Crystal and Molecular Structures of Dicarbonyldichlorobis(diphenylarsino)methanemolybdenum(II) and Dicarbonyldichlorobis(diphenylphosphino)methanemolybdenum(II)–Benzene (1/0.75)

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Crystals of $[MoCl_2(CO)_2(dpam)_2]$ [dpam = bis(diphenylarsino)methane] (I) are orthorhombic, a = 11.134(5), b = 22.715(5), c = 19.138(6) Å, Z = 4, space group $P2_12_12_1$. Crystals of $[MoCl_2(CO)_2(dppm)_2]$ [dppm = bis(diphenylphosphino)methane] (II) are monoclinic, a = 19.863(18), b = 13.972(6), c = 19.064(13) Å, β = 101.30(11)°, Z = 4, space group $P2_1/n$. 1 974 (I) and 2 623 (II) independent reflections were measured by counter methods and refined by least squares to R 0.068 and 0.108. The structure of (I) is a relatively undistorted capped octahedron with a carbonyl group in the capping position [1.73(4) Å], a carbonyl group and two arsenic atoms in the capped face [1.83(4); 2.624(4), 2.596(4) Å], and one arsenic and two chlorine atoms in the uncapped face [2.681(4); 2.520(8), 2.501(8) Å]. The geometry of (II) is similar but more distorted with bond lengths: Mo–C 1.91(2), 1.82(3); Mo–P 2.547(6), 2.487(7), 2.593(6), and Mo–Cl 2.554(6), 2.484(6) Å.

As part of our study of seven-co-ordinate geometry,[1] we have looked at the crystal structures of a number of complexes of general formula $[MX_2(CO)_nL_{3-n}(L\text{–}L)]$ (M = Mo or W; X = Cl, Br, or I; n = 2 or 3; L = unidentate ligand, L–L = bidentate ligand). With X = Br or I these complexes had relatively undistorted capped octahedral geometries in which the two halogens occupied the relatively uncrowded uncapped face with X–M–X angles of *ca.* 90°. We considered that the replacement of bromine by chlorine might well distort the co-ordination sphere by a considerable amount because Cl · · · Cl repulsions were less important in fixing geometry than Br · · · Br repulsions. A related dichloro-complex, though with all-unidentate ligands, namely $[MoCl_2(CO)_2(PMe_2Ph)_3]$,[2] has a geometry intermediate between a capped octahedron (CO) and a capped trigonal prism (CTP). Accordingly we have determined and report here the crystal and molecular structure of two dichloro-complexes namely $[MoCl_2(CO)_2(dpam)_2]$ (I) and $[MoCl_2(CO)_2(dppm)_2]$ (II). Other structures of this type which have been reported are $[MoBr_2(CO)_3(dppe)]$,[3] $[MoBr_2(CO)_2(dpam)_2]$,[4] $[WI_2(CO)_3(dmpe)]$,[5] $[WI_2(CO)_3(difas)]$,[6] $[WI_2(CO)_3(dpam)]$,[7] and $[MoI_2(CO)_3(dimas)]$.[8,†]

EXPERIMENTAL

Crystals were prepared as previously described in refs. 9 (I) and 10 (II) from the halogenocarbonyl and the appropriate ligand.

Crystal Data.—(I), $C_{52}H_{44}As_4Cl_2MoO_2$, Orthorhombic, M = 1 167.4, a = 11.134(5), b = 22.715(5), c = 19.138(6) Å, U = 4 840.2 Å^3, $F(000)$ = 2 320, D_m = 1.57, Z = 4, D_c = 1.60. Mo-K_α radiation, λ = 0.710 7 Å, μ(Mo-K_α) = 32.14 cm^{-1}. Space group $P2_12_12_1$ from systematic absences $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, $00l$, $l = 2n + 1$.

(II), $C_{52}H_{44}P_4Cl_2MoO_2$ + xC_6H_6‡, Monoclinic, M = 991.7, a = 19.863(18), b = 13.972(6), c = 19.064(13) Å, β = 101.30(11)°, U = 5 188.1 Å^3, $F(000)$ = 2 032, D_m = 1.34(2), Z = 4, D_c = 1.27, μ(Mo-K_α) = 5.1 cm^{-1}. Space group $P2_1/n$ from systematic absences $0k0$, $k = 2n + 1$ and $h0l$, $h + l = 2n + 1$.

Data for both crystals were obtained by use of a General

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† Abbreviations: dpam = bis(diphenylarsino)methane, dppm = bis(diphenylphosphino)methane, dppe = bis(diphenylphosphino)ethane, dmpe = bis(dimethylphosphino)ethane, difas = 2,3-bis(dimethylarsino)-1,1,1,4,4,4-hexafluorobut-2-ene, and dimas = *o*-phenylenebis(methylphenylarsine).

‡ Some benzene of crystallisation present; M, D_c, $F(000)$, and μ were calculated assuming $x = 0$.

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Electric XRD 5 diffractometer equipped with manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered molybdenum X-rays were used.

TABLE 1

Final positional co-ordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$) for (I), with standard deviations in parentheses

Atom	x	y	z	U
Mo	−0 472(2)	0.798(1)	1 045(1)	
Cl(1)	0 575(7)	0 393(3)	2 108(4)	
Cl(2)	−2 203(7)	1 036(4)	1 829(4)	
As(1)	0 387(3)	1 764(1)	1 609(1)	
As(2)	1 124(3)	0 087(1)	0 531(1)	
As(3)	−1 274(3)	−0 307(1)	0 890(2)	
As(4)	0 344(3)	2 617(2)	2 991(2)	
C(1)	0 200(33)	1 193(15)	0 377(19)	87(11)
C(2)	−1 622(37)	1 001(17)	0 403(22)	106(13)
O(1)	0 630(21)	1 508(10)	−0 167(12)	92(7)
O(2)	−2 340(23)	1 162(11)	−0 051(14)	105(8)
C(3)	0 363(25)	−0 657(11)	−0 839(13)	53(7)
C(4)	0 071(30)	1 812(15)	2 598(17)	77(10)
C(11)	2 139(26)	1 899(12)	1 589(15)	56(8)
C(12)	2 676(27)	2 135(13)	1 006(17)	66(9)
C(13)	3 923(32)	2 227(16)	0 970(19)	85(10)
C(14)	4 619(35)	2 086(15)	1 578(19)	91(10)
C(15)	4 081(30)	1 811(15)	2 167(17)	79(10)
C(16)	2 827(28)	1 731(14)	2 186(16)	68(9)
C(21)	−0 157(25)	2 485(13)	1 231(14)	58(8)
C(22)	−1 471(26)	2 479(13)	1 074(15)	57(9)
C(23)	−2 070(35)	3 036(17)	0 893(20)	96(12)
C(24)	−1 393(35)	3 524(17)	0 798(20)	100(12)
C(25)	−0 072(34)	3 518(20)	0 903(20)	101(13)
C(26)	0 418(30)	2 982(14)	1 123(16)	72(9)
C(31)	2 697(25)	0 083(13)	0 863(15)	58(8)
C(32)	3 216(34)	−0 439(15)	1 155(20)	92(12)
C(33)	4 455(30)	−0 417(13)	1 348(15)	65(8)
C(34)	5 150(28)	0 068(14)	1 355(16)	69(9)
C(35)	4 644(33)	0 588(14)	1 084(18)	83(10)
C(36)	3 421(27)	0 591(13)	0 839(16)	69(10)
C(41)	1 317(24)	0 014(11)	−0 444(13)	46(7)
C(42)	0 369(32)	0 136(14)	−0 891(16)	78(9)
C(43)	0 441(41)	−0 038(18)	−1 662(21)	111(13)
C(44)	1 460(36)	−0 275(15)	−1 836(19)	93(12)
C(45)	2 464(36)	−0 417(17)	−1 457(20)	100(13)
C(46)	2 351(27)	−0 278(13)	−0 706(15)	63(9)
C(51)	−2 070(30)	−0 572(14)	0 041(15)	67(9)
C(52)	−3 078(35)	−0 241(16)	−0 134(19)	89(11)
C(53)	−3 584(51)	−0 482(22)	−0 833(29)	152(19)
C(54)	−2 947(62)	−0 815(30)	−1 231(33)	174(24)
C(55)	−2 257(55)	−1 097(25)	−1 088(33)	157(21)
C(56)	−1 642(38)	−0 942(19)	−0 428(23)	114(14)
C(61)	−1 992(32)	−0 747(15)	1 547(18)	83(10)
C(62)	−2 013(30)	−0 552(14)	2 313(17)	72(10)
C(63)	−2 500(36)	−0 940(19)	2 839(21)	104(13)
C(64)	−3 083(34)	−1 395(17)	2 659(20)	88(11)
C(65)	−3 176(34)	−1 585(16)	2 002(20)	92(12)
C(66)	−2 671(28)	−1 272(14)	1 464(16)	68(9)
C(71)	0 204(30)	2 411(15)	3 981(17)	74(9)
C(72)	0 990(57)	2 043(25)	4 174(31)	175(22)
C(73)	1 100(76)	1 798(32)	5 012(41)	235(32)
C(74)	0 223(55)	2 054(25)	5 389(29)	156(20)
C(75)	−0 503(67)	2 482(37)	5 152(38)	219(28)
C(76)	−0 662(45)	2 599(21)	4 386(25)	138(17)
C(81)	−1 233(31)	2 987(14)	2 830(19)	70(9)
C(82)	−2 385(38)	2 713(18)	2 905(19)	104(13)
C(83)	−3 392(35)	2 961(17)	2 725(20)	96(13)
C(84)	−3 341(35)	3 532(18)	2 469(20)	96(12)
C(85)	−2 213(41)	3 793(19)	2 396(23)	117(15)
C(86)	−1 164(31)	3 542(14)	2 580(16)	69(9)

TABLE 2

Final positional co-ordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$) for (II), with standard deviations in parentheses

Atom	x	y	z	U
Mo	2 842(1)	3 070(2)	3 970(1)	
Cl(1)	1 894(3)	2 013(5)	4 282(3)	
Cl(2)	1 950(3)	4 327(5)	3 651(3)	
P(1)	2 839(3)	3 705(5)	5 222(3)	
P(2)	3 274(3)	1 467(5)	3 706(3)	
P(3)	2 458(3)	2 447(5)	2 671(3)	
P(4)	1 991(3)	4 718(7)	6 223(4)	
C(1)	4 737(11)	2 867(13)	4 534(12)	57(6)
C(2)	3 403(12)	3 955(18)	3 676(12)	62(7)
O(1)	4 310(8)	2 791(11)	4 868(8)	62(5)
O(2)	3 715(8)	4 590(13)	3 458(9)	73(5)
C(3)	2 570(10)	1 131(15)	2 945(11)	46(6)
C(4)	1 989(10)	4 098(16)	5 379(11)	49(6)
C(11)	3 150(10)	2 926(15)	5 981(10)	44(5)
C(12)	3 420(13)	3 304(8)	6 665(14)	76(8)
C(13)	3 643(13)	2 654(20)	7 244(14)	78(8)
C(14)	3 581(12)	1 728(19)	7 173(13)	71(7)
C(15)	3 335(13)	1 312(20)	6 466(14)	79(8)
C(16)	3 120(11)	1 939(19)	5 876(13)	66(6)
C(21)	3 319(11)	4 783(16)	5 351(11)	53(6)
C(22)	3 059(12)	5 683(18)	5 118(12)	64(7)
C(23)	3 422(15)	6 540(21)	5 155(15)	90(9)
C(24)	4 111(16)	6 466(24)	5 469(17)	100(10)
C(25)	4 428(14)	5 635(22)	5 671(15)	85(8)
C(26)	4 056(14)	4 763(21)	5 680(15)	86(8)
C(31)	3 348(11)	0 533(15)	4 343(11)	54(6)
C(32)	2 846(13)	−0 084(20)	4 424(14)	80(8)
C(33)	2 957(15)	−0 838(22)	4 976(16)	94(9)
C(34)	3 594(15)	−0 916(22)	5 427(16)	92(9)
C(35)	4 122(15)	−0 326(22)	5 371(15)	93(9)
C(36)	4 047(13)	0 468(19)	4 841(14)	78(8)
C(41)	4 056(11)	1 373(17)	3 346(11)	54(6)
C(42)	4 488(11)	2 170(16)	3 294(12)	57(6)
C(43)	5 059(15)	1 988(19)	2 956(13)	70(7)
C(44)	5 193(14)	1 094(22)	2 715(15)	86(8)
C(45)	4 774(13)	0 355(20)	2 724(14)	79(8)
C(46)	4 197(12)	0 433(17)	3 075(12)	63(7)
C(51)	2 968(12)	2 603(18)	2 023(12)	61(7)
C(52)	3 251(11)	3 506(17)	1 939(12)	59(6)
C(53)	3 662(14)	3 707(21)	1 439(15)	89(9)
C(54)	3 799(15)	2 873(23)	1 026(16)	96(9)
C(55)	3 527(15)	2 027(24)	1 040(16)	95(9)
C(56)	3 118(12)	1 865(19)	1 571(14)	74(7)
C(61)	1 595(10)	2 558(16)	2 208(11)	47(6)
C(62)	1 069(10)	2 527(31)	2 576(23)	151(14)
C(63)	0 369(19)	2 533(27)	2 214(23)	130(12)
C(64)	0 184(14)	2 697(20)	1 500(16)	87(8)
C(65)	0 707(14)	2 969(22)	1 135(15)	91(9)
C(66)	1 440(13)	2 831(19)	1 506(14)	82(8)
C(71)	1 142(13)	5 297(21)	6 021(13)	73(7)
C(72)	1 147(15)	6 165(22)	5 881(15)	96(9)
C(73)	0 516(18)	6 771(25)	5 750(20)	125(12)
C(74)	−0 074(16)	6 309(25)	5 801(16)	98(9)
C(75)	−0 106(15)	5 443(27)	5 965(17)	108(10)
C(76)	0 518(14)	5 244(23)	6 068(15)	90(9)
C(81)	1 916(16)	3 848(24)	6 893(17)	102(10)
C(82)	1 678(17)	2 990(37)	6 763(19)	121(11)
C(83)	1 689(24)	2 173(34)	7 401(27)	170(17)
C(84)	1 978(21)	2 669(32)	7 959(14)	145(14)
C(85)	2 279(24)	3 553(38)	8 200(26)	169(17)
C(86)	2 210(24)	4 191(37)	7 613(29)	188(19)

Cell dimensions were measured by least-squares refinement of high-angle reflections, and intensity data obtained by a stationary-crystal–stationary-counter method with take-off angle 4° and counting time 10 s. Individual backgrounds were taken from plots of background as a function of 2θ. Because of crystal decay of (I) four crystals were used for data collection of dimensions *ca.* 0.4 × 0.15 × 0.15 mm and were mounted with *a* parallel to the instrument axis. From the four crystals a total of 2 557 independent reflections with $2\theta < 40°$ was obtained of which 1 974 with $I > \sigma(I)$ were used in subsequent calculations. A linear correction factor was applied to account for crystal decay, and a scale factor, subsequently refined, introduced for each crystal.

For (II) a crystal of size *ca.* 0.5 × 0.3 × 0.1 mm was mounted with the (111) planes perpendicular to the instrument axis. Of 5 052 independent reflections measured with $2\theta < 40°$ 2 623 with $I > \sigma(I)$ were used in subsequent calculations. No crystal decay was observed. No absorption or extinction corrections were applied for either (I) or (II).

TABLE 3

Molecular dimensions in (I) and (II), distances (Å), angles (°) [Y = As in (I), P in (II)]

	(I)	(II)
(*a*) In co-ordination sphere		
Mo–C(1)	1.73(4)	1.91(2)
Mo–C(2)	1.83(4)	1.82(3)
Mo–Cl(1)	2.520(8)	2.554(6)
Mo–Cl(2)	2.501(8)	2.484(6)
Mo–Y(1)	2.624(4)	2.547(6)
Mo–Y(2)	2.596(4)	2.484(7)
Mo–Y(3)	2.681(4)	2.593(6)
C(1)–Mo–C(2)	71.2(18)	73.5(10)
C(1)–Mo–Y(2)	75.4(12)	70.1(7)
C(1)–Mo–Y(1)	73.3(12)	72.4(7)
C(1)–Mo–Cl(1)	125.8(12)	115.5(7)
C(1)–Mo–Cl(2)	131.5(12)	141.5(7)
C(1)–Mo–Y(3)	123.2(12)	123.7(7)
C(2)–Mo–Y(2)	112.4(13)	107.1(8)
C(2)–Mo–Y(1)	108.7(12)	99.5(8)
C(2)–Mo–Cl(1)	163.0(13)	170.4(7)
C(2)–Mo–Cl(2)	79.0(13)	83.9(8)
C(2)–Mo–Y(3)	85.9(12)	91.0(7)
Y(2)–Mo–Y(1)	115.3(1)	124.6(2)
Y(2)–Mo–Cl(1)	76.2(2)	80.0(2)
Y(2)–Mo–Cl(2)	152.7(2)	147.8(2)
Y(2)–Mo–Y(3)	66.6(1)	63.5(2)
Y(1)–Mo–Cl(1)	78.7(2)	81.2(2)
Y(1)–Mo–Cl(2)	81.6(2)	81.4(2)
Y(1)–Mo–Y(3)	161.6(1)	163.1(2)
Cl(1)–Mo–Cl(2)	87.2(3)	86.7(2)
Cl(1)–Mo–Y(3)	84.3(2)	86.4(2)
Cl(2)–Mo–Y(3)	90.6(2)	86.7(2)
(*b*) Not in the immediate co-ordination sphere *		
C(1)–O(1)	1.35(4)	1.20(3)
C(2)–O(2)	1.24(5)	1.20(3)
Mo–C(1)–O(1)	175(3)	176(2)
Mo–C(2)–O(2)	176(3)	174(2)
Y(1)–C(4)	1.93(3)	1.86(2)
Y(1)–C(11)	1.98(3)	1.82(2)
Y(1)–C(21)	1.89(3)	1.77(2)
Y(2)–C(3)	1.98(3)	1.87(2)
Y(2)–C(31)	1.86(3)	1.77(2)
Y(2)–C(41)	1.89(2)	1.82(2)
Y(3)–C(3)	1.99(3)	1.91(2)
Y(3)–C(51)	1.95(2)	1.76(2)
Y(3)–C(61)	1.79(4)	1.78(2)
Y(4)–C(4)	2.00(3)	1.82(2)
Y(4)–C(71)	1.96(3)	1.84(2)
Y(4)–C(81)	1.97(3)	1.79(3)
Y(1)–C(4)–Y(4)	113(2)	116(1)
Y(2)–C(3)–Y(3)	94(1)	90(1)
Mo–Y(1)–C(4)	113(1)	115(1)
Mo–Y(1)–C(11)	119(1)	118(1)
Mo–Y(1)–C(21)	117(1)	109(1)
C(4)–Y(1)–C(11)	101(1)	103(1)
C(4)–Y(1)–C(21)	106(1)	102(1)
C(11)–Y(1)–C(21)	100(1)	108(1)
Mo–Y(2)–C(3)	97(1)	99(1)
Mo–Y(2)–C(31)	121(1)	121(1)
Mo–Y(2)–C(41)	121(1)	120(1)
C(3)–Y(2)–C(31)	107(1)	107(1)
C(3)–Y(2)–C(41)	106(1)	105(1)
C(31)–Y(2)–C(41)	103(1)	104(1)
Mo–Y(3)–C(3)	94(1)	94(1)
Mo–Y(3)–C(51)	122(1)	122(1)
Mo–Y(3)–C(61)	126(1)	121(1)
C(3)–Y(3)–C(51)	105(1)	105(1)
C(3)–Y(3)–C(61)	103(1)	106(1)
C(51)–Y(3)–C(61)	102(1)	106(1)
C(4)–Y(4)–C(71)	98(1)	100(1)
C(4)–Y(4)–C(81)	101(1)	109(1)
C(71)–Y(4)–C(81)	100(1)	104(1)

* Dimensions of phenyl rings are listed in the Supplementary Publication.

Structure Determinations.—The positions of the metal atoms in both structures were obtained from the Patterson functions and further Fourier syntheses gave the positions of the remaining atoms. In both structures carbon and oxygen atoms were refined isotropically and the other heavier atoms anisotropically. For (I) the data from each crystal were consistent with the choice of enantiomorph made from tests of R value with co-ordinates x,y,z and $\bar{x},y,z$. The final R value was 0.068. For (II) a surprisingly high R value of 0.112 was obtained after refinement. A difference-Fourier map was then calculated and regions of significant electron density were observed away from the molecules, and were presumably due to the presence of solvent, but no clear-cut molecular shapes could be observed. The crystals had been recrystallised from benzene–chloroform and the most likely solvent in the lattice was considered to be benzene both from the C,H analysis and the electron-density distribution. The discrepancy between D_m and D_c suggested the presence of about 3 molecules of benzene in the unit cell. We interpreted the difference-Fourier map as indicating three independent benzene rings superimposed, each with a multiplicity of 0.25. Attempts to refine these peaks were not successful, and they were therefore included in the structure-factor calculation with fixed parameters. Subsequently R was reduced to 0.108, and a new difference-Fourier map showed very little residual electron density. No doubt the distortion could be explained in other ways but our treatment was deemed reasonable. Both structures were refined until all shifts were $< 0.10\sigma$. The anisotropic thermal parameters were defined as $\exp(-2\pi^2\sum_i\sum_j U_{ij}b_ib_jh_ih_j)$; $i,j = 1,2,3$ with b_i the i,th reciprocal cell dimension. The isotropic thermal parameter is defined as $\exp(-8\pi^2U\sin^2\theta/\lambda^2)$. The weighting scheme, chosen to give mean values of $w\Delta^2$ for groups of reflections independent of $\sin\theta/\lambda$ and F_o, was $\sqrt{w} = 1$ for $F_o < F^*$ and F^*/F_o for $F_o > F^*$. F^* was 60 for (I) and 70 for (II). Final positions and isotropic thermal parameters are given in Tables 1 and 2, molecular dimensions are compared in Table 3. Anisotropic thermal parameters, positions of the solvent molecules in (II), dimensions of the benzene rings and intermolecular contacts < 3.7 Å, and the structure-factor tables are given in Supplementary Publication No. SUP 21945 (14 pp., 1 microfiche).*

DISCUSSION

The two molecules are illustrated in Figures 1 and 2 together with the atom-numbering schemes, which are equivalent. Both molecules are seven-co-ordinate with the molybdenum atom bonded to two carbonyl groups, two chlorine atoms, and three arsenic [in (I) but phosphorus in (II)] atoms from the potentially bidentate dpam (dppm) ligands. Thus one ligand is uni- and the other bi-dentate.

Compound (I) is best described as a capped octahedron with one carbonyl group in the capping position [1.73(4) Å], another in the capped face [1.83(4) Å] together with two arsenic atoms [2.624(4), 2.596(4) Å], and two chlorine

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

atoms [2.520(8), 2.501(8) Å] together with the third arsenic atom [2.681(4) Å] in the uncapped face. The bidentate dpam ligand occupies an edge between a site in the uncapped and capped faces and this is as expected.[1] The bite of the ligand [66.6(1)°] is much smaller than the usual value of this edge (*ca.* 77°) and this therefore causes considerable distortion in the polyhedra. As noted elsewhere,[5,7] the C(2)–Mo–As(3) angle is much larger (at 85.9°) than this norm because of the relatively small C(2)–Mo–As(3)–C(51) torsion angle. The Mo–As bond lengths are all different, in the sequence Mo–As(3) > Mo–As(1) > Mo–As(2), and the same pattern is found in $[MoBr_2(CO)_2(dpam)_2]$,[4] and in (II) for Mo–P. Presumably As(1) and As(3) are in competition for the metal $d\pi$ electrons, being mutually *trans*, and thus the Mo–As(2) bond, being *trans* to chlorine, is the shortest. It can be argued that Mo–As(3) is the longest bond because it is also somewhat *trans* to the capping carbonyl group, or because of the small C(2)–Mo–As(3) angle. The Mo–Cl distances are probably equivalent as are the Mo–C distances. These latter are often prone to error but in (I) Mo ··· O distances are equivalent and are a more reliable guide.

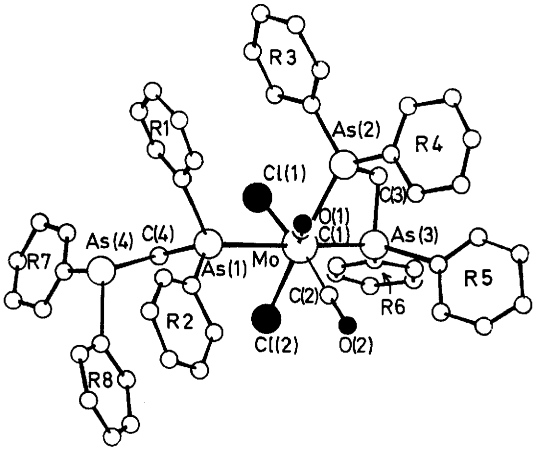

FIGURE 1 The structure of (I)

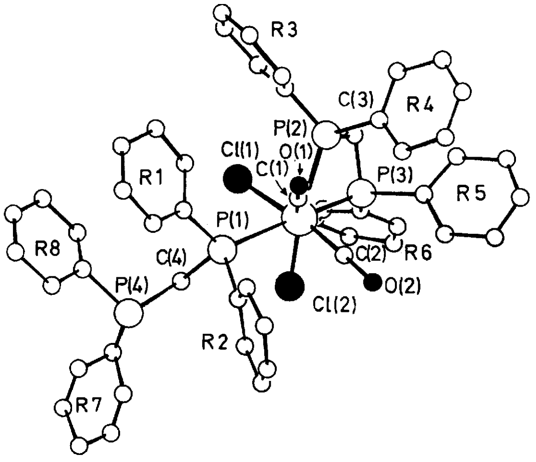

FIGURE 2 The stucture of (II)

The closeness of this geometry to the expected values is not surprising. We have shown elsewhere[1] that introduction of a chelate ring into the capped octahedron distorts it towards a capped trigonal prism, and this trend is accelerated in (II) (Figure 3). In particular in (I) the C(1)–Mo–Cl(2) angle is 131.5(12)° while it is 141.5(7)° in (II); C(1)–Mo–Y(2) is 75.4(12) (I) and

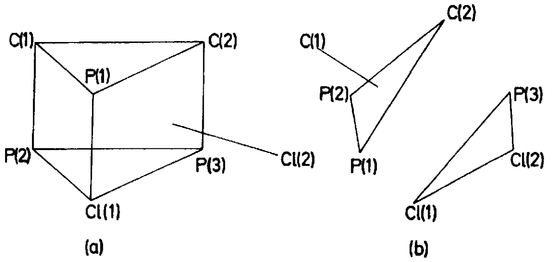

FIGURE 3 The geometry of (II) is almost equally distorted from (a) a capped trigonal prism [with Cl(2) in the unique capping position, P(1), C(2), P(3), Cl(1) in the capped quadrilateral face, and C(1), P(2) in the unique edge] and a capped octahedron (b) [with C(1) in the capping position, C(2), P(1), P(2) in the capped face, and Cl(1), P(3), Cl(2) in the uncapped face]

TABLE 4

Torsion angles (°) in (I) and (II)

	(I)	(II)
(*a*) Angles of the type L–Mo–Y–C, where L–Mo–Y is <100°		
Cl(1)–Mo–Y(1)–C(4)	−47.4	−53.1
Cl(1)–Mo–Y(1)–C(11)	70.3	69.3
Cl(1)–Mo–Y(1)–C(21)	−169.8	−166.9
Cl(2)–Mo–Y(1)–C(4)	41.3	34.9
Cl(2)–Mo–Y(1)–C(11)	159.0	157.3
Cl(2)–Mo–Y(1)–C(21)	−81.0	−78.9
C(1)–Mo–Y(1)–C(4)	179.5	−173.5
C(1)–Mo–Y(1)–C(11)	−62.8	−51.2
C(1)–Mo–Y(1)–C(21)	57.1	72.7
C(1)–Mo–Y(2)–C(3)	−156.3	−173.2
C(1)–Mo–Y(2)–C(31)	88.5	70.8
C(1)–Mo–Y(2)–C(41)	−43.4	−60.8
Cl(1)–Mo–Y(2)–C(3)	70.3	65.0
Cl(1)–Mo–Y(2)–C(31)	−44.9	−51.1
Cl(1)–Mo–Y(2)–C(41)	−176.8	177.3
Y(3)–Mo–Y(2)–C(3)	−19.4	−26.0
Y(3)–Mo–Y(2)–C(31)	−134.7	−142.0
Y(3)–Mo–Y(2)–C(41)	93.5	86.3
Cl(1)–Mo–Y(3)–C(3)	−58.2	−55.3
Cl(1)–Mo–Y(3)–C(51)	−168.4	−165.8
Cl(1)–Mo–Y(3)–C(61)	50.9	55.5
Cl(2)–Mo–Y(3)–C(3)	−145.3	−142.4
Cl(2)–Mo–Y(3)–C(51)	104.4	107.4
Cl(2)–Mo–Y(3)–C(61)	−36.2	−31.6
C(2)–Mo–Y(3)–C(3)	135.7	133.7
C(2)–Mo–Y(3)–C(51)	25.5	23.5
C(2)–Mo–Y(3)–C(61)	−115.2	−115.5
Y(2)–Mo–Y(3)–C(3)	19.2	25.1
Y(2)–Mo–Y(3)–C(51)	−91.1	−85.1
Y(2)–Mo–Y(3)–C(61)	128.3	135.9
(*b*) The smallest torsion angles around each As–C bond in (I) and for comparison the value of the same torsion angle in (II)		
C(4)–Y(1)–C(11)–C(16)	28.2	103.1
C(11)–Y(1)–C(21)–C(26)	−12.9	36.8
C(3)–Y(2)–C(31)–C(32)	11.0	−24.7
Mo–Y(2)–C(41)–C(42)	−25.9	8.6
C(3)–Y(3)–C(51)–C(56)	5.2	28.1
Mo–Y(3)–C(61)–C(62)	−10.8	−31.6
C(81)–Y(4)–C(71)–C(76)	−10.9	−17.0
C(4)–Y(4)–C(81)–C(82)	39.0	−20.6
(*c*) Others		
Mo–Y(1)–C(4)–Y(4)	−165.7	−171.6
Y(1)–C(4)–Y(4)–C(71)	−170.4	162.3
Y(1)–C(4)–Y(4)–C(81)	87.2	−88.7

70.1(7) (II), C(2)–Mo–Y(1) is 108.7(12) (I) and 99.5(8)° (II). The angles found in (II) are in all three cases more typical of the CTP than the CO. However, other changes in angle found in (II) are not; for example C(2)–Mo–Y(2) is 112.4(13) in (I) and 107.1(8) in (II) when an increase might be expected. In (II), the Mo–Cl bond lengths differ by 0.07 Å with the shorter bond [Mo–Cl(2)] being in the unique capping position of the CTP. A similar difference is found in [$MoCl_2(CO)_2(PMe_2Ph)_3$] with lengths of 2.486(16) and 2.561(14) Å, the shorter bond again being in this site. It may not be accidental that both these distorted dichloride structures contain phosphorus rather than arsenic ligands. The smaller-sized atom ensures that the benzene rings are *ca.* 0.20 Å closer to the metal and will clearly affect the geometry of the co-ordination sphere that much more. Thus C(2)–Mo–Y(3) is 91.0(7) in (II), *ca.* 14° larger than the mean for that edge in the CO. An additional factor in distorting the polyhedra of (II) is the small P–M–P angle of 63.5(2)°.

Using our program [1,5] to calculate root-mean-square deviations from ideal geometries we obtained values (after normalisation of bond lengths) of 0.068 (I), and 0.115 Å (II) as a CO, and 0.112 (I) and 0.104 Å (II) as a CTP. Values for (I) are equivalent to those found for [$MoBr_2(CO)_2(dpam)_2$][4] and [$WI_2(CO)_3(dpam)$].[7] Thus (II) is much more distorted from the CO and is much closer to the CTP than is (I).

The orientations of the four-membered chelate rings are similar in (I) and (II) with the carbon atom displaced by 0.65 and 0.81 Å from the MoY_2 plane towards Cl(1) and away from the carbonyl groups C(1),O(1) and C(2),O(2). Despite the differences in molecular geometry the torsion angles (Table 4) around the Mo–Y bonds are very similar (mean difference 5.8°, maximum difference 17.7°). Also listed in Table 4 are the minimum torsion angles around each As–C bond in (I) and their comparable values in (II). These show considerable differences in the relative orientations of the phenyl rings but they are similar enough to conclude that intramolecular forces play the major role in fixing their positions.

The Mo–Y(1)–C(4)–Y(4) torsion angles are −165.7 (I) and −171.6° (II) and this ensures that the Y(4) ligand is kept well away from the co-ordination sphere. The Y(1)–C(4)–Y(4)–C(71) torsion angles are similarly close to 180°, but those for Y(1)–C(4)–Y(4)–C(81) are of opposite sign in the two structures (87.2, −88.7°); as is clear from Figures 1 and 2, this is the major difference between the molecular structures of (I) and (II).

There are no intermolecular contacts significantly less than the sum of van der Waals radii in either (I) or (II). In (II) no atom in the solvent molecules comes closer than 3.25 Å to an atom in the complex. The much lower density in (II) than (I) [1.34 *vs.* 1.60] indicates the loose packing of solvent and complex in (II).

We thank A. W. Johans for assistance with the crystallographic investigations and the University of Reading for a studentship (to A. P. W.).

[6/1328 *Received, 7th July,* 1976]