Structural Investigations of Nickel Complexes. Part II.[1] Crystal and Molecular Structure of *trans*-Dichlorobis-(4,4-dimethoxy-1-phenylphosphorinan)nickel(II)

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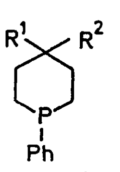
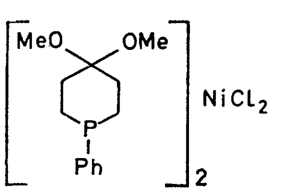
The structure of the title compound (3) has been elucidated by single-crystal *X*-ray analysis from photographic data by the heavy-atom method, and refined by full-matrix least-squares calculations to R 0·099 for 3709 independent reflections. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions: $a = 10{\cdot}49(2)$ $b = 12{\cdot}10(2)$, $c = 23{\cdot}16(3)$ Å, $\beta = 90{\cdot}62(20)°$. The nickel atom co-ordination is *trans* square planar with mean Ni–P and Ni–Cl 2·250(2) and 2·171(2) Å. The phosphorinan ligands are in chair conformations with the phenyl substituent of one ring axial, and that of the other equatorial; the former ring is more flattened at phosphorus.

PREVIOUS *X*-ray analyses of two phosphorinan derivatives, 1-phenylphosphorinan-4-one (1) [2] and 4,4-(dimethoxy)-1-phenylphosphorinan (2),[3] have shown that these molecules adopt chair conformations and that their phenyl substituents are axially oriented. As part of our continuing studies on conformations of phosphorus heterocycles and their complexes, it was important to establish how this conformational preference was affected when the phosphorus lone-pair was occupied in complex formation, and so we have elucidated the crystal structure of *trans*-dichloro-(4,4-dimethoxy-1-phenylphosphorinan)nickel(II) (3). A preliminary account of this analysis has been reported.[4]



(1) R1,R2=O
(2) R1,R2=OMe



(3)

EXPERIMENTAL

Crystal Data.—$C_{26}H_{38}Cl_2NiO_4P_2$, $M = 606{\cdot}2$, Monoclinic, $a = 10{\cdot}49(2)$, $b = 12{\cdot}10(2)$, $c = 23{\cdot}16(3)$ Å, $\beta = 90{\cdot}62(20)°$, $U = 2940$ Å^3, $D_m = 1{\cdot}369$, $Z = 4$, $D_c = 1{\cdot}370$, $F(000) = 1272$. Space group $P2_1/c$ (C^5_{2h}) from systematic absences: $h0l$ when $l \neq 2n$, $0k0$ when $k \neq 2n$. Cu-K_α radiation, $\lambda = 1{\cdot}542$ Å; μ(Cu-K_α) $= 38{\cdot}3$ cm^{-1}.

The dark red crystals were obtained from absolute methanol as small plates, elongated along the crystallographic b axis.

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[1] Part I, A. T. McPhail, R. C. Komson, J. F. Engel, and L. D. Quin, *J.C.S. Dalton*, 1972, 874.

[2] A. T. McPhail, J. J. Breen, and L. D. Quin, *J. Amer. Chem. Soc.*, 1971, **93**, 2574.

[3] A. T. McPhail, J. J. Breen, J. H. Somers, J. C. H. Steele, jun., and L. D. Quin, *Chem. Comm.*, 1971, 1020.

[4] A. T. McPhail, J. J. Breen, J. C. H. Steele, jun., and L. D. Quin, *Phosphorus*, 1972, **1**, 255.

Crystallographic Measurements.—Rotation, oscillation, and Weissenberg photographs were taken with Cu-K_α radiation; precession photographs were taken with Mo-K_α (λ 0·7107 Å) radiation. Unit-cell dimensions were evaluated from precession, rotation, and $h0l$ Weissenberg photographs. Intensities were estimated visually from equi-inclination multiple-film Weissenberg photographs. Spot-shape corrections and the usual Lorentz, polarization, and rotation factors were applied; absorption was neglected. In all, 3709 independent observed structure amplitudes were derived from the intensity estimates.

Structure Analysis.—The structure was solved by the heavy-atom method. Initial co-ordinates for the nickel atom were deduced from the three-dimensional Patterson map and structure factors calculated with this atom alone gave R 0·65.

The first three-dimensional electron-density distribution, evaluated by use of weighted Fourier coefficients[5] and nickel phases, permitted the two chlorine and two phosphorus atoms to be placed although they could not be distinguished. Inclusion of these four atoms, weighted as chlorine, in a structure-factor calculation yielded R 0·43. From a second three-dimensional F_o Fourier synthesis, calculated with the improved phase constants, the approximate positions of all the remaining non-hydrogen atoms were found, although C(10) could only be assigned very roughly. For structure factors calculated with all thirty-five atoms appropriately weighted, R was 0·257. Two cycles of full-matrix least-squares adjustment of the positional and isotropic thermal parameters then followed, and these reduced R to 0·170. It was apparent from the relatively high thermal parameter of C(10) that the position of this atom was much in error, and so it was omitted from the next structure-factor calculation and relocated in a subsequent F_o Fourier synthesis. Two more cycles of least-squares refinement resulted in R 0·154.

The nickel, chlorine, and phosphorus atoms were then allowed to assume anisotropic thermal parameters, and two further least-squares cycles reduced R to 0·106. Positions for all the hydrogen atoms, save those of the methyl groups, were calculated assuming appropriate angles and C–H 1·07 Å, and were found to coincide with significant positive regions in a three-dimensional difference electron-density map. Inclusion of the hydrogen atoms in the next structure-factor calculation decreased R to 0·101. The refinement was concluded after two more cycles of least-squares adjustment of the non-hydrogen positional and thermal parameters. The final R is 0·099.

Theoretical atomic scattering factors for neutral atoms,[6] corrected for the effects of anomalous scattering, were employed in all the structure-factor calculations. For the least-squares iterations the weighting scheme $\sqrt{w} = 1$ for $|F_o| \leqslant 20{\cdot}0$ and $\sqrt{w} = 20{\cdot}0/|F_o|$ for $|F_o| > 20{\cdot}0$ was used; this showed no systematic dependence of $<w\Delta^2>$ on $|F_o|$ and $\sin\theta$ when analysed in ranges of these values.

RESULTS AND DISCUSSION

Final atomic positional and thermal parameters, together with their estimated standard deviations, are given in Table 1. The molecular conformation is illustrated in Figure 1 which also shows the atomic numbering scheme employed. Interatomic distances and valency angles are listed in Table 2. Deviations of selected atoms from the least-squares planes calculated through various groups of atoms are presented in Table 3.*

The nickel atom co-ordination is *trans* square planar with Cl–Ni–Cl′ 179·4(1) and P–Ni–P′ 175·0(1)°. The latter angle departs significantly from linearity as a consequence of non-bonded intramolecular repulsions which result in enlargement of the P–Ni–Cl′ and P′–Ni–Cl′ angles by an average of 2·5° from the ideal of 90° with concomitant reduction in the P–Ni–Cl and P′–Ni–Cl angles. The mean Ni–P and Ni–Cl distances (2·250 and 2·171 Å) agree well with the values estimated from the sums of the appropriate single-bond covalent radii,[7] Ni–P 2·27, Ni–Cl 2·16 Å [we have assumed 1·17 Å as the best estimate available for the

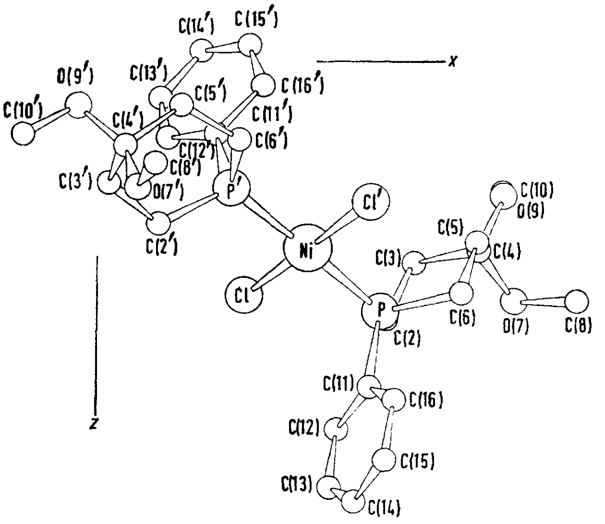

FIGURE 1 Molecular conformation and atom numbering

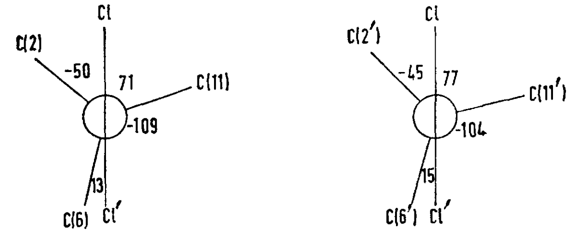

FIGURE 2 Projections along the Ni–P bonds in the complex, torsion angles (°)

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* Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20498 (17 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[5] G. A. Sim, *Acta Cryst.*, 1960, **13**, 511; 'Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis,' eds. R. Pepinsky, J. M. Robertson, and J. C. Speakman, Pergamon Press, Oxford, 1961, p. 227.

[6] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[7] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.

covalent radius of square planar nickel(II), this value being the mean of those suggested recently [8,9]].

TABLE 1

Fractional atomic co-ordinates and thermal parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	B/Å^2
Ni	0·4435(1)	0·1219(1)	0·1809(1)	*
Cl	0·3115(2)	0·0146(2)	0·2262(1)	*
Cl′	0·5741(2)	0·2302(2)	0·1362(1)	*
P	0·5962(2)	0·0610(2)	0·2424(1)	*
P′	0·2809(2)	0·1703(2)	0·1224(1)	*
C(2)	0·6072(7)	−0·0884(6)	0·2498(3)	2·91(12)
C(3)	0·6659(8)	−0·1418(8)	0·1967(4)	3·97(16)
C(4)	0·8020(7)	−0·1004(7)	0·1834(3)	3·35(14)
C(5)	0·8064(8)	0·0251(7)	0·1749(4)	3·60(14)
C(6)	0·7655(7)	0·0931(7)	0·2257(3)	3·18(13)
O(7)	0·8756(6)	−0·1350(5)	0·2324(3)	3·92(11)
C(8)	1·0092(11)	−0·1066(9)	0·2308(5)	5·53(22)
O(9)	0·8489(6)	−0·1455(5)	0·1318(3)	4·77(13)
C(10)	0·8477(13)	−0·2648(12)	0·1284(6)	7·21(30)
C(11)	0·5746(7)	0·1137(7)	0·3159(3)	3·05(13)
C(12)	0·5086(8)	0·0505(8)	0·3569(4)	4·03(16)
C(13)	0·4966(11)	0·0931(9)	0·4132(5)	5·59(22)
C(14)	0·5475(11)	0·1941(10)	0·4266(5)	5·68(22)
C(15)	0·6095(10)	0·2566(9)	0·3875(5)	5·26(21)
C(16)	0·6248(9)	0·2180(8)	0·3301(4)	4·35(17)
C(2′)	0·1308(7)	0·2012(6)	0·1580(3)	2·82(12)
C(3′)	0·0239(7)	0·2436(6)	0·1172(3)	3·07(13)
C(4′)	0·0582(7)	0·3452(7)	0·0822(3)	3·22(13)
C(5′)	0·1729(8)	0·3229(8)	0·0436(4)	3·90(15)
C(6′)	0·2971(7)	0·2938(7)	0·0769(3)	3·27(13)
O(7′)	0·0850(6)	0·4293(5)	0·1229(3)	4·09(11)
C(8′)	0·1216(9)	0·5338(8)	0·0991(4)	4·67(18)
O(9′)	−0·0424(6)	0·3733(5)	0·0432(3)	4·40(12)
C(10′)	−0·1599(11)	0·4100(10)	0·0699(5)	5·59(22)
C(11′)	0·2487(7)	0·0625(6)	0·0703(3)	2·72(12)
C(12′)	0·1475(8)	−0·0123(7)	0·0753(4)	3·62(14)
C(13′)	0·1314(10)	−0·0965(9)	0·0353(5)	5·03(20)
C(14′)	0·2162(10)	−0·1055(9)	−0·0105(5)	5·26(21)
C(15′)	0·3166(10)	−0·0339(9)	−0·0150(5)	5·21(20)
C(16′)	0·3337(9)	0·0480(8)	0·0243(4)	4·50(17)
H(2α)	0·513	−0·119	0·257	5·0
H(2β)	0·665	−0·105	0·288	5·0
H(3α)	0·606	−0·124	0·160	5·0
H(3β)	0·669	−0·230	0·203	5·0
H(5α)	0·745	0·046	0·139	5·0
H(5β)	0·902	0·047	0·165	5·0
H(6α)	0·772	0·179	0·217	5·0
H(6β)	0·821	0·073	0·264	5·0
H(12)	0·473	−0·024	0·346	5·0
H(13)	0·451	0·048	0·448	5·0
H(14)	0·537	0·223	0·467	5·0
H(15)	0·645	0·331	0·398	5·0
H(16)	0·670	0·263	0·300	5·0
H(2′α)	0·152	0·263	0·190	5·0
H(2′β)	0·101	0·127	0·178	5·0
H(3′α)	−0·057	0·263	0·143	5·0
H(3′β)	0·001	0·178	0·088	5·0
H(5′α)	0·191	0·394	0·018	5·0
H(5′β)	0·151	0·254	0·016	5·0
H(6′α)	0·323	0·360	0·105	5·0
H(6′β)	0·373	0·278	0·048	5·0
H(12′)	0·086	−0·005	0·108	5·0
H(13′)	0·058	−0·148	0·039	5·0
H(14′)	0·204	−0·168	−0·039	5·0
H(15′)	0·380	−0·041	−0·048	5·0
H(16′)	0·409	0·100	0·020	5·0

* For the nickel, chlorine, and phosphorus atoms anisotropic temperature factors of the form $B\sin^2\theta/\lambda^2 = b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl$ were employed with parameters ($\times 10^5$).

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni	555(9)	445(8)	122(2)	−107(15)	−15(8)	11(7)
Cl	679(15)	956(17)	268(4)	−391(27)	−86(14)	483(14)
Cl′	723(15)	564(14)	224(4)	−56(24)	135(13)	206(12)
P	495(13)	480(13)	136(3)	−79(22)	−12(11)	51(10)
P′	597(14)	437(12)	111(3)	−37(22)	−49(10)	19(10)

TABLE 2

Interatomic distances (Å) and valency angles (°), with estimated standard deviations in parentheses

(*a*) Bonded distances

Ni–Cl	2·175(2)	C(14)–C(15)	1·352(16)
Ni–Cl′	2·167(2)	C(15)–C(16)	1·420(14)
Ni–P	2·254(2)	P′–C(2′)	1·824(7)
Ni–P′	2·245(2)	P′–C(6′)	1·838(8)
P–C(2)	1·820(8)	P′–C(11′)	1·807(7)
P–C(6)	1·862(8)	C(2′)–C(3′)	1·545(10)
P–C(11)	1·834(8)	C(3′)–C(4′)	1·517(11)
C(2)–C(3)	1·524(12)	C(4′)–C(5′)	1·532(11)
C(3)–C(4)	1·548(12)	C(4′)–O(7′)	1·412(10)
C(4)–C(5)	1·532(12)	C(4′)–O(9′)	1·423(10)
C(4)–O(7)	1·427(10)	C(5′)–C(6′)	1·549(12)
C(4)–O(9)	1·409(10)	O(7′)–C(8′)	1·434(12)
C(5)–C(6)	1·502(11)	O(9′)–C(10′)	1·455(13)
O(7)–C(8)	1·444(13)	C(11′)–C(12′)	1·401(11)
O(9)–C(10)	1·446(15)	C(11′)–C(16′)	1·406(12)
C(11)–C(12)	1·408(12)	C(12′)–C(13′)	1·386(14)
C(11)–C(16)	1·406(12)	C(13′)–C(14′)	1·396(15)
C(12)–C(13)	1·408(14)	C(14′)–C(15′)	1·370(15)
C(13)–C(14)	1·368(16)	C(15′)–C(16′)	1·357(14)

(*b*) Valency angles

Cl–Ni–Cl′	179·4(1)	C(13)–C(14)–C(15)	122·6(11)
Cl–Ni–P	87·3(1)	C(14)–C(15)–C(16)	120·2(10)
Cl–Ni–P′	87·9(1)	C(11)–C(16)–C(15)	118·0(8)
P–Ni–Cl′	92·9(1)	Ni–P′-C(2′)	115·8(2)
Cl′–Ni–P′	91·9(1)	Ni–P′-C(6′)	118·9(2)
P–Ni–P′	175·0(1)	Ni–P′–C(11′)	110·5(2)
Ni–P–C(2)	115·4(2)	C(2′)–P′–C(6′)	100·2(3)
Ni–P–C(6)	118·3(3)	C(2′)–P′–C(11′)	107·1(3)
Ni–P–C(11)	112·2(2)	C(6′)–P′–C(11′)	102·8(3)
C(2)–P–C(6)	99·6(3)	P′–C(2′)–C(3′)	114·6(5)
C(2)–P–C(11)	105·4(3)	C(2′)–C(3′)–C(4′)	114·9(6)
C(6)–P–C(11)	104·3(3)	C(3′)–C(4′)–C(5′)	111·2(7)
P–C(2)–C(3)	111·7(5)	C(3′)–C(4′)–O(7′)	105·9(6)
C(2)–C(3)–C(4)	113·9(7)	C(3′)–C(4′)–O(9′)	110·8(6)
C(3)–C(4)–C(5)	112·0(7)	C(5′)–C(4′)–O(7′)	111·4(6)
C(3)–C(4)–O(7)	103·8(6)	C(5′)–C(4′)–O(9′)	104·6(6)
C(3)–C(4)–O(9)	112·1(7)	O(7′)–C(4′)–O(9′)	113·1(6)
C(5)–C(4)–O(7)	112·1(6)	C(4′)–C(5′)–C(6′)	114·2(7)
C(5)–C(4)–O(9)	105·3(6)	P′–C(6′)–C(5′)	112·8(6)
O(7)–C(4)–O(9)	111·7(6)	C(4′)–O(7′)–C(8′)	115·6(6)
C(4)–C(5)–C(6)	115·6(7)	C(4′)–O(9′)–C(10′)	115·4(7)
P–C(6)–C(5)	109·2(5)	P′–C(11′)–C(12′)	123·1(6)
C(4)–O(7)–C(8)	115·2(7)	P′–C(11′)–C(16′)	118·7(6)
C(4)–O(9)–C(10)	115·5(8)	C(12′)–C(11′)–C(16′)	118·0(7)
P–C(11)–C(12)	120·4(6)	C(11′)–C(12′)–C(13′)	120·4(8)
P–C(11)–C(16)	118·7(6)	C(12′)–C(13′)–C(14′)	119·5(9)
C(12)–C(11)–C(16)	121·0(7)	C(13′)–C(14′)–C(15′)	120·4(10)
C(11)–C(12)–C(13)	118·5(8)	C(14′)–C(15′)–C(16′)	120·5(10)
C(12)–C(13)–C(14)	119·8(10)	C(11′)–C(16′)–C(15′)	121·3(9)

(*c*) Some intramolecular non-bonded distances

C(3) ··· C(10)	2·90	C(6) ··· C(16)	3·22
C(5′) ··· C(8′)	2·91	C(2′) ··· C(12′)	3·22
C(5) ··· C(8)	2·95	C(6′) ··· C(16′)	3·24
C(3′) ··· C(10′)	2·99	Cl′ ··· C(6′)	3·29
P ··· Cl	3·06	Cl′ ··· C(6)	3·32
P′ ··· Cl	3·07	Cl ··· C(2′)	3·34
P′ ··· Cl′	3·17	C(8′) ··· C(10′)	3·37
C(2) ··· C(12)	3·18	Cl ··· C(2)	3·38
P ··· Cl′	3·21	C(8) ··· C(10)	3·48

(*d*) Intermolecular separations $<3·6$Å

C(2′) ··· O(7$^{\mathrm{I}}$)	3·22	O(7′) ··· C(8^{1})	3·57
O(7′) ··· O(7$^{\mathrm{I}}$)	3·46	C(8′) ··· O(9′$^{\mathrm{II}}$)	3·57
C(16) ··· C(3$^{\mathrm{I}}$)	3·54		

Roman numeral superscripts refer to the following co-ordinate transformations:

I $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ II $-x, 1 - y, -z$

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[8] G. R. Davis, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc.* (*A*), 1967, 1750.

[9] B. T. Kilbourn and H. M. Powell, *J. Chem. Soc.* (*A*), 1970, 1688.

Projections along the nickel–phosphorus bonds are shown in Figure 2; the phosphorus–carbon bonds are rotated by *ca.* 16° from the conformation in which the the phosphorus–carbon (phosphorinan) bonds would be equally inclined to the Cl–Ni–Cl′ direction. While the Ni–P–C and C–P–C angles found in the complex accord with the general pattern that M–P–C angles in tertiary phosphine complexes are greater than tetrahedral (109° 28′) and C–P–C angles are significantly less then this, the Ni–P–C angles in the complex reveal a strong dependence on the Cl–Ni–P–C torsion angles. In discussing the torsion angles we refer to one enantiomer. The greatest non-bonded interaction occurs with P–C(6) and P′–C(6′) bonds for which the mean torsion angle[10] (14°) is smallest, and the corresponding mean Ni–P–C valency angle is the greatest (118·6°). For the P–C(2) and P′–C(2′) bonds the mean torsion angle of —48° leads to a decrease in the non-bonded repulsions, and the mean Ni–P–C valency angle is 115·6°. The least interactions occur with the P–C(11) and P′–C(11′) bonds where the mean torsion angles are 74° and the corresponding mean valency angles 111·4°. Similar M–P–C bond-angle distortions which may be ascribed to non-bonded interactions have been noted in other complexes.[1,9,11]

TABLE 3

Displacements (Å) of the atoms from various planes

Plane (1): Ni, Cl, Cl′, P, P′
Ni −0·01, Cl −0·02, Cl′ −0·01, P 0·02, P′ 0·02

Plane (2): P, C(11)—(16)
P −0·01, C(11) 0·00, C(12) 0·01, C(13) 0·00, C(14) −0·01, C(15) 0·00, C(16) 0·01

Plane (3): P′, C(11′)—(16′)
P′ −0·02, C(11′) 0·03, C(12′) 0·01, C(13′) −0·01, C(14′) 0·00, C(15′) −0·01, C(16′) 0·00

Plane (4): C(2), C(3), C(5), C(6)
C(2) 0·01, C(3) −0·01, C(5) 0·01, C(6) −0·01, P 0·91, C(4) −0·67, C(11) 0·38

Plane (5): C(2′), C(3′), C(5′), C(6′)
C(2′) 0·01, C(3′) −0·01, C(5′) 0·01, C(6′) −0·01, P′ 0·78, C(4′) −0·69, C(11′) 2·50

This analysis yields not only the first determination of the dimensions for complexed phosphorinan ligands, but also provides geometric details for a phosphorinan ring with an equatorial *P*-phenyl substituent, although the geometry will probably be modified to some extent from that of the free ligand. However, the magnitude of this change may be assessed by comparing the geometry of the complexed axial-phenyl conformer with that already established[3] for (2), when this difference is found to be small.

Torsion angles for the phosphorinan rings of (2) and (3) are shown in Figure 3. The values show that the phosphorinan ring preferentially adopts a chair conformation with considerably more puckering at phosphorus in the equatorial-phenyl conformer than in the axial-phenyl conformer. Moreover, the valency angles at the α-carbon atoms differ significantly when the phenyl is axial (mean 113·7°) to the ring and when it is equatorial (mean 110·5°). The torsion angles for the axial conformers in (2) and (3) are similar, and there is a small, but significant, increase in the C–P–C angles in the complexed axial-phenyl conformer over those found for the free ligand (2). It therefore seems reasonable to assume that similar small changes occur at the C–P–C angles in the complexed and free equatorial-phenyl conformer. The mean exo- and endo-cyclic angles at phosphorus in the complex are 104·9 and 99·9°, and there is no significant difference between the means for each ligand. For (2), the corresponding values are 102·3 and 97·7°. The larger C–P–C angles found in the complex compared with those for (2) result in a decrease of phenyl ring–hydrogen 1,3-diaxial interactions in the axial-phenyl ligand, and the phosphorus atom lies in the phenyl ring plane. This latter observation contrasts with the marked phosphorus-atom displacements of 0·11 and 0·29 Å from the corresponding planes in (1) and (2).

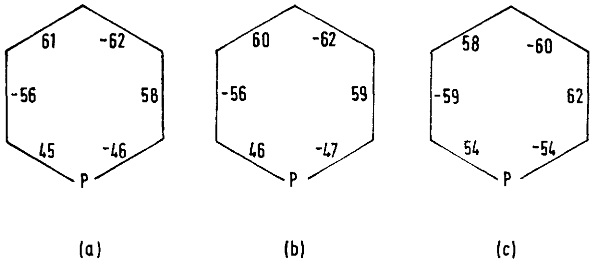

FIGURE 3 Torsion angles (°) in the phosphorinan rings of (2) and (3): (a) free ligand (2); (b) axial-phenyl conformer in (3); and (c) equatorial-phenyl conformer in (3)

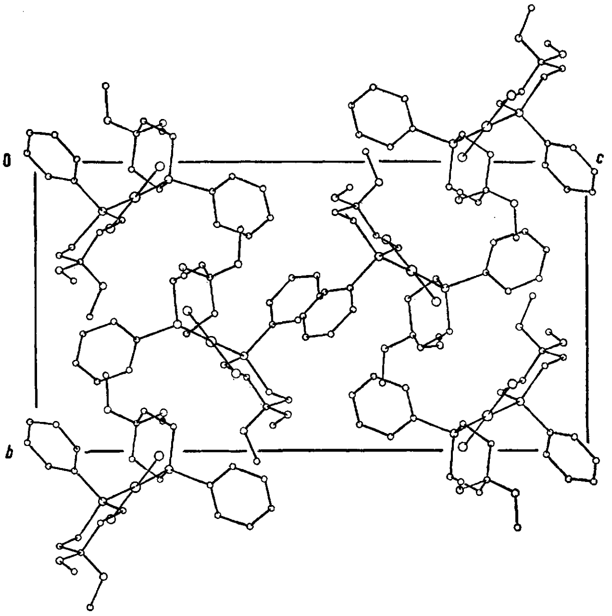

FIGURE 4 Crystal structure viewed in projection on (100)

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[10] W. Klyne and V. Prelog, *Experientia*, 1960, **16**, 521.

The mean P–C(sp^3) and P–C(Ph) distances are 1·836 and 1·820 Å, within the normal ranges for such bonds.[11,12] The mean C(sp^3)–C(sp^3), aromatic C–C bond lengths, and C(sp^3)–O distances (1·531, 1·390, and 1·431 Å) are in good agreement with the corresponding accepted values [1·537(5), 1·394(5), and 1·426 Å].[13]

Approximate C_2 molecular symmetry extends over the central portion of the complex, but it is not continued beyond the phosphorinan α-carbon atoms. Inspection of molecular models fails to reveal any increased number of unfavourable non-bonded intramolecular phosphorinan–phosphorinan repulsions when the phosphorus substituents on both ligands are similarly oriented. Thus, we conclude that the complexed ligands show no preference for axial or equatorial orientation of the phenyl substituent, and crystal packing forces may favour the presence of both conformers. In this respect it is of note that the methyl substituent of 4,4-dimethoxy-1-methylphosphorinan does not appear to have a substantial conformational preference.[14]

A view of the molecular packing in the crystal is shown in Figure 4, and the shorter intermolecular separations are listed in Table 2; none of these distances is abnormal.

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