

Structural Investigations of Nickel Complexes. Part I. Crystal and Molecular Structure of *cis*-Dichlorobis(1-benzyl- Δ^3 -phospholen)nickel(II)

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The crystal and molecular structure of the title compound has been determined by single-crystal X-ray analysis with 3112 independent reflections and refined to R 0.095. The crystals are monoclinic, space-group $P2_1/c$, with $a = 10.40(2)$, $b = 12.91(2)$, $c = 18.00(3)$ Å, $\beta = 112.67(10)^\circ$; $Z = 4$. The molecule has approximate C_2 symmetry and co-ordination around the nickel atom is tetrahedrally distorted square planar with mean Cl–Ni–P angles of 164.7° . A high *trans*-influence of the tertiary phosphine ligands is noted in the complex. The mean Ni–P [2.154(2) Å] and Ni–Cl [2.212(2) Å] bond lengths are respectively 0.12 shorter and 0.05 Å longer than the corresponding values derived from the sum of the covalent radii. The phospholen rings are puckered, mean C–P–C angle $94.0^\circ \pm 0.4^\circ$, and the mean phosphorus atom displacement from the best plane through the ring carbon atoms is 0.385 Å.

FOUR-CO-ORDINATE nickel(II) complexes of general formula $NiX_2(PR_3)_2$ ($X = Cl, Br, \text{ or } I$; $R = \text{alkyl or aryl}$) have been the subject of numerous investigations.^{1–3} Many of these complexes have been characterized by their magnetic and spectroscopic properties, and some of their detailed structures have been elucidated by single-crystal X-ray analysis.^{4–10} In general, dark red dichloro-complexes have been found to be square planar in their nickel-atom co-ordination, but an exception to the use of colour as a means of classification has been noted.⁹ With unidentate ligands the *trans*-configuration is adopted most frequently. We have subjected dichlorobis(1-benzyl- Δ^3 -phospholen)nickel(II) to single-crystal X-ray analysis in order to examine the geometry around the nickel atom and to obtain molecular parameters for the heterocyclic ligand which is a liquid (b.p. $80\text{--}82^\circ$) at room temperature. The less frequently encountered *cis* square-planar ligand configuration which occurs in this complex permits an estimate of the *trans*-influence of the tertiary phosphine ligand on the nickel-chlorine bonds.

EXPERIMENTAL

Preparation.—The addition, in one portion, of a solution of anhydrous nickel chloride (0.13 g, 1.00 mmol) in absolute ethanol (15 ml) to 1-benzyl- Δ^3 -phospholen¹¹ (0.32 g, 1.82 mmol) in absolute ethanol (10 ml) produced a dark red solution which was subsequently stirred for 44 h. Removal of the ethanol yielded a dark red solid (0.35 g), m.p. $139\text{--}141^\circ\text{C}$, which was recrystallized from the minimum of ethanol to give dark red crystals (0.18 g), m.p. $146\text{--}148^\circ\text{C}$.

Crystal Data.— $C_{22}H_{26}Cl_2NiP_2$, $M = 481.7$, Monoclinic, $a = 10.40(2)$, $b = 12.91(2)$, $c = 18.00(3)$ Å, $\beta = 112.67(10)^\circ$, $U = 2230$ Å³, $D_m = 1.45$, $Z = 4$, $D_c = 1.44$, $F(000) = 1000$. Space-group $P2_1/c(C_{2h}^5)$ from systematic absences:

$h0l$ when $l \neq 2n$, $0k0$ when $k \neq 2n$. Cu- K_α radiation, $\lambda = 1.542$ Å; $\mu(\text{Cu-}K_\alpha) = 47.5$ cm^{−1}.

Crystallographic Measurements.—Unit-cell dimensions were evaluated from rotation photographs taken with Cu- K_α radiation and from precession photographs taken with Mo- K_α radiation ($\lambda = 0.7107$ Å). Intensity data for the $0\text{--}9kl$ layers were recorded by the equi-inclination multiple-film Weissenberg method with Cu- K_α radiation. The intensities were estimated visually and were corrected for spot-shape, Lorentz, polarization, and rotation factors. In all, 3112 independent structure-amplitudes were derived.

Structure Analysis.—Initial co-ordinates for the nickel atom were obtained from the three-dimensional Patterson map. With the assumption that the phosphorus and chlorine atoms were in a nearly square-planar arrangement around the nickel atom, several possible sets of trial co-ordinates were derived for these atoms. For each of these sets, however, R was ca. 0.6 when structure-factors were calculated. A three-dimensional nickel-phased F_o Fourier synthesis was then computed and this clearly revealed that the phosphorus and chlorine atoms deviated by substantial amounts from a regular square-planar geometry. Inclusion of the phosphorus and chlorine atoms, all weighted as chlorine, in the next structure-factor calculation reduced R to 0.40. A subsequent three-dimensional F_o Fourier synthesis computed with the improved phase constants enabled the carbon atoms to be placed and permitted identification of the chlorine and phosphorus atoms which were appropriately weighted in all later calculations. For structure-factors calculated with all non-hydrogen atoms included, R was 0.23.

The positional and isotropic thermal parameters were then adjusted by three cycles of full-matrix least-squares calculations which reduced R to 0.144. Further refinement during which the nickel, chlorine, and phosphorus atoms were allowed to assume anisotropic temperature factors resulted in R 0.099 after five cycles. Approximate positions for the hydrogen atoms were then calculated using appropriate

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ate angles and assuming C-H 1.07 Å. All 26 hydrogen atoms were found to lie in positive regions of the difference electron-density map, and they were then included in the

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) and thermal parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	$B/\text{\AA}^2$
Ni	2724(1)	1024(1)	192(1)	*
Cl	1948(3)	1186(2)	-1135(1)	*
Cl'	2529(3)	-678(1)	164(1)	*
P	2882(2)	914(1)	1418(1)	*
P'	3442(2)	2594(1)	225(1)	*
C(1)	1406(10)	210(7)	1494(5)	3.57(15)
C(2)	1175(11)	741(8)	2188(6)	4.21(18)
C(3)	1796(9)	1633(7)	2446(5)	3.47(15)
C(4)	2719(8)	2037(6)	2022(4)	2.51(12)
C(5)	4457(9)	244(7)	2123(5)	3.27(14)
C(6)	5746(8)	877(5)	2319(4)	2.40(11)
C(7)	6217(9)	1530(7)	2990(5)	3.33(14)
C(8)	7372(11)	2158(8)	3158(6)	4.31(18)
C(9)	8084(12)	2137(9)	2638(7)	5.20(22)
C(10)	7629(11)	1522(8)	1972(6)	4.42(19)
C(11)	6478(9)	888(7)	1816(5)	3.37(15)
C(1')	4637(9)	2740(7)	-304(5)	3.27(14)
C(2')	5649(10)	3565(7)	180(5)	3.71(16)
C(3')	5639(9)	3820(6)	876(5)	3.18(14)
C(4')	4627(7)	3271(5)	1140(4)	2.37(11)
C(5')	2036(8)	3562(6)	-250(4)	2.43(11)
C(6')	1166(7)	3676(5)	238(4)	2.25(11)
C(7')	1393(8)	4482(6)	787(4)	2.58(12)
C(8')	629(9)	4553(6)	1267(5)	3.27(14)
C(9')	-388(10)	3828(8)	1204(6)	4.19(18)
C(10')	-650(9)	3022(6)	630(5)	3.14(14)
C(11')	142(8)	2948(6)	186(4)	2.62(12)
H(1 α) [†]	53	28	93	5.0
H(1 β)	168	-59	161	5.0
H(2)	178	100	190	5.0
H(3)	196	129	198	5.0
H(4 α)	374	225	243	5.0
H(4 β)	226	266	162	5.0
H(5 α)	426	7	265	5.0
H(5 β)	453	-47	183	5.0
H(7)	571	153	335	5.0
H(8)	769	263	364	5.0
H(9)	891	259	276	5.0
H(10)	815	153	161	5.0
H(11)	616	43	133	5.0
H(1' α)	512	201	-31	5.0
H(1' β)	404	298	-92	5.0
H(2')	634	394	0	5.0
H(3')	633	437	121	5.0
H(4' α)	402	379	133	5.0
H(4' β)	511	271	159	5.0
H(5')	254	428	-28	5.0
H(6')	144	329	-85	5.0
H(7')	212	500	84	5.0
H(8')	80	512	164	5.0
H(9')	-37	383	121	5.0
H(10')	-138	250	58	5.0
H(11')	-3	238	-19	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:

	$10^4 \cdot b_{11}$	$10^5 \cdot b_{22}$	$10^5 \cdot b_{33}$	$10^5 \cdot b_{12}$	$10^5 \cdot b_{13}$	$10^5 \cdot b_{23}$
Ni	63(1)	261(6)	198(3)	-51(13)	317(9)	-52(7)
Cl	143(3)	517(11)	195(5)	-103(29)	391(17)	-138(12)
Cl'	163(3)	298(9)	409(9)	-240(26)	684(21)	-140(13)
P	53(2)	326(8)	199(5)	21(19)	294(13)	74(11)
P'	49(2)	269(8)	168(4)	-4(18)	273(12)	-11(10)

[†] Hydrogen-atom co-ordinates $\times 10^3$.

structure-factor calculations at their computed positions but were not refined. When structure-factors were cal-

culated R decreased to 0.095. Two further least-squares iterations on all the non-hydrogen atom parameters brought the refinement to convergence. The final value of R is 0.095.

Theoretical atomic scattering factors for neutral atoms,¹² uncorrected for anomalous dispersion effects, were employed

TABLE 2

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

(a) Bonded distances			
Ni-Cl	2.216(2)	Ni-Cl'	2.205(2)
Ni-P	2.155(2)	Ni-P'	2.153(2)
P-C(1)	1.833(10)	P'-C(1')	1.844(9)
P-C(4)	1.857(8)	P'-C(4')	1.852(7)
P-C(5)	1.855(9)	P'-C(5')	1.863(7)
C(1)-C(2)	1.524(14)	C(1')-C(2')	1.515(13)
C(2)-C(3)	1.314(14)	C(2')-C(3')	1.301(13)
C(3)-C(4)	1.530(12)	C(3')-C(4')	1.489(12)
C(5)-C(6)	1.492(12)	C(5')-C(6')	1.492(11)
C(6)-C(7)	1.397(11)	C(6')-C(7')	1.392(10)
C(6)-C(11)	1.390(12)	C(6')-C(11')	1.396(11)
C(7)-C(8)	1.383(14)	C(7')-C(8')	1.383(12)
C(8)-C(9)	1.400(16)	C(8')-C(9')	1.384(13)
C(9)-C(10)	1.361(16)	C(9')-C(10')	1.415(13)
C(10)-C(11)	1.387(14)	C(10')-C(11')	1.354(12)
(b) Some intermolecular nonbonded distances			
Cl...P'	2.96	C(4)...C(4')	3.38
P...Cl'	2.97	C(4)...C(7')	3.44
Cl...Cl'	3.24	C(4')...C(7')	3.54
P...P'	3.26	C(4)...C(11')	3.56
C(4)...C(6)	3.34	C(4')...C(11)	3.58
C(4')...C(6')	3.37		
(c) Intermolecular separations < 3.7 Å			
C(7')...C(7 ^{III})	3.45	C(5')...C(8 ^{IV})	3.61
C(6')...C(8 ^{II})	3.49	C(2')...C(11 ^{III})	3.68
C(6')...C(7 ^I)	3.51	C(8)...C(11 ^{IV})	3.68
Cl(2)...C(10 ^{III})	3.59	C(7')...C(8')	3.69

Roman numeral superscripts refer to the following coordinate transformations:

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

(d) Valency angles

Cl-Ni-P'	85.4(1)	Cl'-Ni-P	85.9(1)
Cl-Ni-Cl'	94.4(1)	P-Ni-P'	98.3(1)
Cl-Ni-P	164.3(1)	Cl'-Ni-P'	165.1(1)
Ni-P-C(1)	111.9(3)	Ni-P'-C(1')	112.2(3)
Ni-P-C(4)	124.0(2)	Ni-P'-C(4')	125.0(2)
Ni-P-C(5)	115.5(3)	Ni-P'-C(5')	114.6(2)
C(1)-P-C(4)	94.4(4)	C(1')-P'-C(4')	93.5(4)
C(1)-P-C(5)	105.2(4)	C(1')-P'-C(5')	105.2(4)
C(4)-P-C(5)	102.7(4)	C(4')-P'-C(5')	103.1(3)
P-C(1)-C(2)	103.8(6)	P'-C(1')-C(2')	103.4(6)
C(1)-C(2)-C(3)	118.2(9)	C(1')-C(2')-C(3')	118.0(8)
C(2)-C(3)-C(4)	116.1(8)	C(2')-C(3')-C(4')	117.1(8)
P-C(4)-C(3)	104.0(5)	P'-C(4')-C(3')	104.6(5)
P-C(5)-C(6)	112.5(6)	P'-C(5')-C(6')	110.0(5)
C(5)-C(6)-C(7)	121.3(7)	C(5')-C(6')-C(7')	121.2(6)
C(5)-C(6)-C(11)	121.3(7)	C(5')-C(6')-C(11')	121.0(6)
C(7)-C(6)-C(11)	117.4(7)	C(7')-C(6')-C(11')	117.8(7)
C(6)-C(7)-C(8)	121.9(8)	C(6')-C(7')-C(8')	120.9(7)
C(7)-C(8)-C(9)	118.8(9)	C(7')-C(8')-C(9')	120.5(8)
C(8)-C(9)-C(10)	120.4(11)	C(8')-C(9')-C(10')	118.9(9)
C(9)-C(10)-C(11)	120.2(10)	C(9')-C(10')-C(11')	119.4(8)
C(6)-C(11)-C(10)	121.4(8)	C(6')-C(11')-C(10')	122.4(7)

in all the structure-factor calculations. For the least-squares calculations the weighting scheme $\sqrt{w} = 1$ for $|F_o| \leq 19.0$ and $\sqrt{w} = 19.0/|F_o|$ for $|F_o| > 19.0$ was used,

¹² 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

and this gave a satisfactory analysis of $\langle w\Delta^2 \rangle$ over ranges of $|F_o|$ and $\sin \theta$.*

TABLE 3

Displacements (\AA) of relevant atoms from selected planes. Atoms not included in the derivation of the plane are italicized

Plane (A):

Cl 0.289, Cl' -0.288, P 0.289, P' -0.288, Ni 0.009

Plane (B):

C(1) 0.002, C(2) -0.005, C(3) 0.005, C(4) -0.002, P -0.388, Ni 0.623

Plane (C):

C(1') 0.001, C(2') -0.001, C(3') 0.001, C(4') 0.000, P' -0.382, Ni 0.617

Plane (D):

C(6) -0.004, C(7) 0.004, C(8) 0.002, C(9) -0.008, C(10) 0.009, C(11) -0.003, C(5) 0.069, C(4') 3.463

Plane (E):

C(6') 0.000, C(7') -0.008, C(8') 0.003, C(9') 0.010, C(10') -0.019, C(11') 0.014, C(5') 0.060, C(4) 3.431

Plane (F):

Ni 0.000, Cl 0.000, Cl' 0.000, P 0.584, P' -0.553

Plane (G):

Ni 0.000, P 0.000, P' 0.000, Cl 0.585, Cl' -0.546

Angles ($^\circ$) between plane normals:

(A)-(B)	40.0	(B)-(E)	9.3
(A)-(C)	40.7	(C)-(D)	10.3
(A)-(D)	50.1	(C)-(E)	18.6
(A)-(E)	18.6	(D)-(E)	13.7
(B)-(C)	17.8	(F)-(G)	20.4
(B)-(D)	18.4		

RESULTS AND DISCUSSION

Final atomic positional and thermal parameters together with their standard deviations are listed in Table 1. Views of the molecular conformation are shown in Figures 1 and 2 with the atomic numbering scheme being given in the former. Interatomic distances and valency angles are provided in Table 2. The packing of molecules is illustrated by Figure 3; there are no abnormally short intermolecular separations. Deviations of selected atoms from the best planes calculated through various groups of atoms are given in Table 3.

The crystal comprises discrete molecular units which have approximate C_2 symmetry, and the geometry around the nickel atom is best described as tetrahedrally-distorted square planar. There are significant deviations from ideal angles of 90° subtended at the nickel atom. Enlargement of the Cl-Ni-Cl' and P-Ni-P' angles to 94.4 and $98.3 \pm 0.1^\circ$, respectively, may be ascribed to ligand-ligand repulsions which would be expected to be greater between the bulkier phospholen ligands than between the chlorine atoms. The nickel atom lies close ($\Delta 0.009 \text{ \AA}$) to the plane calculated through the phosphorus and chlorine atoms which are essentially

all equidistant ($\Delta \pm 0.29 \text{ \AA}$) from this plane. The Cl-Ni-P and Cl'-Ni-P' angles of 164.3 and $165.1 \pm 0.1^\circ$, depart significantly from ideal linear geometry. A number of X-ray structure determinations have revealed that low-spin four-co-ordinate nickel(II) complexes exist

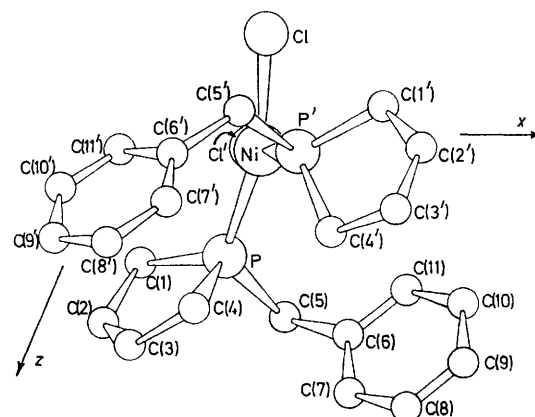


FIGURE 1 The molecular structure viewed in projection along b

preferentially with either perfectly planar or slightly distorted planar geometry about the nickel atom. Highly significant deviations from linearity have been observed with bidentate ligands in biacetylbis(mercaptoethyl-imine)nickel(II),¹³ 173° , and di-iodo[ethylenebis(oxyethylene)]bis(diphenylphosphine)nickel(II)¹⁴ where

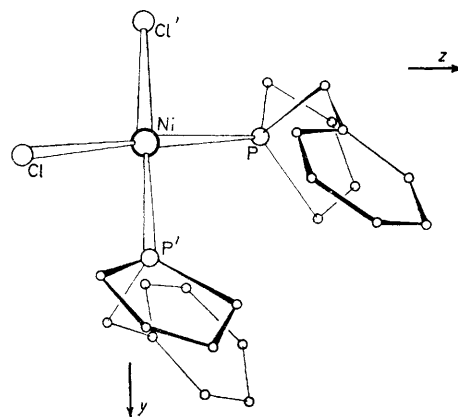


FIGURE 2 The molecular structure viewed in projection along a

I-Ni-I is 162.1° and P-Ni-P 143.5° . The deviations noted in the present work are the largest yet found where unidentate ligands are involved. Further evidence for the severity of the non-bonded phospholen-phospholen interactions is contained in the pattern of angles around the phosphorus atoms where mean Ni-P-C(4) and Ni-P'-C(4') angles are 124.5° in contrast to Ni-P-C(1) and Ni-P'-C(1') angles, mean 112.1° . In the absence

* Observed and calculated structure-factors are listed in Supplementary Publication No. SUP 20304 (18 pp., 1 microfiche). For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

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¹⁴ P. Dapporto and L. Sacconi, *J. Chem. Soc. (A)*, 1971, 1914.

of non-bonded intramolecular repulsions the exocyclic Ni-P-C angles would be expected to be approximately equal.

The mean Ni-P and Ni-Cl bond lengths are 2.154(2) and 2.212(2) Å. The former distance is significantly shorter than the Ni-P length of 2.250(2) Å in square-planar *trans*-dichlorobis(1-phenyl-4,4-dimethoxyphosphorinan)nickel(II)¹⁵ while the Ni-Cl distance is significantly longer than the corresponding length [2.171(2) Å]

is 2.287(2) Å, whereas in *cis*-Pd(PMe₂Ph)₂Cl₂²⁰ the Pd-P and Pd-Cl lengths are 2.260(2) and 2.362(Å). In *trans*-Pt(PEt₃)₂Cl₂²¹ Pt-P is 2.298(2) Å and Pt-Cl 2.294(9) Å while in *cis*-Pt(PMe₃)₂Cl₂²² the corresponding distances are 2.247(8) and 2.376(9) Å.

The present work represents the first X-ray analysis of a phospholen, either complexed or as the free phosphine. The phospholen rings are puckered with a mean phosphorus atom displacement of 0.385 Å from the mean

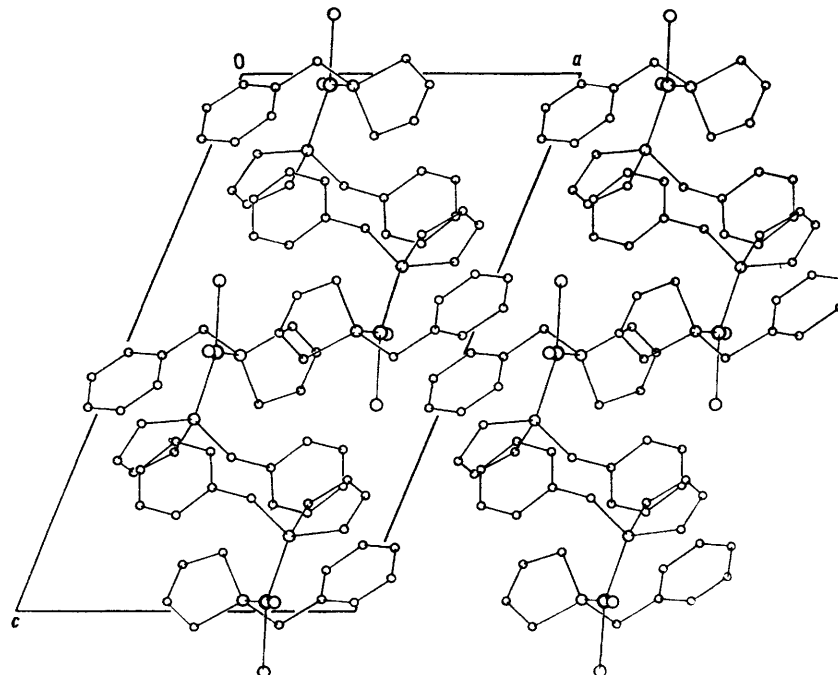


FIGURE 3 The crystal structure viewed in projection along *b*

in this same complex. From the sum of the single-bond covalent radii¹⁶ (taking 1.17 Å as the best estimate for square-planar Ni^{II}, this being the mean of values suggested recently^{9,10}), the predicted lengths would be Ni-P 2.27, Ni-Cl 2.16 Å. Thus the highly significant differences between these values and those found in the present work (Δ Ni-P +0.12, Δ Ni-Cl -0.05 Å) are in the direction which would be expected on the basis of a strong *trans*-influence of the phosphorus which tends to weaken the bond *trans* to it.¹⁷ Similar differences in metal-halogen and metal-phosphorus bond lengths between *cis*- and *trans*-square-planar Pd^{II} and Pt^{II} complexes have been reported. In *trans*-Pd(PMe₂Ph)₂I₂¹⁸ Pd-P is 2.333(7) Å and in *trans*-Pd(Me₂SO)₂Cl₂¹⁹ Pd-Cl

plane through the ring carbon atoms. The C(1)-P-C(4) and C(1')-P'-C(4') angles at 94.4 and 93.5 ± 0.4° do not differ significantly and their mean value, 94.0°, is intermediate between the corresponding internal angles in the doubly unsaturated (phosphole) ring, 90.7° in 1-benzylphosphole¹¹ and 90.5–91.3° in dicyanotris-(5-methyl-5*H*-dibenzophosphole)nickel(II) and dicyanotris-(5-ethyl-5*H*-dibenzophosphole)nickel(II),²³ and the saturated (phospholan) ring value of 96.6° in bis(tetramethylene)diphosphine disulphide.²⁴ The pattern of angles at phosphorus conforms to that generally encountered in other metal-phosphine complexes. All the C-P-C angles (94.4, 105.2, 102.7, 93.5, 105.2, and 103.1°, mean 100.7°) are significantly less than the tetrahedral

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value ($109^{\circ}28'$) while all the Ni-P-C angles (111.9 , 124.0 , 115.5 , 112.2 , 125.0 , and 114.6° , mean 117.2°) exceed this value.

Phosphorus-carbon bond lengths range from 1.833 to 1.863 Å, mean 1.851 , which is close to the sum of the covalent radii¹⁶ (1.87 Å), and not significantly different from the corresponding values reported for other molecules.^{11,15,25} The mean C(sp^3)-C(sp^2) single-bond length, 1.507 Å, and the mean aromatic C-C bond length, 1.387 Å, agree satisfactorily with accepted values.²⁶ The mean carbon-carbon double-bond length in the phospholen ring, 1.308 Å, is not significantly different from that of 1.334 Å in ethylene.²⁷

Atoms C(5) and C(5') are displaced by small amounts from the planes calculated through the carbon atoms of

the phenyl rings to which they are bonded. These deviations presumably arise in order to gain relief from non-bonded interactions between the phenyl groups and the phospholen moieties. The dihedral angle between the planes through C(1)-(4) and C(6')-(11') is 9.3° , and between the planes through C(1')-(4') and C(6)-(11) the corresponding angle is 10.3° .

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