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CRYSTAL AND MOLECULAR STRUCTURE OF TWO MONOCLINIC FORMS OF TRICARBONYLDIIODO[BIS(DIMETHYLPHOSPHINE)ETHANE]-TUNGSTEN(II)

MICHAEL G.B. DREW*
Department of Chemistry, The University, Whiteknights, Reading RG6 2AD (Great Britain)
COLIN J. RIX
Department of Chemistry, The University, Manchester (Great Britain)
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Summary

There are two monoclinic crystal forms of the title compound. In the first, *a* 11.701(6), *b* 15.680(9), *c* 9.316(5) Å, *β* 95.36(5)°, *Z* 4, with 1 molecule in the asymmetric unit, spacegroup $P2_1/n$. In the second, *a* 25.772(14), *b* 15.514(13), *c* 17.432(14) Å, *β* 91.59(8)°, *Z* 16, with 4 molecules in the asymmetric unit, spacegroup $P2_1/a$. In this latter form crystals were twinned with *hk*0 common. Both structures were solved by Patterson and Fourier methods from diffractometer data and refined by least squares methods to *R* 0.072 for 2226 independent reflections and to *R* 0.063 for 3250 independent reflections respectively. The five independent molecules are seven-coordinate monomers with similar geometries, all are distorted capped octahedra with a carbonyl group in the capping position, two carbonyl groups and a phosphorus atom in the capped face and two iodine atoms and a phosphorus atom in the uncapped face. Bond lengths are compatible with values found in similar structures. In all molecules, the two W—P bond lengths differ by about 0.06 Å, the longer bond being to the phosphorus atom in the uncapped face which is *trans* to a carbonyl group.

Introduction

We have determined the structures of a number of seven-coordinate capped octahedral structures of general formula $MX_2(CO)_3L$, M = Mo, W; L = a bidentate ligand, X being Cl, Br, I; among them being $MoBr_2(CO)_3(PPh_2CH_2CH_2PPh_2)$ [1] and $WI_2(CO)_3(AsPh_2CH_2AsPh_2)$ [2]. In these two compounds the phenyl rings on the donor atoms and the ring conformation have some effect upon the geometry of the coordination sphere. Therefore we were interested to see whether the replacement of these rings by methyl groups affected the ring conformation and/or the molecular geometry, and therefore have determined, and report

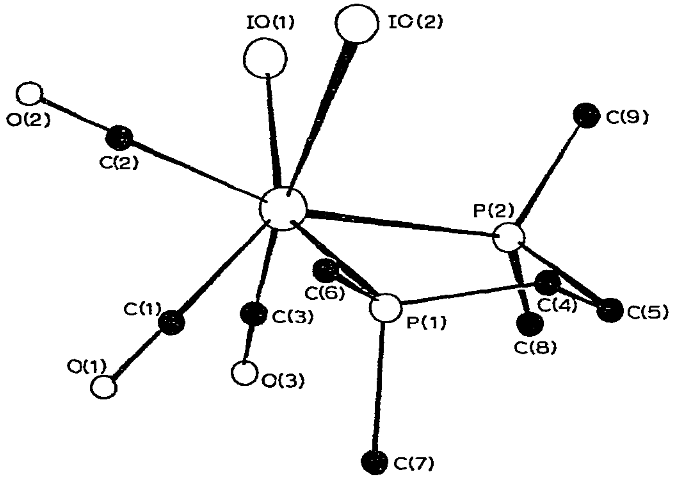

Fig. 1. I.

here, the crystal structure of $WI_2(CO)_3(PMe_2CH_2CH_2PMe_2)$. We found two crystal forms of this compound. In one, hereafter I, there is one molecule in the asymmetric unit, in the other, II, there are four molecules in the asymmetric unit. Therefore from these structure determinations we can compare the geometry of five independent molecules. This is of particular interest as the ligand $Me_2PCH_2CH_2PMe_2$ (dmpe) is very often found to be disordered in the solid state, one example (among many) being the seven-coordinate capped octahedral complex $TaH(CO)_2(dmpe)_2$ [3], indicating that many possible conformations are of equivalent energy. It might be expected therefore that the five molecules would not all have the same geometry.

Experimental

Crystals were prepared as described previously, recrystallised from heptane [4]. Two crystal forms were obtained; I were chunky yellow parallelopipeds and II of which there were very few, were (twinned) yellow-red needles. Crystal data, $C_9H_{16}P_2I_2WO_3$, Mol. wt. 671.8, Mo-K_α radiation, λ 0.7107 Å. For I, monoclinic, a 11.701(6), b 15.680(9), c 9.316(5) Å, β 95.36(5)°, Z 4, U 1701.7 Å^3, d_m 2.61(2), d_c 2.62, μ(Mo-K_α) 108.5 cm^{-1}, spacegroup $P2_1/n$ from systematic absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$. For II, monoclinic, a 25.772(14), b 15.514(13), c 17.432(14) Å, β 91.59(8)°, Z 16, U 6967.1 Å^3, d_c 2.56, d_m not measured due to lack of crystals, μ(Mo-K_α) 106.7 cm^{-1}, spacegroup $P2_1/a$ from systematic absences $h0l$, $h = 2n + 1$ and $0k0$, $k = 2n + 1$.

A General Electric XRD 5 apparatus was used to measure cell dimensions via least squares refinement of high angle reflections and diffraction intensities by the stationary-crystal-stationary-counter method. It was equipped with a manual goniostat, scintillation counter and pulse-height discriminator. Zirconium filtered molybdenum X-radiation was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken from those reflections which were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background as a function of 2θ.

For I a crystal of approximate size 0.5 × 0.5 × 0.7 mm was mounted with the b axis parallel with the instrument axis. 2999 Independent reflections were measured with $2\theta < 45°$ of which 2226 with $I > 2\sigma(I)$ were used in subsequent calculations. For II a needle of approximate size 0.05 × 0.60 × 0.05 mm was mounted with the b axis parallel with the instrument axis. All crystals were twinned in the (usual) monoclinic manner in that $hk0$ zones were common but the two c^* axes were $2\beta°$ apart. In view of the proximity of the β angle to 90°, this twinning resulted in considerable overlap of peaks. We chose a crystal in which the two twins had an approximate intensity ratio of 1.3/1 and measured 6363 independent reflections with $2\theta < 40°$. The $hk0$ data were given an initial scale factor of 1.3/2.3 (subsequently refined) relative to the other reflections. No other corrections for the overlapping of peaks were made until the structure had been solved (vide infra). 3250 reflections with $I > 2\sigma(I)$ were used in subsequent refinement.

Standard reflections were measured repeatedly during the data collection of both crystals but no significant change in intensity was observed. For both crystals, absorption corrections were applied using the program ABSORB [5], transmission factors varying between 0.025 and 0.070 for I and 0.57 and 0.72 for II. No extinction correction was applied.

Both structures were solved by Patterson and Fourier methods and refined by least squares. For II, it became apparent that of the 3250 reflections ca. 720 were seriously affected by the superlap of peaks due to the twinning. For reflections with $|h/l| \geqslant 4$, hkl reflections from one twin and $\bar{h}kl$ reflections from the other were superimposed. At $|h/l| = 4$, the difference in Φ between this pair of reflections was ca. 0.4°, a value sufficiently high for the peaks, which were very sharp, to be separated. Also for $h = 12, 13, 14$ hkl reflections for one twin and $\bar{h} + 1, k, l$ reflections from the other were superimposed. We obtained tables of R for specific values of h, k and l which showed that the other categories of reflections were relatively unaffected by the twinning. We then attempted to remeasure these 720 peaks taking careful measurement of the background. For over half these reflections, this procedure was not successful and we measured the intensity of both peaks and by simultaneous equations obtained a value for the contribution from twin 1 to both reflections*. After these corrections had been made 25 reflections had unreasonably large ΔF's and were given zero weight in the refinement. The structure was refined to an overall R of 0.063. The value of R for the 281 reflections with $|l| = 1$ was 0.120 while for $|l| = 12, 13, 14$ R was 0.081 for 297 reflections. This showed that we had made a reasonable stab at accounting for the twinning and no further corrections were made.

For both structures atomic scattering factors for tungsten, iodine, phosphorus, carbon, oxygen were taken from ref. 6 as were the corrections for the real and imaginary part of the anomalous dispersion of tungsten, chlorine and phosphorus. I was refined with all atoms anisotropic to R 0.072 for 2226 indepen-

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* Intensity of peak 1 = $1.26^*(I_{hkl})_{\text{twin 1}} + 1.00^*(I_{\bar{h}kl})_{\text{twin 2}}$. Intensity of peak 2 = $1.26^*(I_{\bar{h}kl})_{\text{twin 1}} + 1.00^*(I_{hkl})_{\text{twin 2}}$. Hence $1.26^* I_{hkl}$ and $1.26^* I_{\bar{h}kl}$, contributions from twin 1 were calculated.

TABLE 1

FINAL POSITIONAL COORDINATES (X 10^4) FOR I
(*with estimated standard deviations in parentheses*)

Atom	*x*	*y*	*z*
W(1)	1313(1)	1852(1)	1847(1)
IO(1)	1633(2)	2983(1)	—0500(2)
IO(2)	2603(2)	3029(1)	3731(2)
P(1)	1881(5)	0927(3)	3974(5)
P(2)	3203(5)	1144(4)	1268(6)
C(1)	—0070(20)	1277(15)	2363(24)
O(1)	—0910(17)	0950(13)	2590(21)
C(2)	0145(24)	2771(18)	2078(24)
O(2)	—0501(21)	3322(13)	2270(19)
C(3)	0684(20)	1200(14)	0152(25)
O(3)	0428(17)	0797(12)	—0902(19)
C(4)	3424(19)	0744(15)	4152(23)
C(5)	3832(23)	0440(15)	2689(24)
C(6)	1544(23)	1276(16)	5802(25)
C(7)	1304(22)	—0158(15)	3892(29)
C(8)	3177(23)	0452(19)	—0334(25)
C(9)	4384(23)	1890(17)	1024(30)

dent reflections, using full-matrix least-squares. For II five large blocks were used; tungsten and iodine atoms were refined anisotropically for the 3250 independent reflections. The weighting scheme chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_o and $\sin\theta/\lambda$ was $\sqrt{w} = 1$ for $F_o < F^*$ and $\sqrt{w} = F^*/F_o$ for $F_o > F^*$. F^* was 50 in I and 250 in II. Calculations were made on a C.D.C. computer at the University of London Computer Centre with the programs listed in ref. 5 and on an I.C.L. 1904S computer at

TABLE 2

ANISOTROPIC THERMAL PARAMETERS (X 10^3) FOR I
(estimated standard deviations in parentheses)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	42.9(5)	27.9(4)	27.2(4)	—1.6(4)	—9.9(4)	0.7(3)
IO(1)	76.4(11)	53.2(9)	42.4(8)	—10.1(8)	—12.9(8)	15.6(7)
IO(2)	87.5(12)	38.1(8)	50.0(9)	—14.7(8)	—20.8(9)	0.0(6)
P(1)	52(3)	33(3)	29(3)	—2(2)	—7(2)	3(2)
P(2)	44(3)	51(3)	35(3)	—2(3)	—7(2)	1(3)
C(1)	38(13)	46(12)	49(13)	—3(10)	—11(10)	3(10)
O(1)	59(12)	85(14)	63(11)	—13(11)	—7(9)	10(10)
C(2)	67(17)	65(16)	36(12)	—12(14)	1(11)	19(11)
O(2)	115(18)	81(13)	50(10)	60(14)	1(11)	1(10)
C(3)	46(13)	39(11)	51(13)	—13(10)	6(10)	4(10)
O(3)	75(12)	74(12)	52(10)	—16(10)	—24(10)	—18(9)
C(4)	40(12)	53(13)	39(11)	10(10)	—9(9)	5(10)
C(5)	76(18)	45(13)	37(11)	—0(12)	8(11)	10(10)
C(6)	69(17)	57(14)	42(12)	—12(13)	0(11)	3(11)
C(7)	57(15)	38(12)	79(18)	3(11)	—11(13)	6(12)
C(8)	63(16)	86(19)	40(13)	14(14)	0(11)	—34(13)
C(9)	61(15)	66(16)	66(16)	—29(14)	—33(13)	24(13)

TABLE 3

FINAL POSITIONAL COORDINATES (X 10^3) AND ISOTROPIC THERMAL PARAMETERS FOR II

Atom	x	y	z	U(X 10^3)
W(a)	5018(1)	3719(1)	2742(1)	[a]
IO(1a)	4810(1)	4051(2)	1135(2)	[a]
IO(2a)	5863(1)	2656(2)	2269(2)	[a]
P(1a)	5183(5)	2858(8)	3945(6)	[a]
P(2a)	4428(4)	2389(7)	2587(6)	[a]
C(1a)	5038(20)	4549(35)	3560(30)	69(15)
O(1a)	5074(12)	5041(22)	4093(18)	65(9)
C(2a)	5542(23)	4648(38)	2497(32)	80(17)
O(2a)	5870(15)	5107(25)	2291(21)	87(11)
C(3a)	4385(16)	4267(28)	2729(22)	42(11)
O(3a)	3949(13)	4621(21)	2754(17)	64(9)
C(4a)	5065(16)	1779(28)	3807(23)	43(11)
C(5a)	4449(19)	1657(34)	3407(27)	65(15)
C(6a)	5836(16)	2899(29)	4409(23)	44(12)
C(7a)	4750(19)	3148(32)	4741(26)	60(14)
C(8a)	3748(15)	2531(26)	2415(22)	37(11)
C(9a)	4581(20)	1779(35)	1730(29)	72(16)
W(b)	5082(1)	1295(1)	7749(1)	[a]
IO(1b)	5196(1)	0934(2)	6143(2)	[a]
IO(2b)	4241(15)	2429(2)	7312(2)	[a]
P(1b)	5024(5)	2190(9)	8943(7)	[a]
P(2b)	5715(5)	2551(8)	7548(7)	[a]
C(1b)	5104(20)	0520(36)	8625(30)	71(15)
O(1b)	5028(15)	−0004(27)	9134(23)	96(12)
C(2b)	4506(20)	0398(32)	7517(27)	59(14)
O(2b)	4149(19)	−0011(30)	7365(26)	118(15)
C(3b)	5717(18)	0615(31)	7736(24)	52(13)
O(3b)	6084(13)	0168(20)	7738(17)	60(9)
C(4b)	5161(17)	3215(30)	8746(25)	52(13)
C(5b)	5765(17)	3297(29)	8352(24)	51(12)
C(6b)	4393(22)	2153(39)	9503(32)	86(18)
C(7b)	5531(17)	1892(29)	9722(24)	49(12)
C(8b)	6405(18)	2327(30)	7433(26)	56(13)
C(9b)	5548(22)	3227(37)	6711(31)	82(31)
W(c)	2732(1)	0689(1)	0266(1)	[a]
IO(1c)	2317(1)	1488(2)	1599(2)	[a]
IO(2c)	2273(1)	2082(2)	−0609(2)	[a]
P(1c)	2733(5)	0035(8)	−1052(6)	[a]
P(2c)	1850(5)	−0076(9)	0141(7)	[a]
C(1c)	3380(18)	0271(29)	0117(24)	47(12)
O(1c)	3839(16)	0022(26)	0050(22)	100(15)
C(2c)	3183(17)	1631(30)	0482(23)	49(12)
O(2c)	3487(12)	2214(21)	0598(17)	59(9)
C(3c)	2840(16)	−0183(27)	1045(23)	42(11)
O(3c)	2878(13)	−0701(23)	1529(19)	73(10)
C(4c)	2076(19)	−0173(32)	−1478(27)	62(14)
C(5c)	1825(21)	−0746(36)	−0755(30)	77(16)
C(6c)	3033(20)	0618(35)	−1814(29)	74(15)
C(7c)	3019(23)	−1061(38)	−1090(33)	88(18)
C(8c)	1676(19)	−0920(32)	0842(27)	63(13)
C(9c)	1262(22)	0563(39)	0182(32)	88(18)
W(d)	2691(1)	4242(1)	4723(1)	[a]
IO(1d)	2301(1)	3462(2)	3338(2)	[a]
IO(2d)	2173(1)	2860(2)	5485(2)	[a]
P(1d)	2653(5)	4830(9)	6059(6)	[a]
P(2d)	1842(5)	5092(8)	4753(7)	[a]
C(1d)	3391(35)	4628(55)	4945(46)	137(29)
O(1d)	3796(20)	4905(31)	5081(26)	121(16)

(to be continued)

TABLE 3 (continued)

Atom	x	y	z	$U(\times 10^3)$
C(2d)	3215(18)	3308(33)	4587(26)	55(13)
O(2d)	3415(14)	2639(25)	4500(20)	80(11)
C(3d)	2850(20)	5092(35)	3920(29)	66(15)
O(3d)	2938(15)	5695(28)	3477(23)	97(12)
C(4d)	2030(15)	5000(26)	6351(22)	36(11)
C(5d)	1736(20)	5554(34)	5724(28)	68(15)
C(6d)	2933(20)	4105(35)	6843(29)	62(15)
C(7d)	2945(18)	5830(31)	6228(27)	75(14)
C(8d)	1718(24)	5995(42)	4098(35)	74(16)
C(9d)	1210(20)	4387(34)	4574(30)	99(20)

[a] Anisotropic thermal parameters given in Table 4.

Reading University using our unpublished programs. In both structures, refinement was stopped when all shifts were $<0.08\sigma$. The anisotropic thermal parameters are defined as exp $-2\pi^2\Sigma\Sigma_{ij}U_{ij}h_ih_jb_ib_j$; $i, j = 1,2,3$, b_i being the i'th reciprocal cell dimension. The isotropic thermal parameter is defined as $\exp(-8\pi^2U\text{-}\sin^2\theta/\lambda^2)$. The zero weighted reflections in both structures showed no serious discrepancies. The large number of low intensity data found for II is due to the relative positions of the four independent molecules (vide infra). The final difference Fourier maps showed no significant peaks. Final positional coordinates and thermal parameters for I are given in Tables 1 and 2 and for II in Tables 3 and 4. Molecular dimensions for both structures are compared in Table 5. The final observed and calculated structure factors are available from the authors on request.

TABLE 4

ANISOTROPIC THERMAL PARAMETERS ($\times 10^3$) IN II
(estimated standard deviations in parentheses)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(a)	34.1(11)	36.7(12)	32.7(11)	−1.7(10)	−0.3(8)	−0.1(10)
IO(1a)	68.7(23)	67.8(24)	38.4(18)	5.4(19)	−2.3(16)	−0.9(16)
IO(2a)	42.8(19)	84.3(27)	74.8(23)	13.9(19)	18.1(17)	7.8(20)
P(1a)	50(8)	57(9)	28(6)	16(7)	2(5)	1(6)
P(2a)	31(7)	45(8)	40(7)	5(6)	7(5)	2(6)
W(b)	44.9(12)	40.3(13)	25.6(11)	1.4(10)	1.6(8)	−3.3(9)
IO(1b)	112.5(30)	65.2(25)	33.6(18)	1.0(22)	4.5(18)	−0.4(17)
IO(2b)	70.1(25)	81.2(29)	103.4(29)	25.5(22)	−34.9(21)	−16.3(23)
P(1b)	71(9)	54(9)	37(7)	2(7)	7(6)	−10(6)
P(2b)	54(8)	51(8)	41(7)	−13(7)	3(6)	−4(6)
W(c)	35.4(11)	44.6(13)	28.5(10)	1.3(10)	−01.2(8)	−2.6(10)
IO(1c)	78.7(25)	80.1(27)	40.9(18)	7.2(20)	12.3(17)	−1.0(18)
IO(2c)	75.1(24)	66.9(24)	56.9(21)	1.2(20)	−9.7(18)	10.5(19)
P(1c)	50(8)	64(9)	36(7)	8(7)	26(6)	−4(7)
P(2c)	63(9)	54(9)	45(8)	0(7)	14(6)	8(7)
W(d)	33.8(11)	41.8(13)	30.9(10)	−1.4(10)	7.9(8)	−3.6(10)
IO(1d)	105.9(30)	81.0(28)	34.6(18)	−19.8(23)	−1.5(18)	−8.8(18)
IO(2d)	65.3(23)	57.3(22)	54.4(20)	−8.7(18)	10.2(16)	3.9(17)
P(1d)	60(9)	79(10)	31(7)	−7(8)	−8(6)	−6(7)
P(2d)	48(8)	52(9)	47(7)	15(7)	1(6)	8(7)

TABLE 5

DIMENSIONS IN THE FIVE MOLECULES (Å)

	I	IIa	IIb	IIc	IId
W—IO(1)	2.868(2)	2.885(3)	2.878(3)	2.866(3)	2.859(3)
W—IO(2)	2.877(2)	2.871(2)	2.878(3)	2.880(3)	2.870(3)
W—P(1)	2.494(5)	2.512(11)	2.510(12)	2.512(12)	2.503(12)
W—P(2)	2.579(6)	2.574(11)	2.571(13)	2.569(13)	2.554(13)
W—C(1)	1.958(24)	1.92(5)	1.94(5)	1.82(5)	1.93(5)
W—C(2)	1.998(28)	2.03(6)	2.07(5)	1.90(5)	2.00(5)
W—C(3)	1.961(22)	1.84(4)	1.95(5)	1.93(4)	1.97(5)
IO(1)—W—IO(2)	88.27(5)	86.8(1)	87.6(1)	87.0(1)	85.3(1)
IO(1)—W—P(1)	157.12(15)	158.1(3)	157.5(3)	157.8(3)	156.6(3)
IO(1)—W—P(2)	86.07(14)	87.0(3)	86.1(3)	85.4(3)	87.4(3)
IO(1)—W—C(1)	130.2(6)	127.0(16)	130.0(16)	129.5(13)	127.2(24)
IO(1)—W—C(2)	77.3(7)	77.0(16)	76.8(13)	75.2(13)	79.4(13)
IO(1)—W—C(3)	77.0(7)	76.4(12)	77.0(13)	77.5(13)	76.0(15)
IO(2)—W—P(1)	78.62(13)	79.8(3)	79.6(3)	80.2(3)	79.2(3)
IO(2)—W—P(2)	89.59(14)	87.7(3)	88.7(3)	87.2(3)	88.1(3)
IO(2)—W—C(1)	123.1(7)	126.4(15)	126.2(16)	123.9(14)	125.7(25)
IO(2)—W—C(2)	78.4(7)	80.4(17)	80.1(14)	76.6(13)	80.7(14)
IO(2)—W—C(3)	163.8(7)	160.3(12)	162.7(13)	161.2(13)	159.2(15)
P(1)—W—P(2)	75.3(2)	75.3(4)	75.3(4)	76.0(4)	74.8(4)
P(1)—W—C(1)	72.4(7)	74.8(16)	72.0(16)	72.5(13)	76.2(24)
P(1)—W—C(2)	117.5(7)	117.2(16)	118.4(14)	118.5(13)	114.7(13)
P(1)—W—C(3)	112.9(7)	112.6(13)	112.3(13)	110.8(13)	115.5(16)
P(2)—W—C(1)	126.7(7)	128.3(16)	124.9(16)	129.6(14)	129.2(26)
P(2)—W—C(2)	159.7(8)	160.5(16)	159.8(14)	155.2(14)	163.2(14)
P(2)—W—C(3)	82.8(7)	81.3(14)	82.7(14)	81.1(13)	82.2(15)
C(1)—W—C(2)	73.5(10)	71.1(23)	75.0(20)	75.2(20)	67.5(29)
C(1)—W—C(3)	72.4(10)	72.8(20)	70.7(20)	74.6(19)	73.9(28)
C(2)—W—C(3)	104.3(10)	105.3(22)	103.4(20)	108.9(18)	104.2(20)
W—C(1)—O(1)	176(2)	176(4)	168(4)	176(4)	176(7)
W—C(2)—O(2)	177(2)	171(6)	171(5)	177(4)	164(4)
W—C(3)—O(3)	172(2)	177(3)	176(4)	176(4)	173(4)
C(1)—O(1)	1.14(3)	1.20(6)	1.22(7)	1.25(6)	1.14(10)
C(2)—O(2)	1.18(4)	1.17(7)	1.14(7)	1.21(6)	1.17(6)
C(3)—O(3)	1.19(3)	1.25(5)	1.17(6)	1.16(6)	1.24(7)
P(1)—C(4)	1.83(2)	1.72(5)	1.67(5)	1.86(5)	1.72(4)
P(1)—C(6)	1.86(2)	1.85(4)	1.92(6)	1.80(6)	1.90(5)
P(1)—C(7)	1.82(3)	1.86(5)	1.91(4)	1.85(5)	1.75(5)
P(2)—C(5)	1.82(2)	1.82(5)	1.82(5)	1.87(6)	1.87(5)
P(2)—C(8)	1.83(3)	1.78(4)	1.83(5)	1.85(5)	1.83(5)
P(2)—C(9)	1.84(3)	1.82(5)	1.84(6)	1.82(6)	1.98(7)
W—P(1)—C(4)	110.4(7)	112.1(14)	109.9(16)	114.4(16)	113.1(14)
W—P(1)—C(6)	119.3(8)	118.5(14)	118.4(18)	119.0(19)	115.5(18)
W—P(1)—C(7)	116.1(8)	113.8(14)	113.5(18)	114.5(18)	117.0(16)
C(4)—P(1)—C(6)	105.3(11)	104(2)	109(2)	101(2)	102(2)
C(4)—P(1)—C(7)	102.3(11)	103(2)	103(2)	101(2)	103(2)
C(6)—P(1)—C(7)	101.6(12)	103(2)	102(2)	105(3)	104(2)
W—P(2)—C(5)	113.8(9)	114.3(16)	114.1(15)	109.7(18)	111.3(16)
W—P(2)—C(8)	118.0(10)	119.6(14)	119.6(16)	120.0(16)	121.1(20)
W—P(2)—C(9)	114.7(9)	111.2(17)	113.8(18)	118.9(20)	114.4(18)
C(5)—P(2)—C(8)	102.3(12)	102(2)	99(2)	99(2)	104(2)
C(5)—P(2)—C(9)	102.6(12)	109(2)	105(2)	109(2)	102(2)
C(8)—P(2)—C(9)	103.5(13)	99(2)	103(2)	98(2)	101(2)
C(4)—C(5)	1.55(3)	1.73(6)	1.72(6)	1.69(7)	1.57(6)
P(1)—C(4)—C(5)	110.5(15)	109(3)	110(3)	109(3)	108(3)
P(2)—C(5)—C(4)	108.5(16)	105(3)	102(3)	99(3)	110(3)

Discussion

The geometry of I is shown in Fig. 1, together with the atomic numbering scheme. The molecules of II which have very similar geometries are named IIa, IIb, IIc and IId, and contributing atoms which are numbered in an equivalent manner are given the identification letter a,b,c,d in the Tables. All five molecules are distorted capped octahedra with a carbonyl group [C(1), O(1)] in the capping position, two carbonyl groups [C(2), O(2); C(3), O(3)] and one phosphorus atom [P(1)] in the capped face and two iodine atoms [IO(1), IO(2)] and the remaining phosphorus atom [P(2)] in the uncapped face. As can be seen from Table 5, there are no significant differences between the bond lengths in the five molecules. The ten W—IO bonds average to 2.873 Å. This is slightly longer than the 2.842(3) Å found in the capped trigonal prismatic ion [W(CO)$_4$(diars)I$^+$] [7] (diars = *o*-phenylenebisdimethylarsine). The fifteen W—C bonds have a mean value of 1.95 Å with all bond lengths within 2σ of this value. However the W—P(1) bonds (mean 2.51 Å) are significantly shorter than the W—P(2) bonds (mean 2.57 Å). A similar effect was noted in $MoBr_2(PPh_2CH_2CH_2PPh_2)(CO)_3$, (III) [1], where the bond lengths are 2.500(4) and 2.618(5) Å, and ascribed to the fact that the W—P(2) bond is weakened by the *trans* W—C(2) bond.

The 21 angles subtended at the tungsten atom are also very similar in the five molecules, as are the conformations of the five-membered rings, details of which are given in Table 6. We used a best molecular fit routine [8] to check whether the differences in geometry between pairs of the five molecules were significant. We took each of the 10 pairs in turn and calculated the r.m.s. average separation of the 17 equivalent atoms. Values were found to be in the range 0.09 to 0.14 Å suggesting that all molecules have essentially the same geometry which is slightly varied in the crystal due to packing forces.

The conformations of the five-membered rings are asymmetrical puckered with C(5) almost coplanar with W, P(1) and P(2) while C(4) is a ca. 0.70 Å from the plane. Distances of the two carbon atoms from the W, P(1), P(2) plane are respectively I −0.71, −0.04; IIa −0.71, 0.07; IIb −0.74, 0.05; IIc −0.68, 0.27; IId −0.73, −0.06; III −0.71, 0.09 Å. The reasons for this particular ring conformation are shown in Fig. 2. P(2) has four near neighbours in the coordination sphere IO(1), IO(2), P(1) and C(3) and a staggered conformation w.r.t. C(5), C(8), C(9) is not possible. In the event, these three carbon atoms are staggered w.r.t. IO(1) and IO(2), thus resulting in one small torsion angle C(3)—W—P(2)—C(8) which is close to 0°. To compensate the P(2)—W—C(3) angle is increased to 82° from the 75° expected for that particular bite in the capped octahedron. The arrangement around the W—P(1) bond is approximately staggered (see Fig. 2).

This conformation of the five-membered ring is also found in III and thus the replacement of the phenyl rings by the methyl groups has not had any major effect. However there are some significant variations in the angles subtended at the central metal atom; for example P(1)—Mo—C(3)* and P(1)—Mo—C(2) angles are respectively 5° larger and 6° smaller in III than in I. The geom-

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* In III, IVa, IVb the numbering scheme is changed to conform with those of I and II.

TABLE 6

TORSION ANGLES FOR THE FIVE MOLECULES

(a). In the five-membered ring[a]

	I	IIa	IIb	IIc	IId
W—P(1)—C(4)—C(5)	—50.3	—52.7	—56.7	—52.7	—52.0
P(1)—C(4)—C(5)—P(2)	47.6	50.9	54.2	58.4	48.2
C(4)—C(5)—P(2)—W	—26.3	—29.1	—28.8	—43.5	—25.8
C(5)—P(2)—W—P(1)	—1.3	2.3	1.6	8.6	—1.8
P(2)—W—P(1)—C(4)	24.4	26.4	28.0	23.8	27.4

(b). For atoms i—W—j—k, where the i—W—j angle is <100°

	I	IIa	IIb	IIc	IId
IO(1)—W—P(2)—C(5)	165.4	169.3	168.9	176.5	162.8
IO(1)—W—P(2)—C(8)	—74.8	—68.8	—74.2	—70.2	—74.3
IO(1)—W—P(2)—C(9)	47.6	45.9	48.4	50.0	47.3
IO(2)—W—P(1)—C(4)	—68.2	—63.9	—63.3	—65.8	—63.6
IO(2)—W—P(1)—C(6)	54.0	58.0	62.1	54.0	53.9
IO(2)—W—P(1)—C(7)	176.0	179.1	—178.7	178.7	177.5
IO(2)—W—P(2)—C(5)	77.0	82.3	81.2	89.2	77.5
IO(2)—W—P(2)—C(8)	—163.1	—155.7	—161.9	—157.5	—159.7
IO(2)—W—P(2)—C(9)	—40.7	—41.0	—39.3	—37.2	—38.0
C(1)—W—P(1)—C(4)	161.4	163.7	163.0	163.8	165.2
C(1)—W—P(1)—C(6)	—76.4	—74.4	—71.6	—76.4	—77.3
C(1)—W—P(1)—C(7)	45.6	46.7	47.6	48.3	46.3
C(3)—W—P(2)—C(5)	—117.2	—114.0	—113.8	—105.5	—120.9
C(3)—W—P(2)—C(8)	2.6	7.9	3.1	7.8	1.9
C(3)—W—P(2)—C(9)	125.0	122.6	125.7	128.0	123.6

[a] Values in III are respectively —54.9, 58.4, —36.7, 3.1, 23.8°.

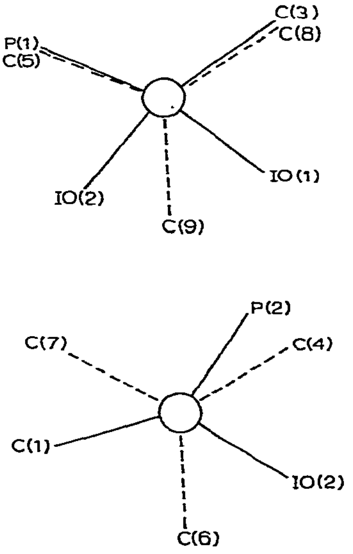

Fig. 2. (a), Projection down the W—P(2) bond; (b), projection down the W—P(1) bond.

etries of Mo{*rac*-*o*-$C_6H_4(AsMePh)_2$}$I_2(CO)_3$, IVa and Mo{*meso*-*o*-$C_6H_4(AsMePh)_2$}-$I_2(CO)_3$, IVb [9] are very similar to I, II and III. These two geometries are equivalent to each other in most respects but have different As(1)—Mo—C(3) and As(1)—Mo—C(2) angles which are 120, 111° in IVa and 112, 116° in IVb. The reason for this is that one of the C—P(1)—[or As(1)]—Mo—C(3) torsion angles is <20° in all eight structures and in III and IVa the C is a phenyl ring carbon in I, II and IVb it is a methyl group. Thus some of the variations in geometry in the coordination sphere can be directly attributed to the influence of the group bonded to the donor atoms in the chelate.

In IVa and IVb the ring conformation is an envelope with both carbon atoms ca. 0.53 Å to the same side of the Mo, As, As plane. The projections down the Mo—As vectors are similar to those shown for I in Fig. 2 with differences in torsion angles of ca. 8° around Mo—As(1) and ca. 12° around Mo—As(2).

The geometries of IVa and IVb have been described [10] as distorted capped trigonal prisms while we would describe them as distorted capped octahedra in common with I and II. Such confusion not uncommon with seven-coordinate geometries merits comment.

While the geometry of most seven-coordinate molecules can be simply described in terms of one of the ideal types, capped octahedron (CO), capped trigonal prism (CTP) or pentagonal bipyramid (PB), there are exceptions; in particular a considerable number of molecules, among them I-IV, which have geometries intermediate between a CO and a CTP. The majority of these molecules (but not all, see for example $[W(CO)_3(PMe_2Ph)_3I]^+$ [11], $MoCl_2(CO)_2(PMe_2Ph)_3$ [12]) are of the type $M(bidentate)(unidentate)_5$. Dewan et al [9] have calculated via simple repulsion theory the minima on the potential energy surface for such molecules. Results show four minima among them a broad one whose characteristics are shown to embrace the geometries of seven molecules of this type including III and IV. However such calculations do not take account of differences in ligands and indeed there are several distinct geometries (vide infra) among these seven molecules which can best be described in terms of distortions from the ideal polyhedra.

However these distortions should be quantified in some way and two recent papers by Dollase [13] and Muetterties and Guggenberger [14] suggest how this can be done. In the first method, the seven ligand positions are fitted by rotation and dilation to an ideal polyhedron of the required symmetry by the method of least squares. The r.m.s. deviation between the observed and the ideal polyhedra is calculated in Å. Thus a direct measure of the distortion from each of the ideal polyhedra can be calculated and compared. This method also allows the shape characteristics of the polyhedra to vary, a necessary feature for C_{2v} and C_{3v}. In the second method, three specific angles (called δ') are calculated between two planes with a common edge. In ref. 14 the method is just applied to ML_7 molecules but with more complicated molecules there are several possible sets of δ' angles that can be considered and it is suggested that the smallest δ' angles are taken. This is not a problem in the present case as for a molecule to be considered as a CTP and a CO only one set of δ' angles can be chosen, those given in Fig. 3. Results for both methods for the seven molecules of ref. 9 together with others including I are given in Table 7. The results are naturally dependent upon bond length and therefore an alternative method is to normalise all M—L bond

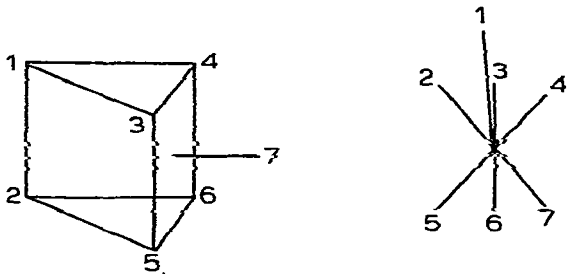

Fig. 3. Alternative ways of describing molecular geometry in terms of a CTP or a CO. δ' angles are those between the planes containing atoms 134 and 347; 123 and 235; 124 and 246. Values of angles calculated from ideal polyhedra obtained from repulsion theory of $M(unidentate)_7$ are for a CO 24.2, 24.2, 24.2 and for a CTP 41.5, 0.0. For any CO (C_{3v}) all three angles are equivalent and for any CTP (C_{2v}) two angles are zero.

TABLE 7

INVESTIGATION OF POLYHEDRA TYPE FOR MOLECULES IN THE CO/CTP CATEGORY[a]

Molecule	r.m.s. distortion (Å) [b] from ideal polyhedra		δ' angles (°)
	CO	CTP	
I	0.092	0.147	13.2, 13.0, 2.7
III	0.086	0.151	12.1, 10.4, 6.0
IVa	0.106	0.159	21.4, 16.7, 3.8
IVb	0.094	0.161	17.5, 10.3, 8.2
V	0.123	0.168	25.1, 21.6, 9.3
VI	0.152	0.155	22.1, 10.4, 6.0
VII	0.168	0.122	33.9, 21.8, 0.2
VIII	0.155	0.089	39.5, 0.0, 0.0
IX	0.066	0.160	22.5, 17.8, 17.8
X	0.090	0.138	14.1, 13.1, 12.8

[a] V is $Mo(Ph_2AsCH_2AsPh_2)_2Br_2(CO)_2$ [15], VI is $Mo(2,2'\text{-bipyridyl})(HgCl)Cl(CO)_3$ [16], VII is $W(2,2'\text{-bipyridyl})(GeBr_3)Br(CO)_3$ [17], VIII is $[W(CO)_4(diars)I]^+$ [7], IX is $Me_3TaCl_2(2,2'\text{-bipyridyl})$ [18], X is $[W(CO)_3(PMe_2Ph)_3I]^+$ [11]. [b] In both cases, the ideal polyhedra have M—L lengths of 1 Å. This enables comparisons to be made between the different structures.

TABLE 8

INVESTIGATION OF POLYHEDRA TYPE FOR MOLECULES IN THE CO/CTP CATEGORY[a]

Molecule	CO	CTP	δ' angles (°)
I	0.044	0.099	24.0, 13.1, 5.2
III	0.039	0.107	19.0, 13.2, 5.4
IVa	0.053	0.115	24.6, 17.4, 2.0
IVb	0.032	0.119	19.7, 17.4, 7.0
V	0.085	0.127	25.0, 21.8, 1.7
VI	0.120	0.079	36.1, 5.8, 0.8
VII	0.128	0.115	26.7, 20.1, 13.0
VIII	0.111	0.017	41.4, 0.0, 0.0
IX	0.066	0.160	22.7, 18.2, 18.2
X	0.083	0.057	32.3, 3.2, 1.6

[a] Bond lengths have been normalised to 1.0 Å.

TABLE 9

NON-BONDED INTERMOLECULAR CONTACTS FOR I < 3.75 Å AND FOR II < 3.50 Å[a]

$\mathrm{C(6)\cdots O(3^{I})}$	3.53	$\mathrm{O(3)\cdots O(3^{III})}$	3.21
$\mathrm{C(7)\cdots O(1^{II})}$	3.58	$\mathrm{C(1)\cdots O(3^{III})}$	3.52
$\mathrm{O(3)\cdots C(1^{III})}$	3.52	$\mathrm{C(6)\cdots O(2^{IV})}$	3.66
$\mathrm{O(3)\cdots C(3^{III})}$	3.48	$\mathrm{C(8)\cdots O(2^{V})}$	3.43
$\mathrm{O(3)\cdots C(7^{III})}$	3.44	$\mathrm{C(9)\cdots O(2^{V})}$	3.54
$\mathrm{O(3)\cdots O(1^{III})}$	3.23		

[a] Roman numeral superscripts refer to the following equivalent positions relevant to the reference molecule at x,y,z: I $x,y,1+z$, II $\bar{x},\bar{y},1-z$, III $\bar{x},\bar{y},\bar{z}$, IV $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$, V $\frac{1}{2}+x,\frac{1}{2}-y,-\frac{1}{2}+z$.

$\mathrm{O(1b)\cdots O(1c^{I})}$	3.50	$\mathrm{O(1b)\cdots O(1b^{III})}$	3.03
$\mathrm{C(6b)\cdots O(2c^{I})}$	3.06	$\mathrm{C(9a)\cdots O(1b^{IV})}$	3.31
$\mathrm{O(2b)\cdots C(6c^{I})}$	3.39	$\mathrm{O(1c)\cdots O(1b^{IV})}$	3.21
$\mathrm{O(3d)\cdots O(3a)}$	3.37	$\mathrm{C(3c)\cdots O(3b^{IV})}$	3.45
$\mathrm{O(2c)\cdots C(9a)}$	3.46	$\mathrm{O(3c)\cdots O(3b^{IV})}$	3.05
$\mathrm{C(8a)\cdots O(2c)}$	3.26	$\mathrm{O(1c)\cdots C(7b^{IV})}$	3.40
$\mathrm{O(1a)\cdots O(1a^{II})}$	3.20	$\mathrm{C(5d)\cdots O(2d^{V})}$	3.28
$\mathrm{O(1a)\cdots O(1d^{II})}$	3.21	$\mathrm{C(4c)\cdots O(3a^{VI})}$	3.42
$\mathrm{C(7a)\cdots O(1a^{II})}$	3.49	$\mathrm{C(5c)\cdots O(2c^{VI})}$	3.28
$\mathrm{C(9b)\cdots O(1a^{II})}$	3.41	$\mathrm{C(4d)\cdots O(3b^{VII})}$	3.49

[a] I $x,y,1+z$, II $1-x,1-y,1-z$, III $1-x,\bar{y},2-z$, IV $1-x,\bar{y},1-z$, V $\frac{1}{2}-x,\frac{1}{2}+y,1-z$, VI $\frac{1}{2}-x,-\frac{1}{2}+y,\bar{z}$, VII $-\frac{1}{2}+x,\frac{1}{2}-y,z$.

lengths to 1.0 Å before doing the calculation. Results are shown in Table 8. The types of polyhedra obtained from this table are equivalent to those obtained from a study of L—M—L angles in the molecules with differences in bond lengths ignored. These tables show that the set of δ' angles are very dependent upon bond lengths. Also that for most molecules the amount and type of the distortion from the ideal geometries is not clear. There are other δ' angles which have specific values in the ideal polyhedra that are ignored. We find the method of Dollase more appropriate for the present set of molecules.

From Tables 7 and 8 it is clear that the geometry of molecules I, III, IVa and IVb is best described as a distorted CO in which the distortions, as described in the present paper, are due to the steric effects of the five-membered ring. V is also of this type though the distortions from ideal symmetry are much greater [15], due to the effect of the four-membered ring. VI is midway between the CO and CTP though more like a CTP after normalisation. VII and VIII are distorted CTP's. The geometry of IX would seem from these Tables to be a distorted CO while the authors described it as a distorted CTP [19]. The geometry of X is equally well described as a CO or a CTP; the changes in r.m.s. deviation and δ' angles after normalisation are particularly striking. Thus there are several distinct geometries among these molecules which can be described in terms of distortions from the ideal polyhedra. It is unjustified to lump them together as a specific stereochemistry, new or otherwise. Indeed it may well be that the geometries listed here illustrate the reaction pathway between the C_{3v} and C_{2v} ideal forms.

The unit cell diagrams, both in the *c* projection, are given in Figs. 4 and 5. Non-bonded contacts, listed in Table 9 show that there are closer contacts between the molecules of II than between the molecules of I. However there are

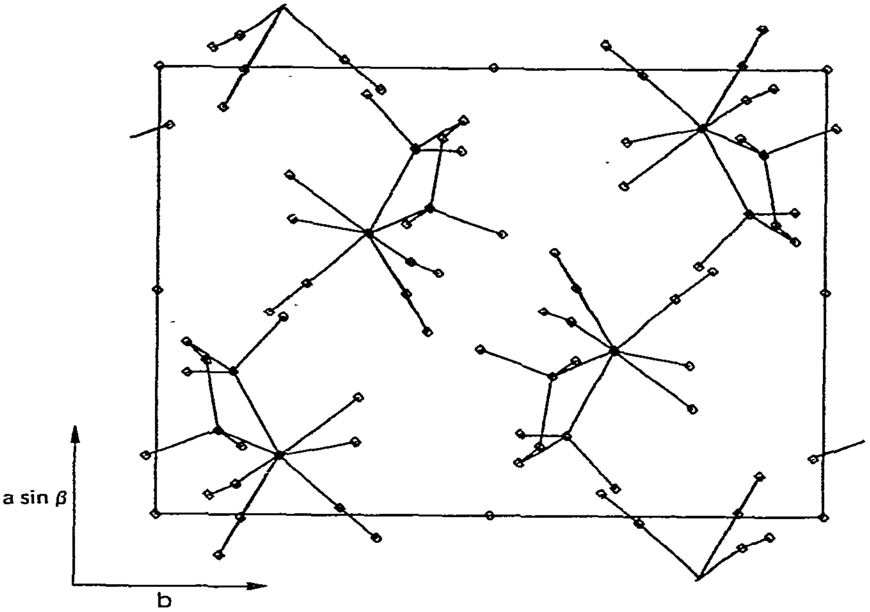

Fig. 4. Unit cell of I in the c projection.

no distances significantly less than the sum of Van der Waals radii. The packing diagram of II illustrates that molecules IIa and IIb are related by the approximate relationship ($x,y,z/1 - x,\frac{1}{2} - y,\frac{1}{2} + z$) and IIc and IId by ($x,y,z/x,\frac{1}{2} - y,\frac{1}{2} - z$).

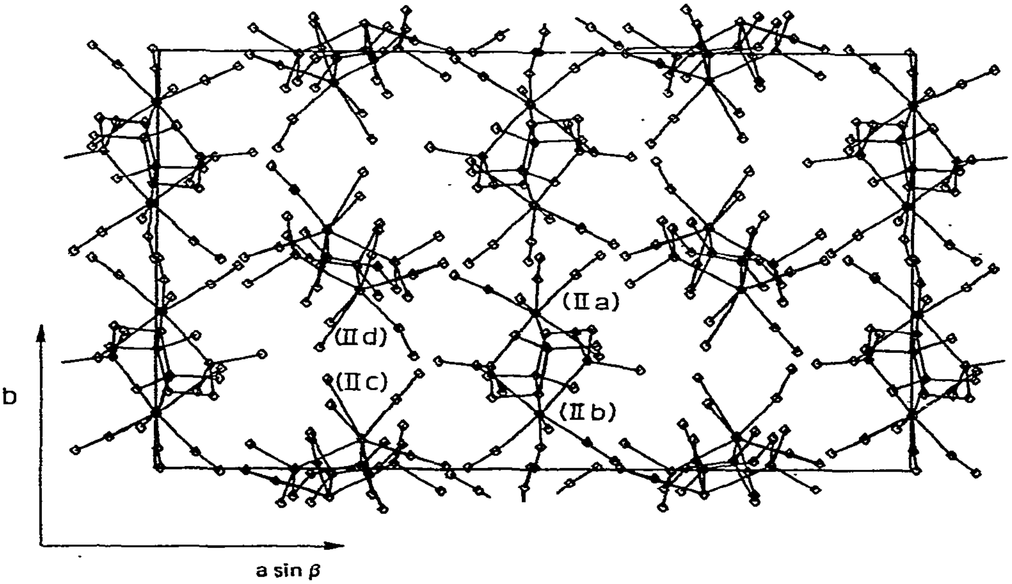

Fig. 5. Unit cell of II in the c projection.

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