4(AsMe_2)_2\}I(CO)_4]I_3$ [j]	(VII)	1·26	D

[a] I. Larking and R. Stomberg, *Acta Chem. Scand.*, 1970, **24**, 2043. [b] D. Grandjean and R. Weiss, *Bull. Soc. chim. France*, 1967, 3044. [c] M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1973, 1830. [d] M. G. B. Drew, *J.C.S. Dalton*, 1972, 626. [e] M. G. B. Drew and R. Mandyczewsky, *Chem. Comm.*, 1970, 292. [f] P. D. Brotherton, J. M. Epstein, A. H. White, and S. B. Wild, *Austral. J. Chem.*, to be published. [g] E. M. Cradwick and D. Hall, *J. Organometallic Chem.*, 1970, **25**, 91. [h] This work. [i] M. G. B. Drew, *J.C.S. Dalton*, 1972, 1329. [j] M. G. B. Drew and J. D. Wilkins, *J. Organometallic Chem.*, 1974, **69**, 271.

Minimum C is related to minimum B if it is considered that the growth of the bidentate ligand puckers the pentagonal plane of the pentagonal bipyramid to form a distorted capped trigonal prism (Figure 7). However, there is a small potential-energy barrier between stereochemistries B and C for $b = 1{\cdot}3$ and $b = 1{\cdot}4$.

Minimum D, corresponding to a new stereochemistry, appears for $b = 1{\cdot}2$—$1{\cdot}4$ which has a symmetry-related pair of unidentate ligands at the highest ϕ (Figure 8), rather than a unique unidentate ligand at highest ϕ, as occurs for minima A, B, and C.

For the particular case of $b = 1{\cdot}2$, calculations have also been carried out for different assumed repulsive laws, namely $n = 1$ and $n = 12$ (Table 4). The main difference is that stereochemistry D becomes somewhat distorted for $n = 12$, with loss of the mirror plane.

TABLE 6

Angular co-ordinates for compounds of structure D

	b	ϕ_A	ϕ_C	θ_C	ϕ_D	θ_D	ϕ_E	θ_E	ϕ_F	θ_F	ϕ_G	θ_G
$n = 6$	1·20	36·9	100	52	100	128	132	208	132	332	77	270
$n = 12$	1·20	36·9	98	61	104	139	154	226	114	339	80	264
Compound *												
(III) [a,b]	1·14	33·4	96	72	104	146	152	223	118	352	80	268
(IV) [c]	1·18	36·1	99	63	100	126	136	196	138	345	81	268
(V) [d]	1·2	36	111	46	95	119	136	194	141	325	78	272
(I) [a]	1·21	37·4	99	68	100	144	153	223	122	348	80	266
(II) [a]	1·24	38·3	100	61	100	134	147	212	125	341	79	264
(VI) [a]	1·24	38·3	101	58	101	133	147	209	126	338	83	257
(VII) [e]	1·26	38·9	100	53	100	127	134	206	134	339	79	270

[a] Halogen atoms occupy F and G sites. [b] Unidentate arsine occupies E site. [c] Chlorine occupies G, mercury D site. [d] Bromine occupies G site, germanium F site. [e] Iodine occupies G site.

* Compound numbers defined in Table 5.

The stereochemistry of complexes of stoicheiometry $[M(\text{bidentate})(\text{monodentate})_5]^{x\pm}$ are listed in Table 5. The structures can be clearly classified as belonging to one of the minima found in these calculations. It is believed that this is a more accurate description of these seven-co-ordinate stereochemistries than are descriptions based on polyhedra corresponding to $[M(\text{monodentate})_7]^{x\pm}$. Similarly, the fitting of bidentate ligands to polyhedral edges of the appropriate length is of little predictive use.

One clear prediction from this work is that the bidentate substituted carbonyl halides of molybdenum and tungsten, of which all seven examples are of stereochemistry D, cannot have this stereochemistry for bidentate ligands of small normalised bite.

Table 6 gives a more detailed comparison of the compounds of structure D, including the present two, with the theoretical structure D. The agreement in the angular co-ordinates is satisfactory, considering that each compound has three or four different types of donor atoms.

The detailed geometry of (I) and (II) differ significantly in their angular disposition; construction of a model shows clearly that the transposition of a phenyl ring from one side of the ligand plane to the other is accompanied by a twist of the ligand relative to the face I(1), C(1)—C(3) so as to accommodate the bulky phenyl group more easily in the vicinity of C(2).

[4/1727 *Received*, 16*th August*, 1974]