Crystal Structures of *fac*-[Bis(2-diphenylphosphinoethyl)phenylphosphine-*PP'P''*]tricarbonyl-chromium(0) and -molybdenum(0)

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The crystal structures of the title compounds, $[M\{Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2\}(CO)_3]$ [(1), M = Cr and (2), M = Mo], have been determined by single-crystal *X*-ray diffraction methods and refined to residuals of 0.055 and 0.071 for 3 653 and 4 345 ' observed ' reflections respectively. Crystals of (1) are monoclinic, space group $P2_1$, with a = 20.989(9), b = 17.825(10), c = 8.784(4) Å, β = 99.70(2)°, and Z = 4; those of (2) are monoclinic, space group $P2_1/n$, with a = 15.181(7), b = 18.799(4), c = 12.053(4), β = 106.62(3)°, and Z = 4. In both (1) and (2), the metal–central phosphorus distance is shorter [(1): 2.334(3), 2.328(4); (2): 2.479(2) Å] than the metal–terminal phosphorus distances [(1): 2.355(4)—2.391(3); (2): 2.504(3), 2.532(3) Å]. In (1) the mean Cr–C length is 1.84 Å; in (2), the mean Mo–C length is 1.97 Å.

In a previous paper,[1] the variation in stereochemistry of the central atom in complexes of the type MLL'_3 (L = tridentate, L' = unidentate ligand) has been developed in terms of a ligand–ligand repulsion model. Complexes of this type whose structures have been established crystallographically are few in number and are predominantly those of ligands with first-row atoms. It was therefore considered to be of interest to extend the available examples of complexes of this type containing tridentate ligands with second-row metal atoms.

Our present studies are concerned with complexes of the type $[M(CO)_3L]$, L = tridentate flexible triphosphine ligand, and the present report describes the structure determination for the case L = ' triphos ' = $PPh(CH_2CH_2PPh_2)_2$ for the metals M = Cr (1) and Mo (2), the smaller metal effectively providing a complex in which the ligand has a larger ' bite '; in this context the previously determined structure[2] of $[Mo\{PPh(NEt\cdot PPh_2)_2\}(CO)_3]$ (3) is also relevant as an example of a complex in which the chelate rings are four-membered so that the ligand bite is small.

The synthesis of the complex $[MoL(CO)_3]$ for the ligand L = triphos has been previously reported,[3] the method consisting of heating $[Mo(CO)_6]$ with 2 equivalents of L in a sealed evacuated tube at 150 °C for 15 h, followed by recrystallization from chloroform. Both the chromium complex (1) and its molybdenum analogue (2) were prepared for the present study by refluxing stoicheiometric amounts of metal carbonyl and ligand in dekalin at 180 °C under nitrogen for *ca.* 1 h, followed by recrystallization from CH_2Cl_2 as pale yellow plates.

EXPERIMENTAL

Crystal Data.—(1). $C_{37}H_{33}CrO_3P_3$, M = 670.6, Monoclinic, space group $P2_1$ (C_2^2, no. 4), a = 20.989(9), b = 17.825(10), c = 8.784(4) Å, β = 99.70(2)°, U = 3 239(5) Å³, D_m = 1.37(1) g cm⁻³, Z = 4, D_c = 1.37 g cm⁻³, $F(000)$ = 1 392. Monochromatic Mo-K_α radiation [likewise for (2)], λ = 0.710 69 Å, μ_{Mo} = 5.2 cm⁻¹, specimen size 0.14 × 0.20 × 0.42 mm (prism).

(2). $C_{37}H_{33}MoO_3P_3$, M = 714.5, Monoclinic, space group $P2_1/n$ (C_{2h}^5 no. 14), a = 15.181(7), b = 18.799(4), c = 12.053(4) Å, β = 106.62(3)°, U = 3 296(2) Å³, D_m = 1.43(1), Z = 4, D_c = 1.44 g cm⁻³, $F(000)$ = 1 464, μ_{Mo} = 6.1 cm⁻¹, specimen size 0.3 mm edge length cuboid.

Structure Determination.—A unique data set measured to $2\theta_{max.}$ 50° on a Syntex $P\bar{1}$ four-circle diffractometer was obtained for each structure, yielding 5 984 and 5 744 independent reflections of which 3 653 and 4 345 with $I > 3\sigma(I)$, for (1) and (2) respectively, were used in the refinement after absorption correction. The structure was solved by the heavy-atom method and $MP_3(CO)_3$ molecular core parameters refined jointly. Other non-hydrogen atoms were refined basically as 9 × 9 blocks, but including any associated hydrogen-atom positional parameters. Anisotropic thermal parameters were used for non-hydrogen atoms; for hydrogen atoms U was constrained at $\langle U_{ii} + 0.01\rangle$ Å² of the parent C, O. Residuals (R,R',S): (1), 0.055, 0.060, 1.43 (both parities); (2), 0.071, 0.070, 0.64. The weighting scheme used was $[\sigma^2(F_o) + 0.000\,3(F_o)^2]^{-1}$ Neutral atom scattering factors were employed for Cr, Mo, and P, corrected for anomalous dispersion ($\Delta f',\Delta f''$).[4-6]

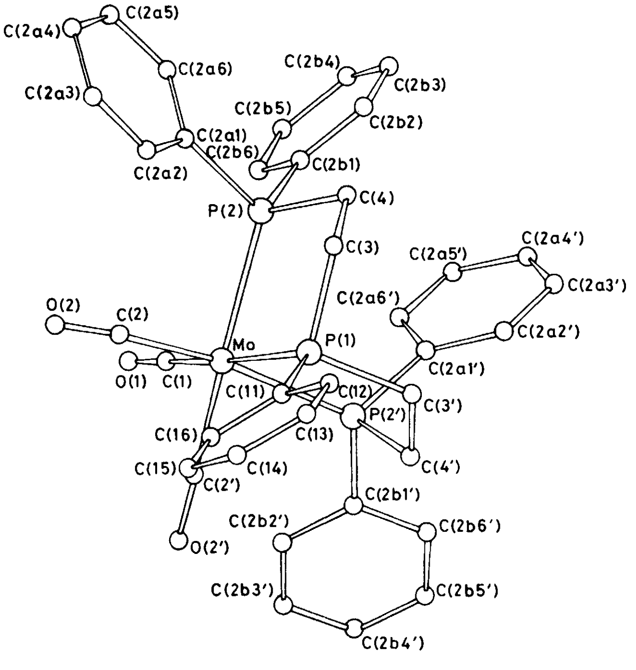


FIGURE 1 Atom labelling (non-hydrogen atoms) of a molecule of compound (2)

TABLE 1

Non-hydrogen atom fractional cell co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

	Cr(1)			Cr(2)			Mo		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Metal	5 367.0(8)	0 000(—)	1 056(2)	284.6(8)	7 480(1)	516(2)	6 047.7(5)	1 659.1(4)	1 867.6(6)
(*a*) Carbonyls									
C(1)	5 040(6)	−816(6)	−80(14)	−97(5)	8 262(6)	−683(12)	5 409(6)	1 651(6)	180(8)
O(1)	4 861(5)	−1 326(5)	−867(10)	−326(4)	8 724(5)	−1 515(9)	5 010(6)	1 652(4)	−795(6)
C(2)	6 206(5)	−302(6)	1 158(13)	1 054(5)	7 954(7)	457(12)	4 862(6)	1 881(5)	2 134(7)
O(2)	6 739(4)	−426(6)	1 027(11)	1 524(4)	8 248(6)	256(10)	4 133(5)	1 967(4)	2 235(6)
C(2′)	5 553(4)	515(5)	−643(10)	489(5)	6 988(6)	−1 161(12)	5 758(6)	657(5)	2 063(7)
O(2′)	5 718(4)	815(5)	−1 644(8)	666(4)	6 691(5)	−2 194(8)	5 567(5)	81(4)	2 208(6)
(*b*) Tridentate ligand									
P(1)	5 665(1)	1 069(2)	2 541(3)	640(1)	6 437(2)	2 016(3)	7 031(2)	1 750(1)	3 896(2)
P(2)	5 242(1)	−498(2)	3 511(3)	159(1)	7 961(2)	2 989(3)	6 481(2)	2 963(1)	1 979(2)
P(2′)	4 354(1)	620(2)	637(3)	−703(1)	6 822(2)	136(3)	7 535(2)	1 190(1)	1 656(2)
C(3)	5 589(5)	943(6)	4 571(11)	571(5)	6 583(6)	4 071(11)	7 307(7)	2 678(5)	4 329(8)
C(4)	5 079(5)	311(6)	4 724(12)	37(5)	7 152(6)	4 214(10)	7 442(7)	3 120(5)	3 322(9)
C(3′)	5 104(5)	1 855(6)	1 920(13)	90(5)	5 635(6)	1 447(12)	8 195(7)	1 393(6)	4 035(8)
C(4′)	4 410(4)	1 553(6)	1 645(11)	−606(5)	5 920(6)	1 208(13)	8 189(7)	849(5)	3 094(8)
(*c*) Phenyl group 1									
C(1)	6 462(5)	1 509(6)	2 605(11)	1 426(5)	5 989(6)	2 097(12)	6 722(6)	1 375(5)	5 130(7)
C(2)	6 565(6)	2 135(9)	1 789(13)	1 571(6)	5 317(8)	2 687(19)	7 268(8)	1 483(8)	6 252(9)
C(3)	7 177(6)	2 410(9)	1 801(16)	2 164(7)	4 991(9)	2 691(19)	7 021(8)	1 196(8)	7 170(8)
C(4)	7 693(6)	2 088(8)	2 643(18)	2 631(6)	5 355(9)	2 110(15)	6 227(8)	830(6)	7 020(8)
C(5)	7 604(6)	1 460(8)	3 483(18)	2 494(7)	6 007(10)	1 432(21)	5 678(8)	712(6)	5 907(9)
C(6)	7 001(5)	1 135(7)	3 518(17)	1 901(6)	6 350(9)	1 457(20)	5 930(6)	989(5)	4 968(8)
(*d*) Phenyl group 2a									
C(1)	4 604(5)	−1 154(6)	3 758(11)	−512(5)	8 605(6)	3 156(12)	5 601(6)	3 601(4)	2 139(7)
C(2)	4 510(5)	−1 806(6)	2 830(12)	−968(6)	8 457(8)	4 105(14)	5 161(7)	3 487(5)	3 001(8)
C(3)	4 059(6)	−2 330(7)	3 041(14)	−1 466(7)	8 963(8)	4 144(18)	4 545(7)	3 959(5)	3 182(8)
C(4)	3 669(6)	−2 229(7)	4 132(7)	−1 508(7)	9 605(9)	3 305(18)	4 293(8)	4 549(6)	2 497(9)
C(5)	3 753(6)	−1 614(8)	5 029(14)	−1 048(7)	9 767(8)	2 369(20)	4 718(7)	4 672(5)	1 630(9)
C(6)	4 204(5)	−1 062(7)	4 859(13)	−549(6)	9 249(7)	2 306(16)	5 378(6)	4 204(5)	1 472(8)
(*e*) Phenyl group 2b									
C(1)	5 905(4)	−987(5)	4 758(10)	820(5)	8 434(6)	4 330(11)	6 900(6)	3 421(5)	890(7)
C(2)	5 915(6)	−1 095(7)	6 308(13)	689(5)	8 737(6)	5 694(13)	7 621(7)	3 882(6)	1 146(9)
C(3)	6 366(7)	−1 514(9)	7 244(13)	1 183(7)	9 050(7)	6 767(13)	7 889(7)	4 237(6)	295(10)
C(4)	6 860(6)	−1 849(7)	6 623(13)	1 807(6)	9 061(7)	6 466(13)	7 434(8)	4 140(6)	−846(10)
C(5)	6 873(6)	−1 725(7)	5 094(15)	1 940(6)	8 760(9)	5 122(15)	6 696(8)	3 675(6)	−1 132(9)
C(6)	6 413(6)	−1 310(7)	4 163(12)	1 438(5)	8 463(8)	4 073(12)	6 436(6)	3 322(6)	−263(8)
(*f*) Phenyl group 2a′									
C(1)	3 599(5)	257(6)	1 125(10)	−992(4)	6 516(6)	−1 878(10)	8 346(6)	1 773(5)	1 215(8)
C(2)	3 473(5)	−513(6)	1 020(12)	−1 401(6)	6 959(7)	−2 888(12)	9 229(8)	1 943(8)	1 911(10)
C(3)	2 890(6)	−805(7)	1 270(15)	−1 639(5)	6 731(7)	−4 383(12)	9 779(9)	2 365(9)	1 431(14)
C(4)	2 424(5)	−317(8)	1 671(14)	−1 452(6)	6 054(7)	−4 886(12)	9 470(10)	2 601(7)	328(14)
C(5)	2 541(5)	435(7)	1 821(13)	−1 042(6)	5 597(7)	−3 906(14)	8 613(9)	2 461(6)	−334(10)
C(6)	3 119(5)	719(7)	1 508(12)	−787(6)	5 855(7)	−2 416(14)	8 046(7)	2 052(6)	126(9)
(*g*) Phenyl group 2b′									
C(1)	4 054(5)	891(6)	−1 403(12)	−1 463(4)	7 193(6)	616(10)	7 552(6)	418(5)	719(7)
C(2)	3 624(5)	428(6)	−2 355(12)	−1 603(5)	7 966(6)	342(12)	6 750(6)	93(5)	90(8)
C(3)	3 386(6)	627(7)	−3 829(12)	−2 199(5)	8 237(7)	602(12)	6 760(7)	−474(5)	−639(9)
C(4)	3 587(5)	1 280(8)	−4 429(12)	−2 638(5)	7 800(7)	1 139(12)	7 573(8)	−695(5)	−777(9)
C(5)	4 037(6)	1 753(7)	−3 525(14)	−2 506(5)	7 052(8)	1 388(13)	8 375(7)	−381(5)	−187(8)
C(6)	4 257(5)	1 539(7)	−2 023(12)	−1 919(5)	6 746(7)	1 111(12)	8 374(7)	184(6)	550(9)

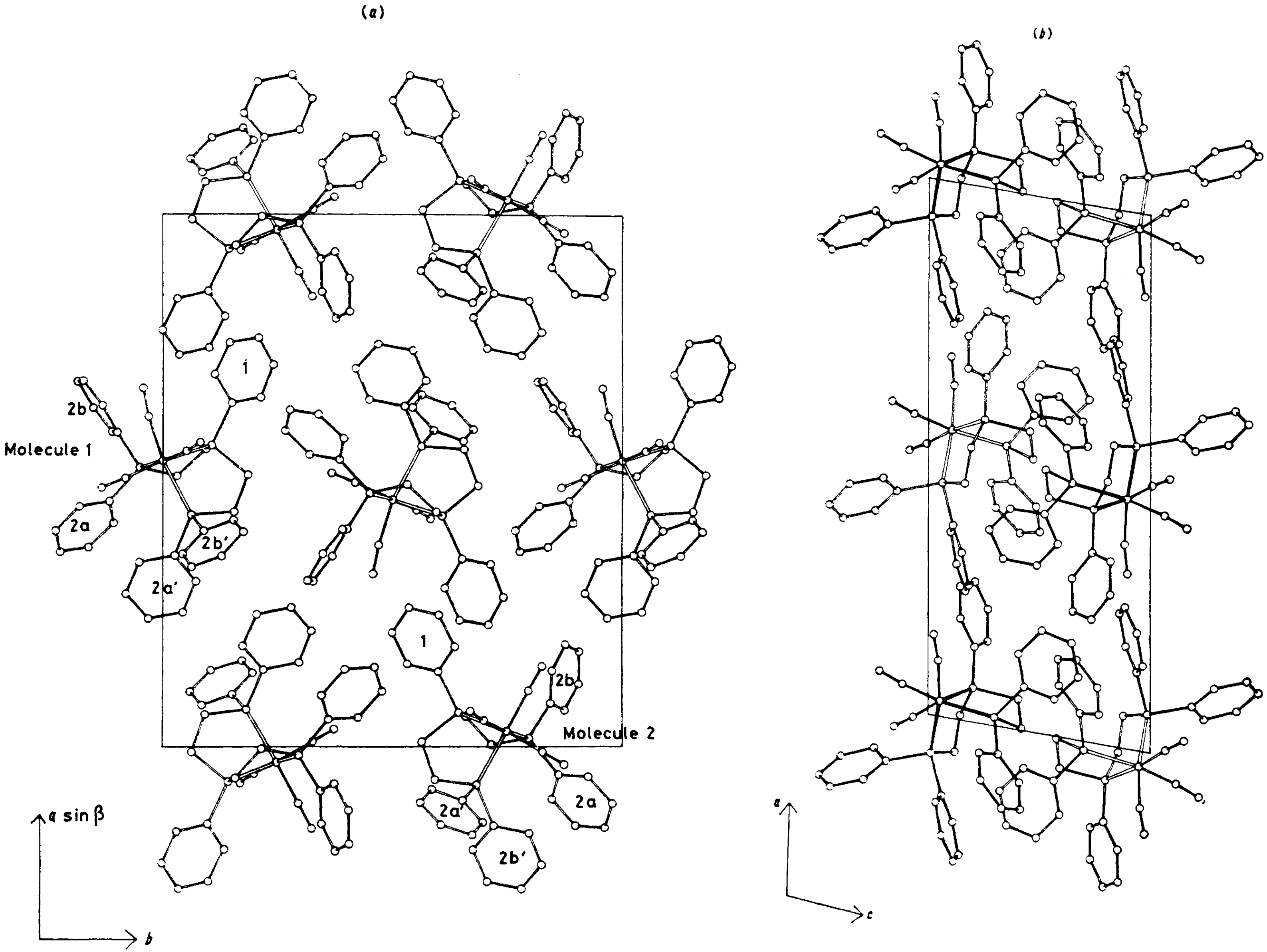


FIGURE 2 (*a*) Unit-cell contents of (1) (non-hydrogen atoms only), projected down *c*; phenyl rings only are numbered. (*b*) Projection of the same structure down *b*, showing the non-crystallographic pseudo-inversion relationship between the two independent molecular sets. Molecules 2 are shown with solid bonds

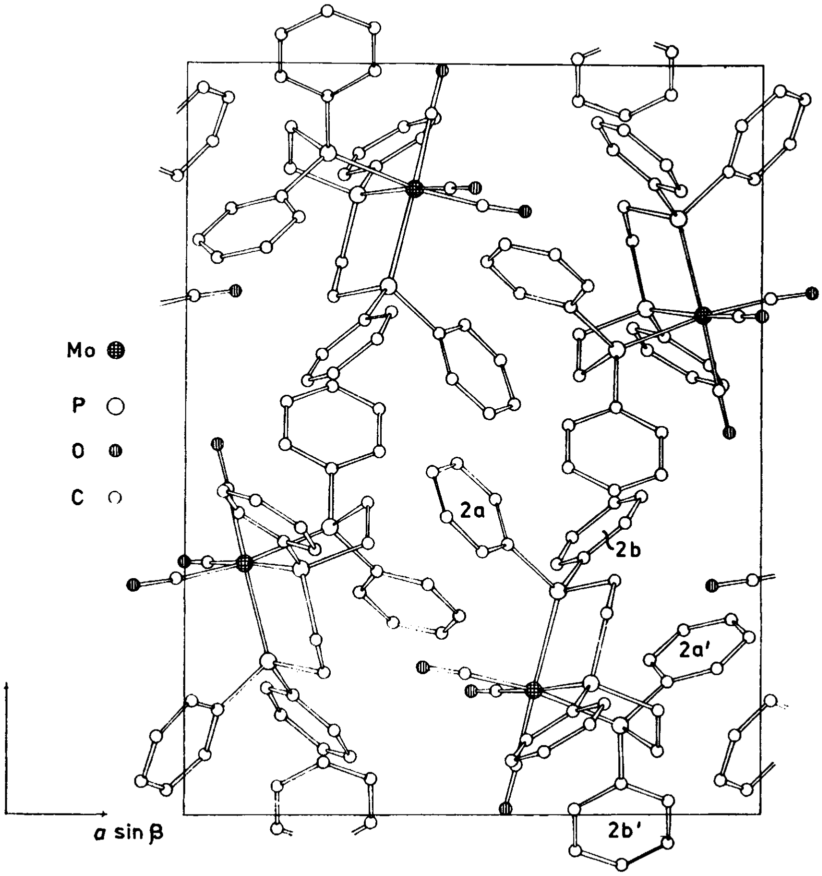


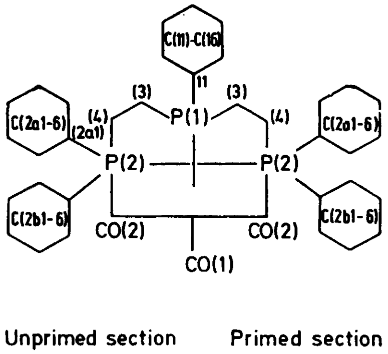
FIGURE 3 Unit-cell contents of (2) (non-hydrogen atoms only), projected down *c*; phenyl rings only are numbered

Calculations were carried out using the '*X*-RAY' '76 program system,[7] on a CYBER 73 computer. The final positions of the non-hydrogen atoms are given in Table 1, with the atoms labelled according to Figure 1. The structure-factor amplitudes, thermal parameters, hydrogen-atom parameters, and the phenyl-ring geometries and planes are contained in Supplementary Publication No. SUP 22656 (66 pp.).*

DISCUSSION

In both (1) and (2) the lattice arrays are composed of discrete molecules of the complex [$ML(CO)_3$], a diagrammatic representation of which is shown below. However, whereas in (2) the asymmetric unit of the structure is a single molecule, in (1) the asymmetric unit comprises two molecules. These are related by a non-crystallographic pseudo-inversion centre. Other than for minor rotations, the molecule contains no intrinsic chirality and the non-centrosymmetric space group of (1) appears to be solely a consequence of crystal packing; as in (2) and (3), the disposition of the tridentate ligand in the six-co-ordinate environment of the metal atom is such that the internal molecular symmetry is pseudo-*m*. Unit-cell contents are shown in Figures 2 and 3.

In both complexes, the chief feature of interest is the metal-atom environment; ligand-atom geometries are conventional and will not be discussed further. Relatively little information concerning chromium(0)–phosphine distances is available in the literature and that which is, is summarized in Table 3. From these data it is apparent that the chromium–phosphorus distances in (1) are much as would be expected. The shorter distances associated with the central [P(1)] atoms relative to the peripheral [P(2),P(2')] are a consequence of the lower degree of phenyl substitution; it is not possible to perceive or argue a concomitant trend in the *trans*-CO–Cr distance. The peripheral P(2,2')–Cr distances are disconcertingly variable, in the range 2.355(4)—2.391(3) Å; the origin of the deviation is uncertain and is equally evident in the geometries of



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

TABLE 2

Molecular non-hydrogen core geometries: bond distances (Å) and angles (°) with estimated standard deviations in parentheses *

	Cr(1)	Cr(2)	Mo
M–C(1)	1.83(1)	1.85(1)	1.99(1)
M–C(2)	1.83(1), 1.85(1)	1.83(1), 1.83(1)	1.96(1), 1.96(1)
M–P(1)	2.334(3)	2.328(4)	2.479(2)
M–P(2)	2.387(3), 2.371(3)	2.391(3), 2.355(4)	2.532(3), 2.504(3)
C(1)–O(1)	1.17(1)	1.15(1)	1.16(1)
C(2)–O(2)	1.17(1), 1.13(1)	1.16(1), 1.17(1)	1.16(1), 1.15(1)
P(1)–C(3)	1.83(1), 1.85(1)	1.85(1), 1.85(1)	1.84(1), 1.85(1)
P(2)–C(4)	1.86(1), 1.88(1)	1.84(1), 1.86(1)	1.87(1), 1.85(1)
C(3)–C(4)	1.58(1), 1.53(1)	1.53(1), 1.53(1)	1.53(1), 1.53(1)
P(1) · · · P(2)	3.093(5), 3.076(9)	3.070(5), 3.095(4)	3.184(3), 3.187(4)
C(1)–M–P(1)	173.6(4)	173.1(4)	171.8(3)
C(1)–M–P(2)	96.3(4), 92.4(4)	98.3(4), 90.5(3)	96.0(3), 94.8(3)
C(1)–M–C(2)	93.6(5), 93.7(5)	86.3(5), 92.3(5)	88.1(4), 93.2(4)
P(1)–M–C(2)	92.7(3), 88.4(3)	100.6(4), 88.7(4)	98.4(2), 92.3(2)
P(1)–M–P(2)	81.9(1), 81.7(1)	81.2(1), 82.7(1)	78.88(8), 79.52(8)
P(2)–M–C(2)	95.6(4), 87.1(3)	95.3(4), 88.1(3)	91.3(3), 85.0(3)
P(2)–M–C(2′)	169.8(3), 167.5(4)	169.1(3), 170.0(3)	170.5(3), 171.0(3)
P(2)–M–P(2′)	94.7(1)	94.5(1)	96.80(9)
C(2)–M–C(2′)	81.6(4)	82.6(5)	86.3(4)
M–C(1)–O(1)	175.6(12)	175.5(10)	177.8(9)
M–C(2)–O(2)	169.6(10), 174.4(8)	172.9(9), 174.9(9)	174.7(7), 177.1(9)
M–P(1)–C(11)	121.4(4)	125.0(4)	123.7(3)
M–P(1)–C(3)	112.7(4), 110.8(3)	111.6(3), 109.7(3)	111.7(3), 110.8(3)
M–P(2)–C(2a1)	122.8(3), 126.0(4)	119.9(3), 114.9(3)	116.7(3), 121.2(3)
M–P(2)–C(2b1)	121.9(3), 114.8(4)	123.5(4), 124.4(3)	123.8(5), 120.7(3)
M–P(2)–C(4)	106.7(4), 110.8(3)	107.3(3), 109.9(3)	109.0(3), 106.6(4)
P(1)–C(3)–C(4)	110.0(7), 108.7(7)	110.6(6), 108.6(7)	111.2(7), 111.9(6)
P(2)–C(4)–C(3)	108.2(8), 111.6(7)	107.1(7), 112.2(8)	110.6(7), 110.6(7)
C(3)–P(1)–C(3′)	102.9(5)	102.9(5)	100.7(5)
C(11)–P(1)–C(3)	104.5(5), 102.5(5)	104.0(5), 102.9(5)	103.0(4), 104.3(4)
C(2a1)–P(2)–C(4)	102.7(5), 101.1(5)	105.0(5), 102.7(5)	102.5(4), 104.7(4)
C(2b1)–P(2)–C(4)	102.7(4), 102.0(5)	98.4(5), 102.6(5)	101.7(4), 101.8(4)
C(2a1)–P(2)–C(2b1)	97.0(4), 98.8(4)	99.5(5), 99.6(4)	100.4(4), 99.4(4)

* Double entries correspond to non-primed and primed sections respectively (see Figures 1—3 and diagram).

both (2) and (3), indicative that (presumably) relatively minor perturbations arising from interspecies interactions are capable of inducing variations in Cr–P distances to the extent of *ca.* 0.04 Å or more.

The greater metal–phosphorus distances of (2) are reflected in a decreased P(1)–Mo–P(2) angle [79.2° (2), *cf.* 81.9° (1)]; as in (1), the peripheral distances are variable and longer than the Mo–P(1) distance, and are comparable with other $Ph_2(CH_2)P$–Mo distances observed in complexes with bidentate ligands. The values quoted in Table 4 suggest that the mean distance (*ca.* 2.5_2 Å) is independent of the P(1)–Mo–P(2) angle over a wide range of angle. By contrast, the Mo–P(1) distance in (3) is considerably shorter than in (2); the probable origin of this difference lies in the considerably different nature of the atoms bound to the phosphorus atom [see the effect of the oxygen atoms on the Cr–P(1) distances in triphenyl phosphite derivatives relative to triphenylphosphine (Table 3)].

TABLE 3

Phosphine–chromium(0) and chromium(0)–*trans*-carbonyl distances (Å) with estimated standard deviations in parentheses

Phosphine group		Ref.	Cr–P		Cr–C
PPh_3		*a*	2.42		1.83
		b	2.422(1)		1.845(4)
$PMePh_2$	*trans*	*c*	2.417(4) 2.385(4)	(2.40_1)	
CH_2PPh_2	α,β isomers	*d*	2.41(1) 2.376(7)	(2.39_3)	1.96(5) 1.77(3)
CH_2PPh_2		*e*	2.391(3) 2.355(4)	(2.37_6)	1.83(1) 1.85(1)
Phosphorine		*f*	2.372(4)		1.82(2)
$(CH_2)_2PPh$		*e*	2.334(3) 2.328(4)	(2.331)	1.83(1) 1.85(1)
$P(OPh)_3$		*b*	2.309(1)		1.861(4)
$P(OPh)_3/P(OPh)_3$ *trans*		*g*	2.252(1)		

[a] O. S. Mills and A. D. Redhouse, *Chem. Comm.*, 1966, 814. [b] H. J. Plastas, J. M. Stewart, and S. O. Grim, *Inorg. Chem.*, 1973, **12**, 265. [c] N. G. Connelly, B. A. Kelly, R. L. Kelly, and P. Woodward, *J.C.S. Dalton*, 1976, 699. [d] P. H. Bird, N. J. Coville, I. S. Butler, and M. L. Schneider, *Inorg. Chem.* 1973, **12**, 2902. [e] This work. [f] H. Vahrenkamp and H. Nöth, *Chem. Ber.*, 1973, **106**, 2227. [g] H. S. Preston, J. M. Stewart, H. J. Plastas, and S. O. Grim, *Inorg. Chem.*, 1972, **11**, 161.

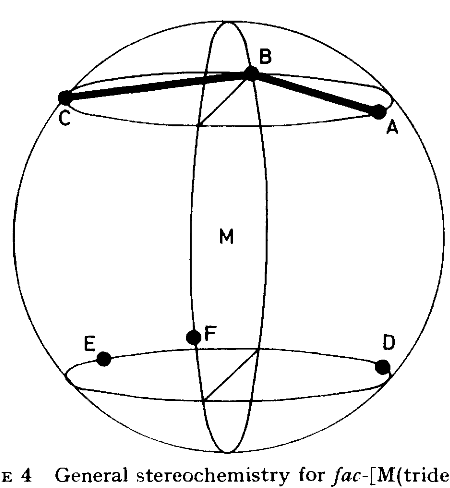

FIGURE 4 General stereochemistry for *fac*-[M(tridentate)(unidentate)$_3$]

TABLE 4

Phosphine–molybdenum(0) geometries in bi- and tri-dentate phosphine carbonylmolybdenum derivatives with estimated standard deviations in parentheses

Compound	Angle (°) P(1)–Mo–P(2)	Bond distances (Å)			
		Mo–P(1)	Mo–P(2)	Mo–CO(P *trans*)	Mo–CO(CO *trans*)
$[MoL(CO)_3]$ (i) [a]	78.88(8)	2.479(2)	2.504(3)	1.96(1)	
	79.52(8)		2.532(3)	1.96(1)	
(ii) [b]	65.0(1)	2.425(4)	2.527(4)	1.98(2)	
	65.3(1)		2.477(4)	2.00(2)	
$[MoL'(CO)_4]$ (i) [c]	65.4(2)		2.516(6)	1.93(2)	2.03(2)
			2.537(5)	1.94(2)	2.01(2)
	65.8(2)		2.519(5)	1.94(2)	2.02(2)
			2.518(2)	1.91(2)	1.99(2)
(ii) [d]	67.3(1)		2.535(3)	1.94(1)	2.02(2)
			2.501(2)	1.92(1)	2.07(1)

[a] This work. [b] Ref. 2 [compound (3), L = $PPh(NEtPPh_2)_2$]. [c] M. A. Bush and P. Woodward, *J. Chem. Soc.* (*A*), 1968, 1221; L′ = pentaethylcyclopentaphosphane. [d] K. K. Cheung, T. F. Lai, and K. S. Mok, *J. Chem. Soc.* (*A*), 1971, 1644; L′ = bis-(diphenylphosphino)methane.

The general stereochemistry for *fac*-[M(tridentate)-(unidentate)$_3$] is shown in Figure 4. One axis through the metal atom is placed normal to the three donor atoms ABC of the tridentate ligand, such that $\phi_A = \phi_B = \phi_C$. Atoms B and F lie on a mirror plane, so that $\theta_B = 180°$, $\theta_F = 0$. The most stable stereochemistry has been calculated by minimization of the total repulsion energy assuming a completely flexible tridentate ligand, the angular parameters being reported previously.[1] The tridentate angle ABC, θ_A, is of particular importance to the stereochemistry of complexes containing tridentate ligands. It is shown in Figure 5 for both *fac* and *mer* isomers as a function of normalized bite, b = AB/MA, and the ratio R, which is the distance between M and the centre of repulsion of each metal–unidentate ligand bond, divided by the distance between M and the centre of repulsion of each metal–tridentate ligand bond.

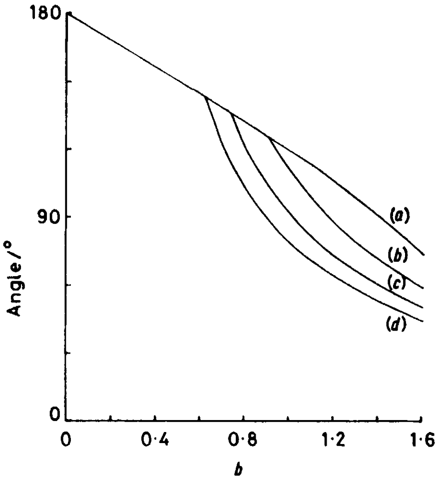

FIGURE 5 Tridentate angle A–B–C as a function of normalised bite b: (*a*) *mer* complexes; (*b*) *fac* complexes, $R = 1.5$; (*c*) *fac* complexes, $R = 1.0$; (*d*) *fac* complexes, $R = 0.7$

Averaged parameters for structurally characterized molecules are shown in Table 5. For the first four compounds there is good agreement between the observed angular parameters and those calculated assuming a completely flexible tridentate ligand and R *ca.* 1.0. The three trioxo-complexes have low values of ϕ_D and ϕ_F, and large DME and DMF angles, due to greater repulsion from these unidentate ligands, and correspond to R *ca.* 0.7. The next four complexes contain tridentate ligands with bulky phenyl groups attached to the terminal donor atoms, namely $PPh(NEtPPh_2)_2$, $NEt(CH_2CH_2PPh_2)_2$, and $PPh(CH_2CH_2PPh_2)_2$. The steric

TABLE 5

Structural parameters for compounds of the type *fac*-[M(tridentate)(unidentate)$_3$]

Compound	b	θ_A	ϕ_A	ϕ_D	θ_D	ϕ_F	DME	DMF	MF/MD	Ref.
$[Zn\{S(CH_2CO_2)_2\}(OH_2)_3]\cdot H_2O$	1.28	70	51	126	123	116	85.1	98.1	1.00	*a*
$[Cr\{NH(CH_2CH_2NH_2)_2\}Cl_3]$	1.33	64	52	124	119	118	92.2	95.5	1.01	*c*
$[Cr\{NH(CH_2CH_2NH_2)_2\}(CO)_3]$	1.26	66	49	131	120	126	81.7	85.9	1.00	*d*
$[Mo\{NH(CH_2CH_2NH_2)_2\}(CO)_3]$	1.21	70	47	131	120	124	82.4	86.7	1.01	*e*
$[Mo\{NH(CH_2CH_2NH_2)_2\}O_3]$	1.19	65	45	114	120	110	105.3	106.8	1.00	*f*
$K_3[Mo\{N(CH_2CO_2)_3\}O_3]$	1.17	65	44	115	119	108	102.1	107.1	1.00	*g*
$Na_4[O_3Mo\{(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2\}MoO_3]\cdot 8H_2O$	1.19	62	44	114	120	111	104.9	107.5	1.00	*h*
$[Mo\{PPh(NEtPPh_2)_2\}(CO)_3]$	1.08	86	47	134	118	113	79.2	91.6	0.95	*i*
$[Cr\{NEt(CH_2CH_2PPh_2)_2\}(CO)_3]$	1.31	74	55	131	119	120	82.4	89.1	0.99	*j*
$[Cr\{PPh(CH_2CH_2PPh_2)_2\}(CO)_3]$	1.31	68	52	127	125	122	81.6	93.6	0.99	*k*
	1.30	68	52	130	121	122	82.6	89.3	1.01	*k*
$[Mo\{PPh(CH_2CH_2PPh_2)_2\}(CO)_3]$	1.27	72	52	129	119	120	86.3	90.6	1.02	*k*
$[Co(As_3)(CO)_3]$	0.97	60	34	115	120	115	103.6	103.6	1.00	*l*

Units of θ, ϕ, DME, and DMF are degrees.

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interaction between groups attached to the ends of a facially co-ordinated tridentate ligand is much more important than for bidentate ligands, and models clearly show that such ligands cannot form ABC angles approaching 60° as required for $b > 1.2$ and $R < 1.1$ (Figure 5). The consequent increase in ABC over that calculated assuming a completely flexible ligand leads to an increase in ϕ_A and ϕ_D, a decrease in θ_F, a large decrease in DME, and a smaller increase in DMF. However the steric effect of these terminal phenyl groups will directly lead to an increase in ϕ_F and decrease in DMF. It is therefore not possible to obtain a meaningful value of R for these complexes. These steric effects are absent in $[\mathrm{Co}(\overline{\mathrm{As{-}As{-}As}})(\mathrm{CO})_3]$, the angular parameters of which correspond to R *ca.* 0.8.

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