Structural Studies in the [M(bidentate ligand)(unidentate ligand)$_5$] System. A New Co-ordination Type for [MI$_2$(CO)$_3${Ph$_2$P(CH$_2$)$_n$PPh$_2$}] (M = Mo or W ; n = 1—3) †

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The crystal structures of [MoI$_2$(CO)$_3${Ph$_2$P(CH$_2$)$_2$PPh$_2$}]·CH$_2$Cl$_2$ (1), [MoI$_2$(CO)$_3${Ph$_2$P(CH$_2$)$_3$PPh$_2$}] (2), and [WI$_2$(CO)$_3$[{Ph$_2$P(CH$_2$)PPh$_2$}] (3) have been determined by single-crystal *X*-ray methods at 295 K and refined by least squares to residuals of 0.082, 0.061, and 0.051 for 7 358, 4 572, and 4 522 'observed' reflections respectively. Crystals of (1) are monoclinic, space group $P2_1/n$, with a = 19.338(6), b = 14.674(6), c = 11.577(5) Å, β = 92.39(3)°, and Z = 4; (2) is monoclinic, space group $P2_1/n$, with a = 20.85(1), b = 14.64(2), c = 10.510(4) Å, β = 104.11(5)°, and Z = 4; (3) is monoclinic, space group $P2_1/c$, with a = 20.880(5), b = 8.646(5), c = 16.706(6) Å, β = 104.17(2)°, and Z = 4. For compounds (1) and (2), with bidentate ligands of large bite, the metal-atom stereochemistry is that usually found for complexes of this type, a capped trigonal prism with the bidentate ligand spanning one of the prism edges. For (3), in which the ligand has only one methylene group bridging the two phosphorus atoms, the bite is smaller and a novel stereochemistry is observed, a pentagonal bipyramid with the bidentate ligand spanning one of the pentagonal edges.

REPULSION energy calculations[1] predict that for complexes of the type [M(bidentate)(unidentate)$_5$] the number of isomers, and the detailed stereochemistry of each isomer, is dependent upon the 'normalised bite' b of the bidentate ligand, defined as the distance between the donor atoms of the chelate ring divided by the metal–ligand distance.

Below a normalised bite of 1.1, there is a shallow potential energy trough which incorporates the capped trigonal prism with the bidentate ligand spanning the prism edge *trans* to the capping atom (stereochemistry A), and the pentagonal bipyramid with the bidentate ligand spanning one of the pentagonal edges (stereochemistry B). As the value of the normalised bite increases, both these stereochemistries progressively distort, and momentarily traverse various isomers of the capped trigonal prism, capped octahedron, and pentagonal bipyramid. Both stereochemistries contain a mirror plane, which contains the bidentate ligand and one unidentate ligand in stereochemistry A, and three unidentate ligands in stereochemistry B.

A third potential energy minimum, corresponding to stereochemistry D, appears only at higher values of the normalised bite ($b > ca.$ 1.15). Stereochemistry D is a capped trigonal prism with the bidentate ligand spanning one of the prism edges *cis* to the capping atom, and possesses a mirror plane containing only one unidentate ligand.

The most common type of structurally characterised seven-co-ordinate complex containing one bidentate ligand is [MX$_2$(CO)$_3$(bidentate)], where M is Mo^{II} or W^{II}, the bidentate is a diphosphine or a diarsine, and X is Br or I.[1-5] These compounds have bidentate ligands with normalised bites in the range b = 1.11—1.24, and are all of stereochemistry D. (In these compounds the mirror plane is destroyed as the capped face comprises the bidentate ligand, one carbonyl group, and one halogen atom, and the stereochemistry may alternatively be described as the unsymmetrical capped octahedron with the bidentate ligand spanning one of the edges between the capped face and the uncapped face.) In searching for a new structural type for these complexes in accordance with the above predictions, this series is now extended to both lower and higher values of the normalised bite. A low normalised bite was obtained by using a four-membered chelate ring, phosphorus donor atoms rather than the larger arsenic, and tungsten rather than the smaller molybdenum, as in [WI$_2$(CO)$_3$(Ph$_2$PCH$_2$PPh$_2$)] (3). Larger normalised bites were obtained by using five-membered chelate rings, [MoI$_2$(CO)$_3$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)]·CH$_2$Cl$_2$ (1) and six-membered chelate rings, [MoI$_2$(CO)$_3$(Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$)] (2). The compounds were prepared by standard methods.[6]

EXPERIMENTAL

Cell determination for each sample was carried out by a least-squares fit of the angular parameters of *ca.* 15 reflections with 2θ *ca.* 25° centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer. The initial data set gathered was for the molybdenum analogue of (3), with which it is isomorphous. It was found that it deteriorated rapidly in the *X*-ray beam and the rapidly collected data set did not yield a satisfactory solution and refinement due to serious disorder in the crystal. This disorder was also present in (3), which was stable in the *X*-ray beam; the data on (3), however were more intense and extensive and the problem of solving and refining the structure was overcome satisfactorily. For each compound a unique data set was gathered within a preset 2θ range using a conventional θ—2θ scan at 295(1) K with monochromatic molybdenum K_α radiation (λ = 0.710 69 Å); those reflections with $I > 2\sigma(I)$ were considered 'observed' in each case and used in the structure solution and refinement after correction for absorption.

Crystal Data.—(1). $C_{30}H_{26}Cl_2I_2MoO_3P_2$, M = 917.1, Monoclinic, space group $P2_1/n$ (variant of C_{2h}^5, no. 14), a = 19.338(6), b = 14.674(6), c = 11.577(5) Å, β =

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† Systematic names for the complexes (1)—(3), whose structures have been determined, are [1,2-bis(diphenylphosphino)ethane-*PP'*]tricarbonyldi-iodomolybdenum–methylene dichloride (1/1), [1,3-bis(diphenylphosphino)propane-*PP'*]tricarbonyldi-iodomolybdenum, and [bis(diphenylphosphino)methane-*PP'*]tricarbonyldi-iodotungsten, respectively.

TABLE 1

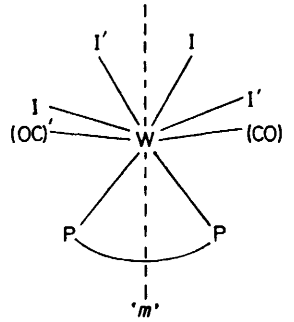
Non-hydrogen atom fractional cell co-ordinates ($\times 10^5$ for Mo, W, I; $\times 10^4$ for other atoms)

	(1)				(2)		
Atom	*x*	*y*	*z*		*x*	*y*	*z*
Mo	26 815(4)	29 384(6)	491(7)		36 119(5)	21 132(7)	59 655(10)
I(1)	23 439(4)	12 784(5)	12 150(6)		42 786(4)	12 221(7)	42 207(8)
I(2)	34 479(4)	34 996(5)	21 051(6)		24 448(4)	17 281(7)	38 864(8)
C(1)	1 958(6)	3 365(8)	1 130(9)		3 578(8)	3 083(10)	4 599(14)
O(1)	1 544(4)	3 587(6)	1 751(8)		3 578(6)	3 648(8)	3 850(10)
C(2)	2 036(5)	3 675(7)	−902(9)		3 724(6)	3 259(11)	6 909(13)
O(2)	1 656(4)	4 147(5)	−1 426(7)		3 769(5)	3 990(8)	7 381(10)
C(3)	3 178(5)	4 072(8)	−426(10)		2 814(7)	2 298(9)	6 655(13)
O(3)	3 422(4)	4 737(5)	−706(7)		2 364(5)	2 431(8)	7 062(10)
P(1)	2 231(1)	1 978(2)	−1 612(2)		4 812(2)	2 158(3)	7 346(3)
C(111)	2 188(5)	2 540(7)	−3 023(8)		5 319(6)	2 933(10)	6 611(12)
C(112)	1 650(6)	2 386(8)	−3 818(9)		5 743(6)	2 587(11)	5 890(13)
C(113)	1 643(6)	2 802(8)	−4 886(9)		6 137(8)	3 188(12)	5 342(15)
C(114)	2 159(7)	3 396(9)	−5 182(9)		6 076(8)	4 120(14)	5 486(18)
C(115)	2 703(6)	3 565(8)	−4 390(10)		5 654(10)	4 478(13)	6 234(29)
C(116)	2 712(5)	3 153(7)	−3 304(9)		5 271(9)	3 873(12)	6 798(22)
C(121)	1 377(5)	1 475(6)	−1 469(8)		4 980(6)	2 557(11)	9 059(14)
C(122)	841(5)	1 957(7)	−1 036(10)		5 613(8)	2 903(16)	9 664(19)
C(123)	195(6)	1 557(9)	−948(11)		5 722(10)	3 115(20)	11 007(20)
C(124)	80(6)	667(9)	−1 289(11)		5 251(11)	3 004(17)	11 702(15)
C(125)	613(6)	178(9)	−1 704(13)		4 637(10)	2 680(16)	11 128(15)
C(126)	1 265(5)	565(8)	−1 797(10)		4 506(7)	2 462(11)	9 777(12)
P(2)	3 796(1)	2 106(2)	−661(2)		3 596(2)	514(2)	7 099(3)
C(211)	4 521(5)	2 786(7)	−1 167(9)		3 005(7)	−231(7)	6 003(11)
C(212)	4 767(5)	3 504(7)	−469(9)		2 346(6)	−260(10)	6 073(12)
C(213)	5 352(5)	3 999(8)	−786(10)		1 881(9)	−779(13)	5 189(16)
C(214)	5 665(5)	3 810(8)	−1 782(11)		2 079(9)	−1 312(12)	4 248(14)
C(215)	5 420(6)	3 092(8)	−2 485(10)		2 749(9)	−1 279(12)	4 155(16)
C(216)	4 856(5)	2 590(7)	−2 176(9)		3 207(8)	−736(9)	5 022(14)
C(221)	4 224(5)	1 330(7)	407(8)		3 334(6)	363(8)	8 634(11)
C(222)	4 711(5)	1 673(7)	1 210(9)		3 150(6)	1 104(10)	9 332(12)
C(223)	5 031(6)	1 088(9)	2 035(11)		2 942(7)	955(11)	10 495(14)
C(224)	4 844(6)	181(8)	2 059(10)		2 918(7)	54(12)	10 942(13)
C(225)	4 364(6)	−156(7)	1 251(10)		3 088(7)	−696(11)	10 262(12)
C(226)	4 050(5)	412(7)	425(9)		3 297(6)	−535(10)	9 087(12)
C(11)	2 818(5)	1 018(6)	−1 872(9)		5 273(6)	1 089(9)	7 588(12)
C(12)	3 557(5)	1 364(7)	−1 912(8)		4 383(6)	−154(9)	7 381(13)
C(13)					4 981(6)	340(10)	8 291(13)
C	3 621(9)	1 173(11)	4 016(13)	methylene chloride			
Cl(1)	2 860(3)	942(4)	4 658(4)				
Cl(2)	4 333(3)	1 107(5)	4 969(4)				

	(3)		
Atom	*x*	*y*	*z*
W	25 530(2)	10 960(6)	39 751(3)
I(1) *	12 756(9)	5 179(19)	30 274(12)
I(1′) *	38 238(11)	7 527(26)	37 850(16)
I(2) *	29 135(9)	−6 633(21)	26 917(9)
I(2′) *	22 471(13)	−8 624(26)	24 802(13)
C(1) *	3 560(10)	826(23)	4 122(12)
O(1) *	4 127(9)	760(20)	4 324(12)
C(1′) *	1 440(15)	735(35)	3 343(19)
O(1′) *	951(13)	771(28)	3 200(15)
C(2)	2 617(5)	−958(15)	4 592(8)
O(2)	2 668(5)	−2 118(11)	4 918(6)
C(3)	2 496(5)	2 987(14)	3 233(7)
O(3)	2 456(4)	3 993(11)	2 798(6)
P(1)	1 846(1)	2 260(3)	4 835(2)
C(111)	1 404(5)	1 064(14)	5 414(6)
C(112)	1 243(6)	1 657(16)	6 112(7)
C(113)	922(7)	728(18)	6 567(8)
C(114)	765(7)	−789(18)	6 350(9)
C(115)	925(7)	−1 364(16)	5 658(10)
C(116)	1 238(6)	−451(17)	5 180(8)
C(121)	1 279(5)	3 820(13)	4 388(6)
C(122)	1 508(6)	5 122(14)	4 078(8)
C(123)	1 097(8)	6 252(14)	3 684(9)
C(124)	443(7)	6 080(18)	3 603(10)
C(125)	176(7)	4 846(20)	3 909(10)
C(126)	602(6)	3 668(16)	4 296(9)
P(2)	3 187(1)	2 511(3)	5 220(2)
C(211)	3 694(5)	1 397(13)	6 057(7)
C(212)	3 394(6)	417(15)	6 513(7)
C(213)	3 789(8)	−409(17)	7 170(8)
C(214)	4 476(7)	−328(17)	7 346(8)
C(215)	4 757(7)	594(17)	6 869(9)
C(216)	4 384(6)	1 430(16)	6 227(8)
C(221)	3 678(5)	4 251(12)	5 172(7)
C(222)	3 828(6)	4 756(15)	4 466(7)
C(223)	4 162(6)	6 145(17)	4 473(8)
C(224)	4 382(6)	6 964(15)	5 196(8)
C(225)	4 253(6)	6 415(15)	5 902(8)
C(226)	3 894(6)	5 044(15)	5 911(7)
C(11)	2 489(5)	3 216(15)	5 623(8)

* Populations: I(1,1′), 0.575(4), 0.429(4); I(2,2′), 0.567(3), 0.421(3); C,O(1), 0.570(—), and C,O(1′), 0.430(—), both constrained.

92.39(3)°, $U = 3\,282(2)$ Å^3, $D_m = 1.86(1)$, $D_c = 1.88$ g cm^{-3}, $Z = 4$, $F(000) = 1\,768$, crystal size $0.09 \times 0.20 \times 0.24$ mm (prism), $\mu_{Mo} = 25.9$ cm^{-1}, data range $2\theta < 60°$, yielding 9 677 independent reflections (7 358 ' observed ').



Primed: unprimed population ratio *ca.*0.43:0.57

(2). $C_{30}H_{26}I_2MoO_3P_2$, $M = 846.3$, Monoclinic, space group $P2_1/n$ (variant of C_{2h}^5, no. 14), $a = 20.85(1)$, $b = 14.64(2)$, $c = 10.510(4)$ Å, $\beta = 104.11(5)°$, $U = 3\,111(5)$ Å^3, $D_m = 1.82(1)$, $D_c = 1.81$ g cm^{-3}, $Z = 4$, $F(000) = 1\,632$, crystal size $0.20 \times 0.08 \times 0.08$ mm (prism), $\mu_{Mo} = 26.8$ cm^{-1}, data range $2\theta < 50°$, yielding 5 526 independent reflections (4 572 ' observed ').

(3). $C_{28}H_{22}I_2O_3P_2W$, $M = 906.2$, Monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 20.880(5)$, $b = 8.646(5)$, $c = 16.706(6)$ Å, $\beta = 104.17(2)°$, $U = 2\,924(1)$ Å^3, $D_m = 2.06(1)$, $D_c = 2.06$ g cm^{-3}, $Z = 4$, $F(000) = 1\,696$, crystal size $0.15 \times 0.08 \times 0.18$ mm (prism), $\mu_{Mo} = 59.1$ cm^{-1}, data range $2\theta < 50°$ yielding 5 173 independent reflections (4 522 ' observed '). For the Mo analogue [isomorphous with (3)]: $C_{28}H_{22}I_2MoO_3P_2$, $M = 818.2$, Monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 20.885(9)$, $b = 8.673(2)$, $c = 16.714(7)$ Å, $\beta = 104.05(3)°$, $U = 2\,937(2)$ Å^3, $D_c = 1.85$ g cm^{-3}, $Z = 4$, $\mu_{Mo} = 25.2$ cm^{-1}.

The structures were solved by the heavy-atom method. In (1) and (2) solution proceeded normally and the parameters of the non-hydrogen atoms were refined with anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$ by least squares, those of the $MoI_2(CO)_3P_2$ molecular core being refined as a single block and those of the remaining individual atoms as 9×9 blocks. For (1), hydrogen atoms were located in difference maps but would not refine successfully positionally, so they were included in the refinements in calculated positions, r(C–H) being held invariant at 1.08 Å, $U_H = 0.08$ Å^2. The data for structure (2) were less accurate and hydrogen atoms were ignored. Refinement was terminated when parameter shifts had fallen below 0.2 σ, final residuals being $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.082$ for (1), 0.061 for (2) and $R' = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}} = 0.083$ for (1), 0.062 for (2) where the weighting scheme was of the form $w = [\sigma^2(F_o) + n \times 10^{-4}(F_o)^2]^{-1}$ the appropriate values of n being 2 for (1) and 2 for (2). The higher residuals of (1) appear to be a consequence of the more extensive data set, the data collected in the range of $50 < 2\theta < 60°$ being largely weak and ineffective.

The data of (3) were superior to those of (1) and (2), which was fortunate, considering the nature of the disorder problem encountered. The molecular geometry is approximately that of the pentagonal bipyramid with C(1) and C(2) axial about the tungsten and the remaining co-ordinated atoms lying in a pseudo-equatorial plane. Careful refinement and examinations of difference maps showed that their disposition was an unequal composite of two arrays related by a mirror exchange (see opposite).

Refinement was carried out by refining the parameters of all ordered and disordered atoms of the $WI_2(CO)_3P_2$ molecular core with anisotropic thermal motion as a single block in the least-squares routine, with the remaining non-hydrogen atoms anisotropic as 9×9 blocks. All hydrogen atoms were located in difference maps and their positional parameters refined with U held at 0.08 Å^2. The molecular-core refinement included variable population parameters for the disordered iodine atoms which gratifyingly refined so as to give populations uniformly and closely consistent with the above ratio. For the sake of consistency, carbonyl populations were constrained in the final refinement stages to be equal to those of the relevant iodines. Final parameter shifts were all $< 0.2\sigma$; the final R was 0.051 and R' 0.052 ($n = 2$).

Neutral atom scattering factors were used throughout, all except C, O, and H being corrected for anomalous dispersion ($\Delta f', \Delta f''$).[7-9] Computation was carried out using the ' X-RAY ' 72' program system,[10] on a CYBER 73 computer. The final positions of the non-hydrogen atoms, bond distances, and angles are given in Tables 1 and 2. Material deposited as Supplementary Publication No. SUP 22655 (78 pp.)† comprises tables of structure factor amplitudes, thermal parameters, refined hydrogen-atom para-

TABLE 2

Molecular non-hydrogen geometries: distances (Å), angles (°) with estimated standard deviations in parentheses

(*a*) The molybdenum and carbonyl geometry [compound (1), compound (2)]

Mo–I(1)	2.873(1), 2.870(2)
Mo–I(2)	2.872(1), 2.902(2)
Mo–C(1)	2.02(1), 2.01(1)
Mo–C(2)	1.96(1), 1.93(2)
C(2)–O(2)	1.16(1), 1.17(2)
I(1)–Mo–I(2)	88.47(4), 83.01(6)
I(1)–Mo–P(2)	87.60(7), 86.9(1)
I(1)–Mo–C(2)	125.5(3), 134.8(4)
I(2)–Mo–P(1)	161.17(7), 162.3(1)
I(2)–Mo–C(1)	75.2(3), 73.8(4)
I(2)–Mo–C(3)	75.7(3), 71.3(4)
P(1)–Mo–C(1)	114.9(3), 104.2(4)
P(1)–Mo–C(3)	114.2(3), 125.2(4)
P(2)–Mo–C(2)	126.2(3), 123.6(4)
C(1)–Mo–C(2)	74.6(4), 74.5(6)
C(2)–Mo–C(3)	71.9(4), 72.7(6)
Mo–C(2)–O(2)	177(1), 174(1)
Mo–P(1)	2.511(3), 2.568(4)
Mo–P(2)	2.638(3), 2.631(5)
Mo–C(3)	2.01(1), 1.99(2)
C(1)–O(1)	1.15(1), 1.14(2)
C(3)–O(3)	1.14(1), 1.14(2)
I(1)–Mo–P(1)	78.79(7), 79.4(1)
I(1)–Mo–C(1)	78.1(3), 78.6(5)
I(1)–Mo–C(3)	162.0(3), 150.8(4)
I(2)–Mo–P(2)	89.49(6), 93.8(1)
I(2)–Mo–C(2)	127.1(3), 122.0(4)
P(1)–Mo–P(2)	76.29(8), 83.4(1)
P(1)–Mo–C(2)	71.7(3), 73.0(4)
P(2)–Mo–C(1)	159.2(3), 161.9(4)
P(2)–Mo–C(3)	83.8(3), 81.5(4)
C(1)–Mo–C(3)	105.4(4), 106.1(6)
Mo–C(1)–O(1)	179(1), 177(1)
Mo–C(3)–O(3)	176(1), 178(1)

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

(*b*) The tungsten geometry in (3)

(*i*) non-disordered geometry

W–P(1)	2.508(4)	W–P(2)	2.495(3)
W–C(2)	2.04(1)	W–C(3)	2.04(1)
C(2)–O(2)	1.13(2)	C(3)–O(3)	1.12(2)
P(1)–W–P(2)	65.9(1)	P(1)–W–C(2)	92.0(4)
P(1)–W–C(3)	94.1(4)	C(2)–W–C(3)	172.8(5)
P(2)–W–C(2)	92.9(4)	P(2)–W–C(3)	93.1(3)
W–C(2)–O(2)	178(1)	W–C(3)–O(3)	177(1)

(*ii*) disordered geometries; entries are organized in parallel columns so that the two molecules may be directly compared

non-primed molecule		primed molecule	
W–I(1)	2.794(3)	W–I(1′)	2.765(4)
W–1(2)	2.875(2)	W–I(2′)	2.955(3)
W–C(1)	2.07(2)	W–C(1′)	2.33(3)
I(1)–W–P(1)	77.4(1)	I(1′)–W–P(2)	79.6(1)
I(1)–W–P(2)	143.0(1)	I(1′)–W–P(1)	145.5(1)
I(1)–W–C(2)	93.8(3)	1(1′)–W–C(2)	91.0(3)
I(1)–W–C(3)	83.9(3)	I(1′)–W–C(3)	86.0(3)
1(1)–W–I(2)	82.6(1)	I(1′)–W–I(2′)	81.7(1)
I(1)–W–C(1)	148.1(6)	I(1′)–W–C(1′)	144.4(8)
I(2)–W–P(1)	159.62(7)	I(2′)–W–P(2)	161.1(1)
I(2)–W–P(2)	134.33(9)	I(2′)–W–P(1)	132.7(1)
I(2)–W–C(2)	85.4(4)	I(2′)–W–C(2)	84.4(4)
I(2)–W–C(3)	87.6(4)	I(2′)–W–C(3)	88.7(3)
I(2)–W–C(1)	65.5(6)	I(2′)–W–C(1′)	63.5(8)
C(1)–W–P(1)	134.4(6)	C(1′)–W–P(2)	135.4(8)
C(1)–W–P(2)	68.9(6)	C(1′)–W–P(1)	69.7(8)
C(1)–W–C(2)	84.4(6)	C(1′)–W–C(2)	92.8(8)
C(1)–W–C(3)	94.0(6)	C(1′)–W–C(3)	85.9(8)
W–C(1)–O(1)	170(2)	W–C(1′)–O(1′)	164(3)

(*c*) Methylene geometries [compounds (1), (2), and (3)]

C(11)–P(1)	1.84(1), 1.82(1), 1.83(1)
C(11)–P(1)–C(111)	101.8(4), 104.5(6), 104.6(5)
C(11)–P(1)–C(121)	105.9(4), 99.6(4), 104.5(5)
C(111)–P(1)–C(121)	104.9(4), 102.8(6), 106.0(5)
M–P(1)–C(11)	110.9(3), 117.7(4), 99.4(4)
M–P(1)–C(111)	115.6(3), 110.9(4), 121.6(4)
M–P(1)–C(121)	116.4(3), 119.2(4), 118.4(4)
C(12) *–P(2)	1.85(1), 1.87(1), 1.85(1)
C(12) *–P(2)–C(211)	103.8(4), 102.6(6), 105.0(6)
C(12) *–P(2)–C(221)	104.5(4), 103.6(6), 104.1(6)
C(211)–P(2)–C(221)	102.7(4), 100.5(6), 104.0(5)
M–P(2)–C(12) *	109.6(3), 115.5(5), 99.3(4)
M–P(2)–C(211)	119.4(3), 109.1(4), 118.3(4)
M–P(2)–C(221)	115.2(3), 122.9(4), 123.7(4)
P(1) · · · P(2)	3.182(4), 3.459(6), 2.722(5)

Compound (1) only:

C(11)–C(12)	1.52(1)		
P(1)–C(11)–C(12)	109.7(7)	P(2)–C(12)–C(11)	112.0(6)

Compound (2) only:

C(11)–C(13)	1.53(2)	C(12)–C(13)	1.55(2)
P(1)–C(11)–C(13)	115.0(9)	P(2)–C(12)–C(13)	113.3(9)
C(11)–C(13)–C(12)	113(1)		

Compound (3) only:

P(1)–C(11)–P(2)	95.3(6)

(*d*) Methylene chloride geometry [compound (1) only]

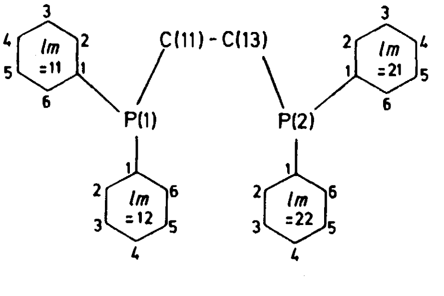
C–Cl(1)	1.71(2)	C–Cl(2)	1.73(2)
Cl(1)–C–Cl(2)	112.9(9)		

* C(11) for compound (3).

meters for (3), and phenyl ring planes and geometries. Non-hydrogen atom numbering within the molecules is as shown in Figures 1—3 and below; carbon atoms in the methylene bridge are numbered 11—13, and phenyl-ring atoms C(*lm* 1—6), where *l* is the number of the phosphorus atom to which they are attached and *m* = 1 or 2, the number of the phenyl ring.

DISCUSSION

Unit-cell contents for each of the three compounds are depicted in Figures 1—3. In each case the asymmetric unit of the compound comprises one molecule of the complex, together with a methylene chloride solvate molecule in the case of (1). In (3), the molecule is disordered in its ' equatorial ' plane; the precision of the determination is sufficient, however, to ensure that this does not preclude separation of the detailed geometries of the two superimposed species sufficiently well to establish that, whereas the stereochemistry in both (1) and (2) is D, the unsymmetrical capped octahedron, (3), comprises a pair of superimposed B type pentagonal bipyramids (Figure 3). This is confirmed by the more detailed comparison provided by the angular co-ordinates calculated relative to the axes defined in Figure 4 and given in Table 3; clearly compound (3) is of stereochemistry B and different to all other complexes of this type, and the aim of preparing a new co-ordination type by reducing the normalised bite of the bidentate ligand has been successful. The angular co-ordinates for compounds of stereochemistry D are reasonably constant, and as predicted from the repulsion calculations are not particularly sensitive to the value of the normalised bite. The ϕ co-ordinates are slightly higher for (2) than for complexes containing five-membered or four-membered chelate rings, which is predicted; the high values for the θ co-ordinates in $[\mathrm{MoI_2(CO)_3}\{rac\text{-}\mathrm{C_6H_4(AsMePh)_2}\}]$ are readily attributed to the expected twisting of this asymmetric ligand relative to all the unidentate ligands. Within the co-ordination spheres of the molybdenum atoms in (1) and (2), significant discrepancies are observed in bonds to similar atom types. Mo–P(1) is shorter than Mo–P(2) by 0.12_7 Å in (1) and 0.063 Å in (2); Mo–C(2) is likewise considerably shorter than Mo–C(1) and Mo–C(3) which are equal.



Phosphine ligand numbering

In a previous[11] report, the structure determinations of complexes $[\mathrm{Pd(NCS)_2L}]$ have been carried out for the above three ligands, revealing a change in the mode of thiocyanate co-ordination from $(\mathrm{SCN})_2$ in the methylene-bridged compound, to (SCN)(NCS) in the dimethylene, and $(\mathrm{NCS})_2$ in the trimethylene analogues. Although the $\mathrm{PdP_2}$ bonding pattern may be influenced both in that series and the present series by the number and nature of the opposed substituents in the co-ordination sphere and the overall co-ordination geometry, the expected correlation between increased methylene chain length, increased P · · · P distance, and increased P–M–P angle with decreased metal–ligand distance for constant

TABLE 3

Angular co-ordinates for $[MX_2(CO)_3(bidentate)]$

	b	ϕ_{AB}	ϕ_{C_1}	θ_{C_1}	ϕ_{C_2}	θ_{C_2}	ϕ_{C_3}	θ_{C_3}	ϕ_{X_1}	θ_{X_1}	ϕ_{X_2}	θ_{X_2}	Ref.
Stereochemistry B													
$[WI_2(CO)_3(Ph_2PCH_2PPh_2)]$ (unprimed molecule)	1.09	33	93	89	94	269	102	174	167	170	110	355	*a*
(primed molecule)							103	356	165	12	113	180	
Stereochemistry D													
$[WI_2(CO)_3(Ph_2AsCH_2AsPh_2)]$	1.11	34	101	65	97	141	146	216	125	345	79	265	*c*
$[MoI_2(CO)_3\{rac\text{-}C_6H_4(AsMePh)_2\}]\cdot CHCl_3$	1.21	37	99	68	100	144	153	223	122	348	80	266	*d*
$[WI_2(CO)_3(Ph_2PCH_2CH_2PPh_2)]$	1.22	38	99	64	102	138	152	214	123	344	82	263	*e*
$[WI_2(CO)_3\{Me_2AsC(CF_3)=C(CF_3)AsMe_2\}]$	1.23	38	101	67	102	139	148	223	125	344	79	265	*f*
$[MoI_2(CO)_3\{meso\text{-}C_6H_4(AsMePh)_2\}]$	1.24	38	100	61	100	134	147	212	125	341	79	264	*d*
$[MoI_2(CO)_3(Ph_2PCH_2CH_2PPh_2)]\cdot CH_2Cl_2$	1.24	38	101	65	100	138	150	215	127	344	81	263	*a*
$[MoBr_2(CO)_3(Ph_2PCH_2CH_2PPh_2)]\cdot Me_2CO$	1.24	38	101	58	101	133	147	209	126	338	83	257	*g*
$[MoI_2(CO)_3(Ph_2PCH_2CH_2CH_2PPh_2)]$	1.33	42	107	55	100	130	143	208	133	336	81	264	*a*

Units of ϕ and θ are degrees. [a] This work. [c] Ref. 5. [d] Ref. 1. [e] Ref. 4. [f] Ref. 3. [g] Ref. 2.

metal atom holds (Table 4) in the palladium derivatives, but not in (**1**) and (**2**) [(**3**), containing tungsten rather than molybdenum, is not directly comparable]; the reason for this is elusive since the disparities in Mo–P distances in these two compounds is very great and influenced considerably by the overall stereochemistry (see above). A plot of P $\cdots$ P distance (Figure 5) against P–M–P angle for the two series of compounds reveals two sets of independent ' straight ' lines as might be expected; interestingly, however, the lower limit for the two series for P $\cdots$ P is almost identical in the two series, the disparity widening as the number of carbon atoms in the bridge increases. The angle at the methylene-bridge carbon, subtended by the two phosphorus atoms, is almost identical for both palladium and tungsten compounds, and strain in the four-membered chelate ring may well be the limiting factor in setting this apparent lower limit to the bite for that ligand.

The chelate-ring conformations are of interest throughout the two series (Table 5). In the methylene-bridged ligand complexes (**3**) (W) and (**4**) (Pd), we find that the four-membered chelate ring is not rigorously planar, and in the case of (**4**), the carbon atom deviates from the plane of the other three by 0.25 Å (Table 5); this in turn is reflected in the deviations of the phenyl-ring-junction atoms from the plane, the two on the side of the plane opposite the carbon deviation being much greater than the other two on the same side. In (**4**), the phenyl atoms above and below the plane are disposed differently, so that the overall symmetry of the $M(PPh_2)C$

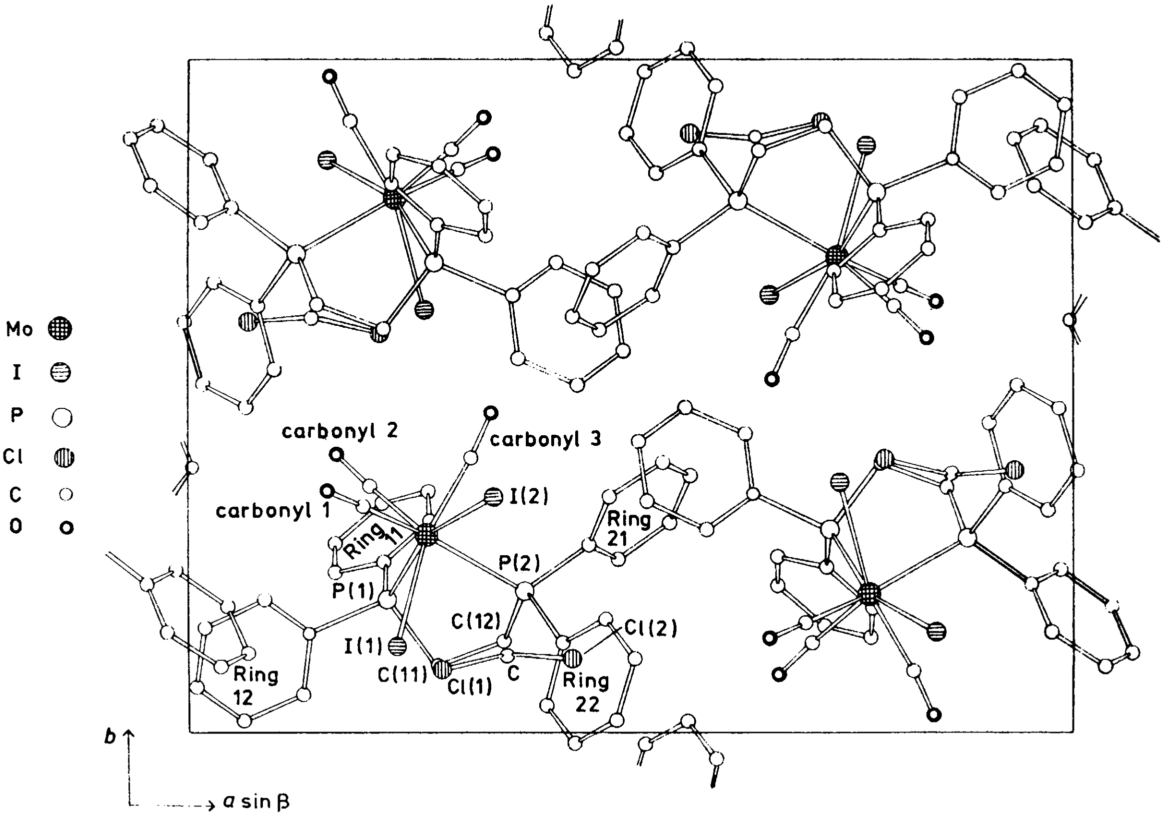


FIGURE 1 Unit-cell contents of (**1**) projected down c, showing non-hydrogen atoms and atom labelling; in this and subsequent figures, carbon atoms are designated by numbers 1—6 only within each phenyl ring (see text)

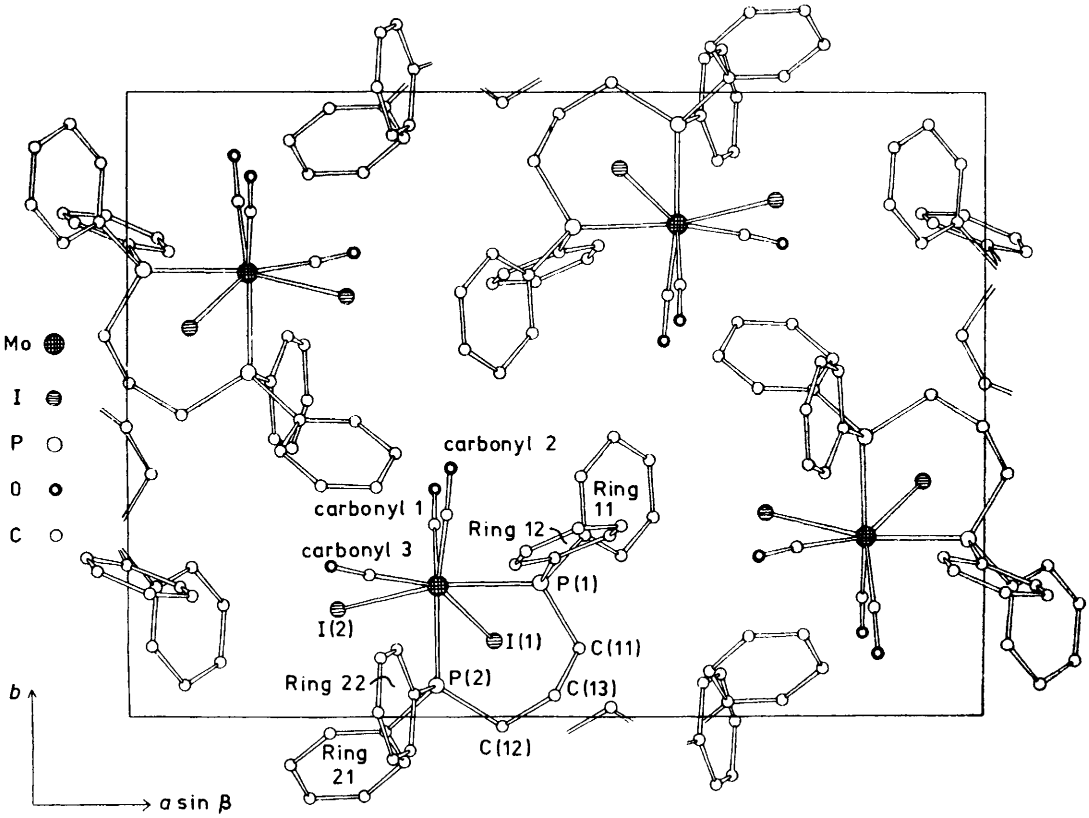


FIGURE 2 Unit-cell contents of (2) projected down *c*

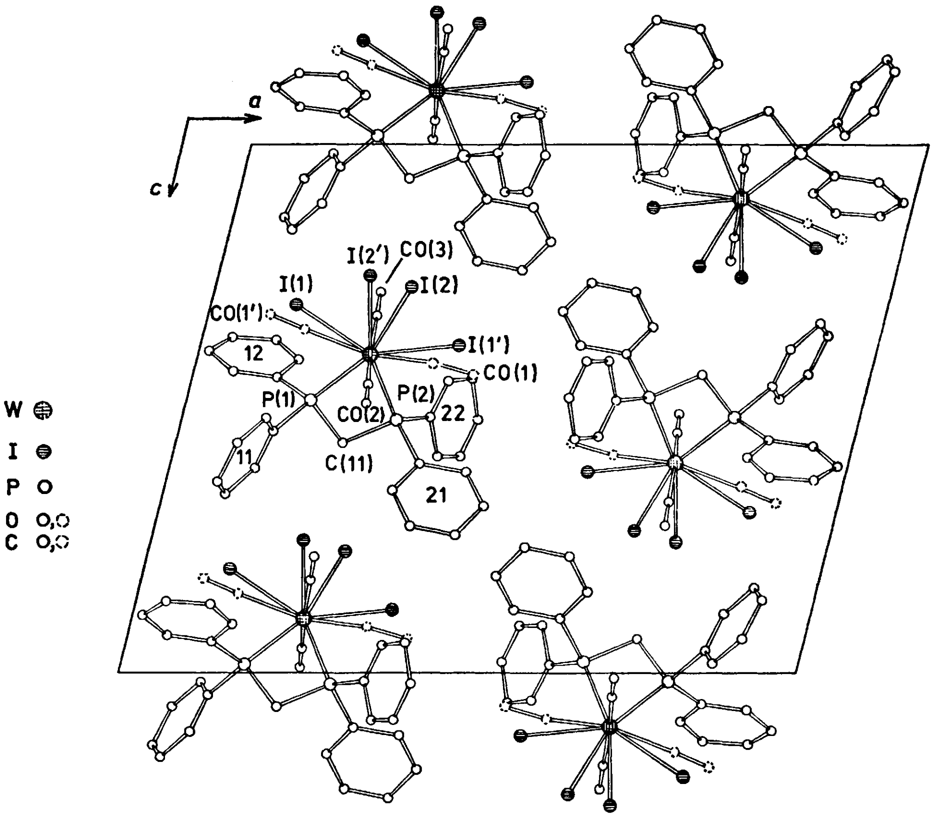


FIGURE 3 Unit-cell contents of (3) projected down *b*. Disordered carbonyl atoms are shown with broken circles

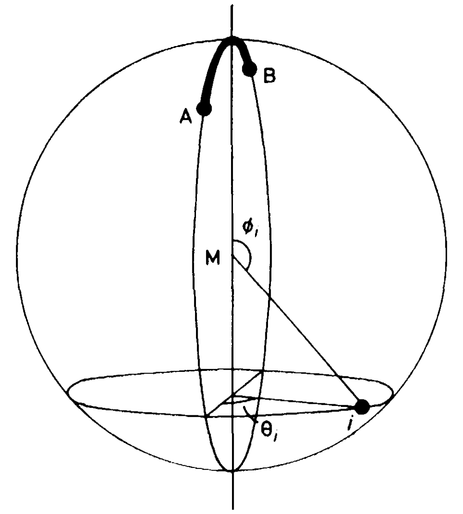


FIGURE 4 Co-ordinates for $[M(bidentate)(unidentate)_5]^{x\pm}$

group is pseudo-*m*, *m* being normal to the MP_2C ' plane ' and passing through M and C; in (3) the overall symmetry of this group is pseudo-2, the 2 passing through the same atoms. The conformations of the five-membered chelate rings in (2) and (5) are almost identical, one of the carbon atoms deviating appreciably from the ring ' plane ' in each case, giving an ' envelope ' conformation. While the conformations of the two six-membered chelate rings in (3) and (6) are both chair, they differ in disposition; in (3), the ring has *m* symmetry with respect to a plane normal to MP_2, passing through M and the unique carbon, while in (6) it has 2 symmetry relative to an axis through these two atoms. C(4) is exactly coplanar with MP_2 in (6). The cause of this is not clear, but in (6), the endocyclic angles at the carbon atoms are curiously enlarged to $116._0$, $116._7$°, indicative of considerable strain.

TABLE 4

Comparison of structural parameters in the phosphine ligands in (3), (1), and (2), and their palladium di(iso)-thiocyanate analogues (4), (5), and (6)

Compound	(3)	(1)	(2)	(4)	(5) *	(6)
n,$(CH_2)_n$	1	2	3	1	2	3
M–P/Å	2.50_2	2.57_5	2.60_0	2.27_3	2.25_1	2.241
P–M–P/°	65.9	76.2_9	$83._4$	73.3_3	$85._1$	89.3_2
P · · · P/Å	2.72_2	3.18_2	3.45_9	2.71_4	3.04_3	3.15_0
P–C–P/°	$95._3$			$94._7$		
M–P–C (chelate)/°	$99._3$	$110._3$	$116._6$	$95._3$	$108._9$	$114._4$

* The assumption is made in our calculations for this compound that the *a* cell dimension is consistently misprinted in the paper[11] as 17.773 rather than the value of 13.773 which reproduces all values quoted.

TABLE 5

Carbon-atom deviations (Å) in the phosphine ligands relative to the MP_2 plane; C(a,a′) are the carbon atoms adjacent to P(1,2), C(b) is the central carbon atom in the trimethylene-bridged ring, and C(1,1′), C(2,2′) are the respective phenyl-ring-junction atoms above and below the ring planes

Cmpd.	(3)	(1)	(2)	(4)	(5)	(6)
δC(a)	−0.07	−0.66	0.95	0.25	−0.64	−0.77
δC(a′)		0.02	1.00		0.13	0.77
δC(b)			0.50			0.00
δC(1)	1.44	1.65	0.69	1.33	1.36	1.66
δC(1′)	1.50	1.39	0.83	1.31	1.70	1.01
δC(2)	−1.47	−0.97	−1.60	−1.56	−1.51	−1.01
δC(2′)	−1.37	−1.49	−1.54	−1.56	−1.00	−1.66

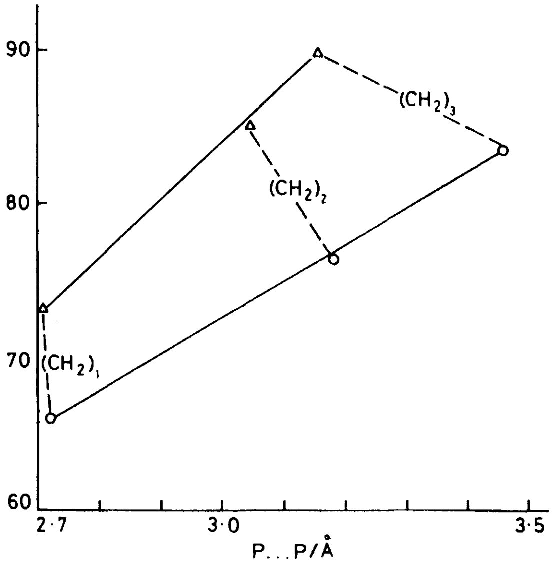


FIGURE 5 Plot of the angle subtended at the metal atom by the phosphine chelate ligand against ligand bite, (O) for the W and Mo series of compounds, (Δ) for palladium analogues

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