

TETRAKIS(DIMETHYLPHENYLPHOSPHINE)MOLYBDENUM(0):

AN X-RAY STRUCTURAL CHARACTERISATION OF THE COMPLEX AS $\text{Mo}(\text{PMe}_2\text{Ph})_3(\eta\text{-PhPMe}_2)$

RONALD MASON, K. MARK THOMAS and GRAHAM A. HEATH

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

(Received November 20th, 1974)

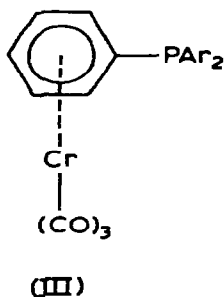
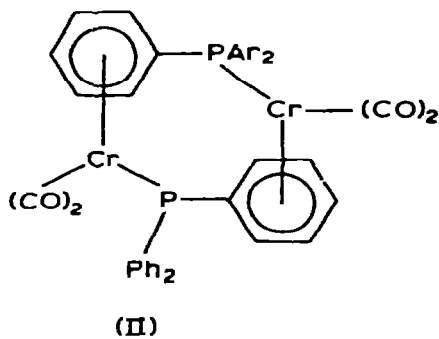
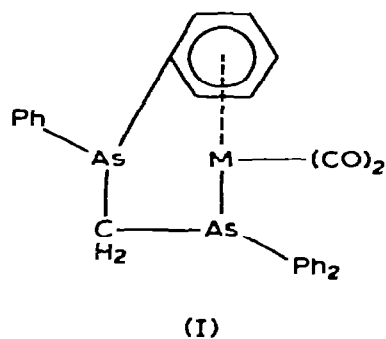
Summary

Tetrakis(dimethylphenylphosphine)molybdenum(0) is shown to be an eighteen electron complex, $\text{Mo}(\text{PMe}_2\text{Ph})_3(\eta\text{-PhPMe}_2)$. Crystals are triclinic, space group $P\bar{1}$, with $a = 11.424(2)$, $b = 16.210(3)$, $c = 9.413(2)$ Å, $\alpha = 82.84(1)$, $\beta = 111.02(1)$, $\gamma = 85.67(1)^\circ$. Intramolecular bond lengths are reported from an X-ray analysis of 1203 independent reflexion intensities ($\text{Mo-K}\alpha$) with $R_1 = 0.068$ and $R_2 = 0.102$; the mean Mo—P and Mo—C lengths are 2.44 and 2.88 Å respectively. There is no significant distortion of the coordinated phenyl ring from six-fold symmetry.

Introduction

Nyholm et al. [1-3] were the first to study the reactions of Group VI carbonyls with *o*-phenylenebis(dimethylarsine), L, and obtain compounds which were formulated as $\text{M}(\text{CO})_4\text{L}$ and $\text{M}(\text{CO})_2\text{L}_2$. Similar reactions have been reported with 1,2-bis(dimethylarsino)tetrafluorocyclobutene [4], $\text{Me}_2\text{AsSnMe}_2\text{AsMe}_2$ [5] and 1,2-bis(diphenylarsino)ethane [6] as ligands; Colton et al. have reported the reactions of bis(diphenylarsino)methane (dam) [7], tris(*p*-tolyl)phosphine (ppt), tris(*m*-tolyl)phosphine (pmt) and tris(*o*-tolyl)phosphine (pot) with $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr, Mo, W}$) [8,9] and found that in addition to the expected substitution products, compounds with stoichiometry $\text{M}(\text{CO})_2(\text{dam})$ ($\text{M} = \text{Cr, Mo}$), $\pi\text{-(pot)M}(\text{CO})_3$ ($\text{M} = \text{Cr, Mo and W}$), $\text{Cr}(\text{CO})_3\text{L}$ ($\text{L} = \text{ppt, pmt and PPh}_3$) and $[\text{Cr}(\text{CO})_2\text{L}]_2$ ($\text{L} = \text{pot, ppt, PPh}_3$) could be isolated. The formulations [9] have been confirmed for I and II by X-ray diffraction methods [10,11].

Chatt and Wedd [12] have isolated, in small yield, the complex $(\text{Me}_2\text{PhP})_4\text{-Mo}$ through the reduction of $[\text{MoCl}_3(\text{thf})_3]$ in the presence of excess phosphine. The compound was monomeric and diamagnetic in solution and, like the Colton et al. complexes, would provide an unusual electron-configuration complex unless the tertiary phosphine coordinated through an aryl-substituent. Difficulties of synthesis prevented a comprehensive spectroscopic study of the complex



but we have been able to characterize the complex using a single crystal selected from the original sample [12].

Experimental

Crystal data

$\text{MoP}_4\text{C}_3\text{H}_{14}$, monoclinic, $a = 11.424(2)$, $b = 16.210(3)$, $c = 9.413(2)$ Å; $\alpha = 82.84(1)$, $\beta = 111.02(1)$, $\gamma = 85.67(1)^\circ$; mol. wt. = 648.59, $V = 1600.8$ Å³, $Z = 2$, $D_{\text{calc}} = 1.34$ g cm⁻³, $F(000) = 1060$, $\mu(\text{Mo-K}\alpha) = 6.2$ cm⁻¹. Space group $P\bar{1}$ (structure solution and refinement).

Crystallographic measurements

$\text{Mo}(\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5)_4$ crystallizes from benzene as brown prisms. Weissenberg and precession photographs were used to determine initial cell dimensions and Laue group. The cell dimensions were refined by least-squares analysis of the angular settings of twelve reflexions on a Hilger and Watts Y290 automatic diffractometer (Mo-K α ; graphite monochromator; $\lambda = 0.70926$ Å). The data crystal (0.35 × 0.55 × 0.60 mm) had prominent faces (10 $\bar{1}$)($\bar{3}01$)(100)(0 $\bar{1}0$)(001)(00 $\bar{1}$) and was mounted along its c axis. The mosaic spread was examined by the ω -scan method, the width at half-height for a typical strong reflexion being 0.20°.

Intensity measurements were based on an $\omega - 2\theta$ scan routine, background measurements being made at the extremities of the peak scan for 50 s (each side) with stationary counter and crystal. The peak was scanned for 100 s in 0.01° steps/s and the diffracted rays were collected by a circular aperture of diameter 3.5 mm positioned 250 mm from the crystal. Instrument stability and crystal

alignment were monitored by following the intensities of three reflexions, 020, 002 and 600; all intensity standards varied by less than 1.5 standard deviations.

All crystallographically non-equivalent reflexions having $4.0 \leq 2\theta \leq 30.0^\circ$ were surveyed and 1203 reflexions having $I_{\text{obs}} > 3.0 \sigma (I_{\text{obs}})$ were regarded as being observed. The value of P in the standard deviation calculation, based on countering statistics alone, was chosen as 0.04. All intensities were corrected for Lorentz and polarisation effects but an absorption correction was not made.

Structure solution and refinement

All calculations were performed using the XRAY70 System [13]. An unsharpened Patterson synthesis provided the position of the molybdenum atom and a single cycle of least squares refinement of its atomic coordinates and isotropic temperature factor gave $R_1 = 0.48$. An electron density synthesis using F_{obs} as the Fourier coefficients gave the positions of the phosphorus atoms, and refinement of the positional and thermal parameters of the molybdenum and phosphorus atoms gave $R_1 = 0.32$. A difference electron density synthesis then provided the positions of all the carbon atoms. Least-squares refinement of all positional parameters, molybdenum and phosphorus anisotropic temperature factors and isotropic temperature factors for all the carbon atoms was now begun in a full-matrix scheme based on a weighting scheme $1/\sigma$ and minimizing $\Sigma \omega \{ |F_o| - |F_c| \}^2$, and this refinement converged to $R_1 = 0.068$ and $R_2 = 0.102$. An analysis of $\omega \Delta^2$ against $|F_o|$ confirmed that the weighting scheme was satisfactory. Maximum shifts of positional parameters in the last cycle of refinement were 0.18σ and a difference Fourier synthesis showed no excursions greater than $1.2 e/\text{\AA}^3$, some being associated with hydrogen atoms which were not, however, included in the structure factor calculations. The error for an observation of unit weight was $2.5 e$. Atomic scattering factors were taken from Cromer and Waber, f_{Mo} and f_{P} being corrected for anomalous dispersion [14,15].

Final atomic positional and thermal parameters are given in Table 1. Observed and calculated structure factors are listed in a table which may be obtained from the authors.

Discussion

The molecular stereochemistry and atom labelling is depicted in Figure 1, geometrical data being listed in Table 2. The present complex is seen to link with the chemistry of complexes of Group VI carbonyls with tertiary arsines and phosphines, in that it adds to the list of those molecules in which a tertiary aryl-phosphine or -arsine coordinates through an aryl substituent [10,11,16]; the present complex, like $[\text{RuH}(\text{PPh}_3)_2(\eta\text{-PhPPh}_2)]^+$, does not have the thermodynamic benefits of chelation but is ensured by the rare gas rule alone. The stereochemistry can, according to taste, be described as quasi-tetrahedral, octahedral, or 3-6 coordination, with the phosphorus molybdenum-phosphorus bond averaging $91.5(16)^\circ$; the small but apparently significant deviations of two-bond angles from this mean reflect non-bonded interactions.

The metal-carbon (arene) bond lengths average $2.28(2) \text{\AA}$ which is considerably shorter than one might have anticipated from, say, the molybdenum-

(continued on p. 200)

TABLE 1
 (PM₂Ph)₄Mo: ATOMIC COORDINATES, TEMPERATURE FACTORS AND THEIR STANDARD DEVIATIONS

	x/a	y/b	z/c	U(\AA^2)	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Mo	0.2253(1)	0.2372(1)	-0.0086(2)		2.60(18)	4.05(17)	3.41(17)	-0.20(11)	0.78(12)	-1.31(10)
P(1)	0.3847(4)	0.1432(3)	0.2076(6)		3.1(4)	5.7(4)	4.2(4)	-0.5(3)	0.8(3)	-1.4(3)
P(2)	0.1205(5)	0.2847(3)	0.1583(6)		3.8(4)	4.6(4)	4.9(4)	-0.3(3)	1.3(3)	-1.7(3)
P(3)	0.3491(5)	0.3531(3)	0.0310(6)		4.0(4)	4.7(4)	5.3(4)	-0.7(3)	1.3(3)	-1.0(3)
P(4)	-0.0853(5)	0.3363(3)	-0.3224(6)		3.9(4)	8.2(5)	5.4(3)	0.4(4)	0.9(3)	-1.7(3)
C(1)	0.3513(15)	0.0355(10)	0.2240(18)	3.9(6)						
C(2)	0.2537(16)	0.0160(11)	0.2759(19)	5.2(6)						
C(3)	0.2200(16)	-0.0644(11)	0.2848(19)	5.3(6)						
C(4)	0.2838(18)	-0.1203(11)	0.2441(20)	6.1(6)						
C(5)	0.3803(18)	-0.1122(10)	0.1914(19)	4.8(5)						
C(6)	0.4138(15)	-0.0312(11)	0.1816(18)	4.7(5)						
C(7)	0.4339(16)	0.1500(10)	0.4185(20)	5.6(6)						
C(8)	0.5482(17)	0.1288(11)	0.2038(20)	5.9(6)						
C(11)	0.0374(16)	0.2001(10)	0.2417(20)	4.1(5)						
C(12)	-0.0695(18)	0.1817(11)	0.1421(21)	5.5(6)						
C(13)	-0.1348(18)	0.1221(12)	0.1938(24)	7.3(7)						
C(14)	-0.0911(19)	0.0930(12)	0.3536(24)	7.5(7)						
C(16)	0.0172(18)	0.1210(11)	0.4563(20)	6.0(6)						
C(16)	0.0808(16)	0.1779(10)	0.3983(20)	4.6(5)						
C(17)	0.2039(17)	0.3313(10)	0.3300(20)	5.9(6)						
C(18)	-0.0150(17)	0.3707(11)	0.0703(21)	6.6(6)						
C(21)	0.4333(17)	0.3711(10)	-0.1058(19)	4.3(5)						
C(22)	0.3726(17)	0.4220(11)	-0.2502(22)	6.2(6)						
C(23)	0.4330(19)	0.4327(11)	-0.3581(21)	6.6(6)						
C(24)	0.5505(20)	0.3884(12)	-0.3189(24)	7.1(6)						
C(25)	0.6070(18)	0.3418(11)	-0.1834(23)	6.5(6)						
C(26)	0.5534(17)	0.3285(11)	-0.0710(20)	5.6(6)						
C(27)	0.2946(17)	0.4640(11)	0.0008(20)	6.6(6)						
C(28)	0.4786(18)	0.3615(11)	0.2165(21)	7.1(6)						
C(31)	0.0529(15)	0.2662(10)	-0.2367(18)	3.5(5)						
C(32)	0.1652(16)	0.2810(10)	-0.2685(18)	4.2(5)						
C(33)	0.2713(16)	0.2129(10)	-0.2194(18)	4.2(5)						
C(34)	0.2632(15)	0.1380(10)	-0.1428(18)	3.9(5)						
C(35)	0.1532(16)	0.4213(10)	-0.1062(18)	4.3(5)						
C(36)	0.0512(15)	0.1874(10)	-0.1562(18)	3.8(5)						
C(37)	-0.0485(18)	0.4420(12)	-0.3514(23)	8.1(7)						
C(38)	-0.1508(21)	0.3237(14)	-0.5290(26)	10.3(8)						

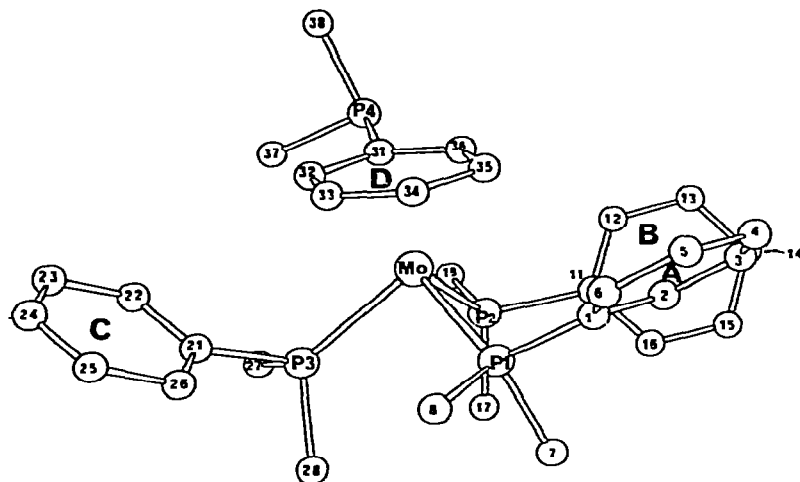


Fig. 1.

TABLE 2

(PMe₂Ph)₄Mo: INTERATOMIC DISTANCES (Å), BOND ANGLES (°) AND THEIR STANDARD DEVIATIONS

Bond lengths

Mo—P(1)	2.434(4)	Mo—P(2)	2.451(6)
Mo—P(3)	2.423(5)	Mo—C(31)	2.30 (1)
Mo—C(32)	2.29 (2)	Mo—C(33)	2.30 (2)
Mo—C(34)	2.27 (2)	Mo—C(35)	2.27 (2)
Mo—C(36)	2.25 (2)	P(1)—C(1)	1.82 (2)
P(1)—C(7)	1.88 (2)	P(1)—C(8)	1.88 (2)
P(2)—C(11)	1.87 (2)	P(2)—C(17)	1.84 (2)
P(2)—C(18)	1.87 (2)	P(3)—C(21)	1.87 (2)
P(3)—C(27)	1.91 (2)	P(3)—C(28)	1.87 (2)
P(4)—C(31)	1.82 (2)	P(4)—C(37)	1.85 (2)
P(4)—C(38)	1.87 (2)	C(1)—C(2)	1.41 (3)
C(2)—C(3)	1.39 (3)	C(3)—C(4)	1.40 (3)
C(4)—C(5)	1.39 (3)	C(5)—C(6)	1.40 (2)
C(6)—C(1)	1.42 (3)	C(11)—C(12)	1.39 (2)
C(12)—C(13)	1.41 (3)	C(13)—C(14)	1.41 (3)
C(14)—C(15)	1.42 (3)	C(15)—C(16)	1.39 (3)
C(16)—C(11)	1.39 (2)	C(21)—C(22)	1.40 (2)
C(22)—C(23)	1.42 (3)	C(23)—C(24)	1.37 (3)
C(24)—C(25)	1.31 (3)	C(25)—C(26)	1.41 (3)
C(26)—C(21)	1.39 (3)	C(31)—C(32)	1.45 (3)
C(32)—C(33)	1.47 (2)	C(33)—C(34)	1.36 (2)
C(34)—C(35)	1.45 (3)	C(35)—C(36)	1.42 (2)
C(36)—C(31)	1.41 (3)		

Bond angles

P(1)—Mo—P(2)	91.6 (2)	P(1)—Mo—P(3)	93.0 (2)
P(2)—Mo—P(3)	89.9 (2)	P(1)—Mo—C(31)	153.6 (4)
P(1)—Mo—C(32)	141.9 (5)	P(1)—Mo—C(33)	104.6 (4)
P(1)—Mo—C(34)	82.3 (4)	P(1)—Mo—C(35)	87.6 (4)
P(1)—Mo—C(36)	119.3 (4)	P(2)—Mo—C(31)	97.5 (5)
P(2)—Mo—C(32)	126.5 (5)	P(2)—Mo—C(33)	163.5 (4)
P(2)—Mo—C(34)	149.4 (5)	P(2)—Mo—C(35)	112.9 (6)
P(2)—Mo—C(36)	92.4 (5)	P(3)—Mo—C(31)	111.7 (4)
P(3)—Mo—C(32)	87.7 (4)	P(3)—Mo—C(33)	92.6 (5)
P(3)—Mo—C(34)	120.3 (5)	P(3)—Mo—C(35)	157.3 (6)

(continued)

TABLE 2 (continued)

Bond angles

P(3)—Mo—C(36)	147.6	(4)	C(31)—Mo—C(32)	36.8	(7)
C(31)—Mo—C(33)	66.4	(6)	C(31)—Mo—C(34)	77.2	(6)
C(31)—Mo—C(35)	66.0	(5)	C(31)—Mo—C(36)	36.0	(6)
C(32)—Mo—C(33)	37.4	(6)	C(32)—Mo—C(34)	64.9	(6)
C(32)—Mo—C(35)	78.1	(6)	C(32)—Mo—C(36)	65.2	(6)
C(33)—Mo—C(34)	35.6	(6)	C(33)—Mo—C(35)	65.4	(7)
C(33)—Mo—C(36)	76.9	(7)	C(34)—Mo—C(35)	37.3	(7)
C(34)—Mo—C(36)	65.5	(6)	C(35)—Mo—C(36)	36.6	(6)
Mo—P(1)—C(7)	127.6	(6)	Mo—P(1)—C(8)	116.6	(6)
Mo—P(1)—C(1)	113.9	(5)	C(7)—P(1)—C(8)	96.9	(8)
C(7)—P(1)—C(1)	96.2	(8)	C(8)—P(1)—C(1)	101.0	(8)
Mo—P(2)—C(17)	122.5	(7)	Mo—P(2)—C(18)	117.6	(7)
Mo—P(2)—C(11)	118.6	(6)	C(17)—P(2)—C(18)	96.1	(8)
C(17)—P(2)—C(11)	99.9	(9)	C(18)—P(2)—C(11)	97.1	(8)
Mo—P(3)—C(27)	119.1	(6)	Mo—P(3)—C(28)	124.4	(6)
Mo—P(3)—C(21)	113.9	(6)	C(27)—P(3)—C(28)	95.6	(8)
C(27)—P(3)—C(21)	99.3	(8)	C(28)—P(3)—C(21)	100.2	(9)
C(31)—P(4)—C(37)	105.0	(8)	C(31)—P(4)—C(38)	103.1	(9)
C(37)—P(4)—C(38)	95.7	(10)	P(1)—C(1)—C(6)	124.4	(15)
P(1)—C(1)—C(2)	118.6	(13)	C(2)—C(1)—C(6)	116.9	(15)
C(1)—C(2)—C(3)	121.4	(18)	C(2)—C(3)—C(4)	120.6	(19)
C(3)—C(4)—C(5)	119.6	(17)	C(4)—C(5)—C(6)	119.8	(17)
C(5)—C(6)—C(1)	121.7	(18)	P(2)—C(11)—C(12)	118.4	(14)
P(2)—C(11)—C(16)	122.3	(13)	C(12)—C(11)—C(16)	110.3	(17)
C(11)—C(12)—C(13)	122.3	(16)	C(12)—C(13)—C(14)	117.4	(17)
C(13)—C(14)—C(15)	120.7	(20)	C(14)—C(15)—C(16)	119.5	(17)
C(15)—C(16)—C(11)	120.7	(15)	P(3)—C(21)—C(22)	120.6	(15)
P(3)—C(21)—C(26)	120.4	(12)	C(22)—C(21)—C(26)	118.8	(19)
C(21)—C(22)—C(23)	121.1	(17)	C(22)—C(23)—C(24)	117.6	(16)
C(23)—C(24)—C(25)	121.2	(24)	C(24)—C(25)—C(26)	123.9	(19)
C(25)—C(26)—C(21)	117.1	(15)	P(4)—C(31)—C(32)	123.5	(11)
P(4)—C(31)—C(36)	117.4	(14)	C(32)—C(31)—C(36)	118.2	(14)
C(31)—C(32)—C(33)	119.2	(14)	C(32)—C(33)—C(34)	119.7	(17)
C(33)—C(34)—C(35)	122.8	(15)	C(34)—C(35)—C(36)	116.7	(15)
C(35)—C(36)—C(31)	123.4	(18)			

π -cyclopentadienyl bond lengths in $(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3(\text{C}_7\text{H}_5)$ where the mean value is 2.37(2) Å, compared with 2.35 to 2.37 Å in other π -cyclopentadienyl organometallic species [18]. Metal-carbon (arene) distances are not very dependent on whether the arene is a five- or six-membered ring and the present short bond lengths are attributed to the absence of relatively strong π -acids such as carbonyl groups and, therefore, of enhanced metal-to-arene π -bonding. There is no significant distortion of the individual carbon-carbon bond lengths in the coordinated arene from an average value of 1.43(2) Å, but it is noteworthy that the phosphorus atom, P(4), is displaced 0.32 Å out of the mean plane defined by the carbon atoms, C(31) to C(36), and away from the metal. This is the more usual sense of displacement of substituent groups on coordinated cyclic ligands and it has received a semi-quantitative explanation in terms of a maximum overlap criterion [19]. By contrast, the X-ray and neutron diffraction analyses of benzenechromium tricarbonyl at 78 K indicate [20] that the hydrogen atoms are displaced by an average of 0.03 Å towards the chromium atom; this work appears to open up again the vexed question of electron localisation in a ligated benzene. Theoretically, there seem to be no valid reasons for believing that local-

isation would be more facile in benzenechromium tricarbonyl than in dibenzenechromium, for which very low lying excited states have to be postulated to accommodate a geometrical distortion based on the Second Order Jahn–Teller effect [21]. The value of the quasi-localised bonding scheme [20], offered by way of a rationalisation of the ring distortion, is not obvious; and, in spite of the apparently very high accuracy of the structure determination, it would be of interest to have an independent refinement analysis of the X-ray and neutron diffraction data in the non-centrosymmetric space group, $P2_1$. One would then be reassured that the structural results do not suffer from systematic errors conditioned by an assumption of strict C_s molecular symmetry in the crystal.

Both the intra- and inter-molecular arrangements of the phenyl substituents of the phosphine ligands are of interest. The angles between the rings A, B and C (Figure 1) are 81° (A–B), 60° (B–C) and 65° (A–C) with ring D making angles of 35° (to A), 66° (to B) and 38° (to C). Whereas the phosphorus atom P(4) is considerably removed from the mean plane containing the carbon atoms of ring D, the deviations from trigonal symmetry of atoms C(1), C(11) and C(21) are smaller: P(1) is displaced 0.06 \AA away from the metal, the corresponding displacements of P(2) and P(3) being 0.04 and 0.12 \AA respectively (the r.m.s. deviations of the carbon atoms from the mean planes are 0.00_4 (A), 0.01_1 (B), 0.01_2 (C) and 0.00_6 (D)). The consistent sense of these displacements and the lack of any precise symmetry in the intra- and inter-molecular non-valence interactions suggested an examination of the accurately determined parameters in the bis- and tris-(dimethylphenylphosphine) complexes of several third row transition metal halides [22]. Again, the phosphorus atoms are not co-planar with the carbon atoms of the phenyl-substituent groups; the displacements are very small (0.01_2 and 0.02_2 \AA) in $\text{OsCl}_4(\text{PMe}_2\text{Ph})$ and $\text{ReCl}_4(\text{PMe}_2\text{Ph})$, whereas they range

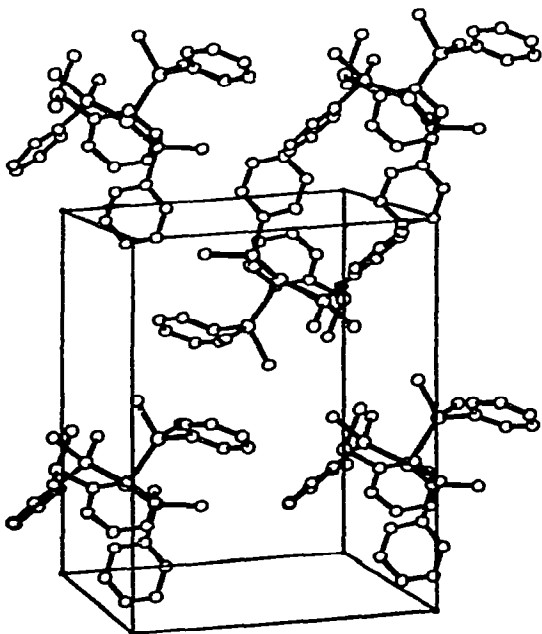


Fig. 2.

from 0.04 and 0.14 Å in the trihalides. The trihalide data are valuable for the pattern of the displacements is identical in the two crystallographically-independent molecules and possible intermolecular packing determination of the distortions can be assumed to be small. One is accordingly left with the view that the distortions reflect non-bonded repulsions of the phosphorus lone pairs with (probably) the hydrogen atoms of the substituent groups and/or repulsions between atoms in the several substituents. The first effect would, for a given tertiary phosphine, be reduced in complexes based on metals in high oxidation states for then much of the ligand lone pair density would be transferred to the metal; a systematic survey would be of interest.

The intermolecular packing is depicted in Figure 2. That tertiary arylphosphine complexes are often arranged in their crystals so as to provide intermolecular face-to-face packing of phenyl-substituents has been commented upon by many workers, and the pattern is repeated here. The ligands themselves, for example triphenylphosphine, pack in centrosymmetric space groups so as to provide a mixture of molecules of opposite chirality; there seems to be strong circumstantial evidence that intermolecular charge transfer between phenyl groups provides a considerable contribution to the lattice energy.

Acknowledgements

We are grateful to the Science Research Council for support of these studies and to Professor J. Chatt and Dr. A. Wedd for the crystal.

References

- 1 H.L. Nigham and R.S. Nyholm, *Proc. Chem. Soc.*, (1957) 321.
- 2 H.L. Nigham, R.S. Nyholm and D.V. Romanc Rao, *Spec. Publ. Chem. Soc.*, No. 13, 1959, 120.
- 3 H.L. Nigham, R.S. Nyholm and M.H.B. Studdard, *J. Chem. Soc.*, (1960) 1803.
- 4 W.R. Cullen, P.S. Dhaliwal and C.J. Stewart, *Inorg. Chem.*, 6 (1967) 2256.
- 5 E.W. Abel, J.P. Crow and S.M. Illingworth, *J. Chem. Soc. A*, (1969) 1631.
- 6 F. Zingales, F. Canziani and R. Ugo, *Gazz. Chim. Ital.*, 92 (1962) 761.
- 7 R. Colton and C.J. Rix, *Aust. J. Chem.*, 24 (1971) 1157.
- 8 J.A. Bowden, R. Colton and C.J. Commons, *Aust. J. Chem.*, 26 (1973) 655.
- 9 J.A. Bowden and R. Colton, *Aust. J. Chem.*, 26 (1973) 43.
- 10 G.B. Robertson, P.O. Whimp, R. Colton and C.J. Rix, *Chem. Commun.*, (1971) 573.
- 11 G.B. Robertson and P.O. Whimp, *J. Organometal. Chem.*, 60 (1973) C11.
- 12 J. Chatt and A.G. Wedd, *J. Organometal. Chem.*, 27 (1971) C15.
- 13 J.M. Stewart, F.A. Kundell and J.C. Baldwin, *XRAY 70 System*, July 1970, as implemented on the LC.L. 1960A at the S.R.C. Atlas Computer Laboratory, Chilton, Didcot, Berks.
- 14 D.T. Cromer and J.T. Waber, *Acta Crystallogr.*, 18 (1965) 104.
- 15 D.T. Cromer, *Acta Crystallogr.*, 18 (1965) 17.
- 16 J.C. McConway, A.C. Skapski, L. Phillips, R.J. Young and G. Wilkinson, *J. Chem. Soc. Chem. Commun.*, (1974) 327.
- 17 M.J. Bennett and R. Mason, *Proc. Chem. Soc.*, (1963) 273.
- 18 J. Rajaram and J.A. Ibers, *Inorg. Chem.*, 12 (1973) 1313.
- 19 S.F.A. Kettle, *Inorg. Chim. Acta*, 1 (1967) 303.
- 20 B. Rees and P. Coppens, *Acta Crystallogr., Part B*, 29 (1973) 2515.
- 21 D.H.W. den Boer, F.C. den Boer and H.C. Longuet-Higgins, *Mol. Phys.*, 5 (1962) 387; R. Mason, *Chem. Soc. Rev.*, 1 (1972) 431.
- 22 L. Aslanov, R. Mason, A.G. Wheeler and P.O. Whimp, *Chem. Commun.*, (1970) 30; A.G. Wheeler, Ph. D. thesis, University of Sheffield, 1969.