Stereochemistry of Five-co-ordinate Compounds ML_3X_2: Crystal and Molecular Structure of Dichlorotris(5-ethyl-5*H*-dibenzophosphole)-nickel(II)

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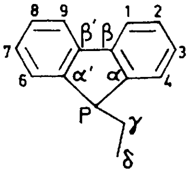
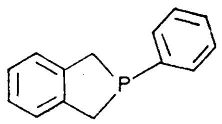
The nickel atom in the title compound is five-co-ordinate. It has a trigonal bipyramidal disposition of its bonds with two chlorine atoms in equatorial positions. This isomeric form is different from the three previously found in eight closely related compounds.

Variation of isomeric form among the compounds ML_3X_2 is related to possible overcrowding of the five immediate atomic neighbours of the metal atom and to other factors. Details concerning particular valency angles in the series are explained by steric effects and an interaction between two of the three aromatic ligands.

In compounds $[ML_3X_2]$ [M = Ni, Pd, or Pt; L = (I) or (II); X = CN or Br][1-3] three different forms of five-co-ordination have been found. One, (*a*), (X = CN), has tetragonal pyramidal metal bonds with one phosphorus atom at the apex and the other two in *trans*-equatorial positions. Another, (*b*), (X = CN), has a trigonal bipyramidal arrangement of metal bonds with three phosphorus atoms occupying equatorial positions. Form (*c*) found for M = Pd or Pt and X = Br has one bromine atom at the apex of a tetragonal pyramid with one bromine and three phosphorus atoms in basal positions. When L = (I) the basal bonds to bromine and the phosphorus atom *trans* to it are considerably below the basal plane through the metal; the other two basal bonds are above this plane. These four bonds point to the corners of a distorted flattened tetrahedron. When L = (II) the disposition of basal bonds is similar except that only one bond to phosphorus is above the plane. The other, *trans* to it, is almost in the plane. The occurrence of these forms of distortion has been related to the non-bonded contact distances X $\cdots$ P and P $\cdots$ P. At suitable M–X and M–P bond distances it becomes impossible to achieve normal X $\cdots$ P or P $\cdots$ P separations without some such distortion. The crystal structure of the title compound was determined in order to find the effect of a diminution in the bonded distances. In this compound distances Ni–P 2.2 and Ni–Cl 2.35 replace Pd–P 2.3 and Pd–Br 2.55 Å. For a hypothetical (*c*) type molecule which has the bond angles of $[PdL_3Br_2]$ [L = (I), R = Et][2] the shortest Cl $\cdots$ P separations have calculated values 3.10 and 3.12 Å, not much less than the minimum estimated for no overcrowding. The non-bonded distances P $\cdots$ P for adjacent atoms are 3.31 and 3.18 Å. Both these are less than the value 3.48 Å deduced as the minimum for no overcrowding; the second is also noticeably less than the minimum so far observed in any molecule of the series, including those known to be overcrowded. It seemed possible that some other stereochemical form would be preferred to type (*c*), if this obviated the short P $\cdots$ P distance.



(I)



(II)

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[1] H. M. Powell, D. J. Watkin, and J. B. Wilford, *J. Chem. Soc.* (*A*), 1971, 1803.

[2] K. M. Chui and H. M. Powell, *J.C.S. Dalton*, 1974, 1879.

[3] K. M. Chui and H. M. Powell, *J.C.S. Dalton*, 1974, 2117.

Figure 1 shows an asymmetric unit of the structure and Table 1 summarises the stereochemistry of the nickel atom. The metal bond angles are those of a trigonal bipyramidal arrangement with two chlorine atoms in equatorial positions; P(I) and P(III) are axial and P(II) equatorial. This type, different from those enumerated earlier, is designated form (*d*). Deviations of the equatorial angles from the ideal 120° are small (6.6, 7.4, and 0.8°). There is little difference between the axial and equatorial nickel–phosphorus bond lengths. As in all members of the ML_3X_2 series [L = (I)], ligands L(II) and L(III) defined by the condition P(II)–M–P(III) < P(I)–M–P(III) have their aromatic systems approximately parallel plane-to-plane and overlapping with a mean separation (3.51 Å) which is in the range found for aromatic molecular complexes. An attractive interaction between them results in the angle A [P(II)–Ni–P(III)] being smaller than the otherwise stereochemically equivalent angle B [P(II)–Ni–P(I)]. The difference (3.4°) is comparable with those already reported. The observation strengthens the previous conclusion that this interaction occurs whatever the basic stereochemical form.

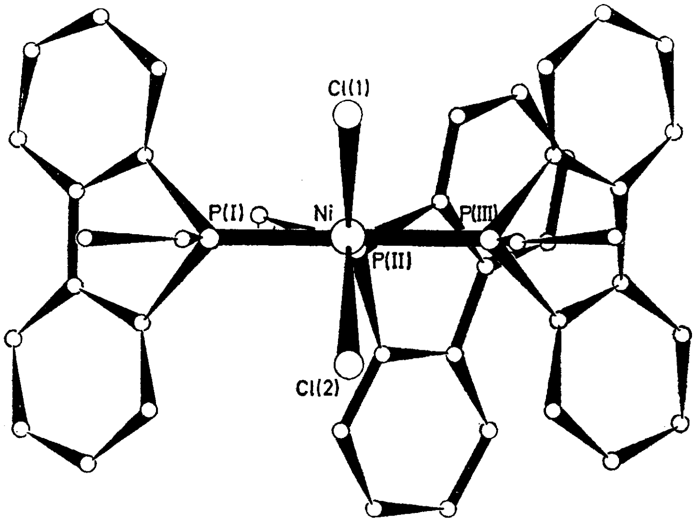

FIGURE 1 The molecule $[NiL_3Cl_2]$ {L = (I), R = Et} projected on to the best plane through the atoms C(α,1), C(α′,I), C(α,III), and C(α′,III)

TABLE 1

Bond lengths (Å) and angles (°) at the nickel atom, with estimated standard deviations in parentheses

(*a*) Bond lengths			
Ni–P(I)	2.210(2)	Ni–Cl(1)	2.344(2)
Ni–P(II)	2.192(2)	Ni–Cl(2)	2.350(3)
Ni–P(III)	2.206(2)		
(*b*) Bond angles			
P(I)–Ni–P(II)	98.18(8)	Cl(1)–Ni–P(III)	87.13(8)
P(I)–Ni–P(III)	166.96(9)	Cl(2)–Ni–P(I)	85.88(8)
P(II)–Ni–P(III)	94.80(9)	Cl(2)–Ni–P(II)	119.17(9)
Cl(1)–Ni–P(I)	85.96(8)	Cl(2)–Ni–P(III)	86.75(8)
Cl(1)–Ni–P(II)	127.43(9)	Cl(1)–Ni–Cl(2)	113.40(9)

In view of the interaction, the nickel stereochemistry is referred to an equatorial plane defined by the nickel atom and the two chlorine atoms. The +*Z* axis in the direction of P(III) is taken through the nickel atom and perpendicular to the plane, the bisector of the Cl–Ni–Cl angle defines the *X* axis, and the *Y* axis is perpendicular to *X* and *Z* in a right-handed system. The nickel bonds are described (Table 2) by an angle θ between the bond and *Z*, and an angle φ between the *XZ* plane and that containing the bond and the *Z* axis. For an ideal trigonal bipyramid the values in parentheses would apply. Some of the differences from ideal values are explained by the requirements of a minimum non-bonded distance P · · · P. This, even more than in the palladium and platinum compounds, requires P–M–P >90°. On the assumption of P · · · P 3.48 and Ni–P 2.20 Å the angle calculated is 104°. The ligand–ligand attraction will diminish angle P(II)–Ni–P(III) so that the values 104 and 100° might be predicted for those which are observed to be 98 and 95°. However, such bond angles diminish the distances between equatorial Cl atoms and axial phosphorus atoms P(I) and P(III). On the basis of Ni–P 2.2, Ni–Cl 2.345, and P · · · Cl estimated as 3.16 Å the angles Cl–Ni–P should be 88°. This would permit P–Ni–P angles very little greater than 90°. The observed angles must compromise between the two requirements. Lack of symmetry about the equatorial plane is caused by the ligand–ligand interaction.

TABLE 2

Angles defining nickel bond positions

	θ/°	φ/°
Cl(1)	90 (90)	303.3 (300)
Cl(2)	90 (90)	56.7 (60)
P(I)	172.7 (180)	0 (0)
P(II)	89.3 (90)	176.0 (180)
P(III)	5.4 (0)	0 (0)

This molecule cannot have the form and bond angles of $[NiL_3(CN)_2]$, [L = (I), R = Me[1]], in either (*a*) or (*b*) form for reasons similar to those applicable to $[Pt(Pd)L_3Br_2]$ [2,3] in which there would be steric difficulties between bromine atoms and the carbon atoms of L.

Occurrence of the new form (*d*) supports the conclusion that these steric difficulties cannot be alleviated by conformational changes and small changes of the nickel valency angles of forms (*a*) or (*b*). The non-bonded P · · · P and P · · · Cl distances in the observed form (*d*) are shown with those for a hypothetical form (*c*) in Table 3. In the hypothetical form the valency angles of $[PdL_3Br_2]$ (R = Et) are used with nickel–ligand distances of the title compound. The P · · · P distances observed in form (*d*) are, like the calculated values for (*a*), shorter than the 3.48 Å referred to earlier as the minimum for no overcrowding. The distance P(I) · · · P(II) (3.33 Å) is not less than the lowest value previously observed in an overcrowded molecule in the series, but the distance P(II) · · · P(III) (3.24 Å) is a new lowest value. For the hypothetical form (*c*) P(II) · · · P(III) has to be even lower (by 0.05 Å). This is now taken to be the critical factor excluding stereochemistry (*c*) for this compound.

TABLE 3

Non-bonded distances (Å) in observed and hypothetical forms of $[NiL_3Cl_2]$ (R = Et)

	P(I) · · · P(II)	P(II) · · · P(III)	P(I) · · · P(III)	Cl(2) · · · P(I)	Cl(2) · · · P(II)
(1) Hypothetical form (*c*)	3.321	3.185	4.394	3.443	4.028
(2) Real form (*d*)	3.327	3.237	4.387	3.108	3.918
Difference (1) − (2)	−0.006	−0.052	0.007	0.335	0.110
	Cl(2) · · · P(III)	Cl(1) · · · P(1)	Cl(1) · · · P(III)	Cl(1) · · · P(II)	Cl(1) · · · Cl(2)
(1) Hypothetical form (*c*)	3.402	3.111	3.126	4.358	4.006
(2) Real form (*d*)	3.131	3.106	3.137	4.068	3.923
Difference (1) − (2)	0.271	0.005	−0.011	0.290	0.083

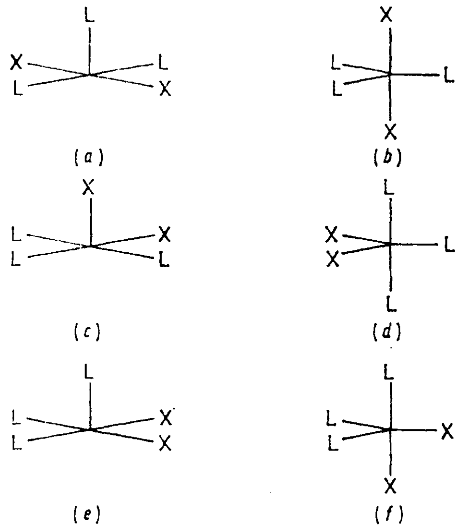

FIGURE 2 Isomeric forms of $[ML_3X_2]$

Form and Disposition of Ligands.—The ligand has the same form as previously reported, including the slight inclination to butterfly form. In accordance with the definitions in ref. 1 the relative positions of L(II) and L(III) are described by an angle of inclination of 4° 22′, a mean separation of 3.51 Å, and an angle of twist of 23° 25′.

Stereochemical Form in the Series ML_3X_2.—Determination of this structure brings the number of geometrical variants to four. The variants are basically the forms (*a*)—(*d*) shown in Figure 2 of the six tetragonal pyramidal or trigonal bipyramidal isomers of ML_3X_2. Figure 2 shows the relative positions of ligands L and X. Although angles of 90 or 120° between adjacent bonds are drawn, the descriptions (*a*)—(*f*) are intended to cover cases where the angles differ from these values within a certain range, *e.g.* where a tetragonal pyramid is recognisable and the angles α between apical and basal bond lie in a range 85—112°. The known forms for particular compounds are summarised in Table 4.[1-4]

TABLE 4

Ligand L = (I) with R as indicated, except for L = (II)

R	CN	Cl	Br
Ni	(*b*) Me3;[a] Et3[a] (*a*) Me4[a]	(*d*) Et	(*d*) Et[b] Me[b]
Pd			(*c*) Et;[c] L = (II)[d]
Pt			(*c*) Me;[c] Et[c]

[a] Ref. 1. [b] Ref. 4. [c] Ref. 2. [d] Ref. 3.

In the absence of steric difficulties forms (*a*) and (*b*) are observed. Of the six isomers, these give the greatest separation of the more electronegative X ligands and, for this reason, are taken to be the most stable forms. Some theoretical considerations relating to simpler AB_5 complexes (B monatomic) suggest almost equal stability for the trigonal bipyramid and the tetragonal pyramid with angle α of *ca.* 105°. Existence of the allogon isomers of $[NiL_3(CN)_2]$ (R = Me) as forms (*a*), Me4, with α in the range 98—112° and (*b*), Me3, shows empirically that there is little difference in stability. The allogons show two ways in which the aromatic ligands can be arranged, and interconversion is sterically possible. This implies that some variation in the disposition of the ligands is also sterically possible. When the small change of Me to Et is made, which means no variation in the five central bonds, there is no change in stereochemistry; the trigonal bipyramidal Et3 is very similar to Me3 (so far attempts to obtain the form Et4 have failed). All other molecules listed in Table 4

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[4] D. J. Watkin, personal communication.

differ significantly from these cyanides in the five central bonds. None has form (*a*) or (*b*).

Steric difficulties between a large X and carbon atoms of the bulky L prevent the formation of (*a*) or (*b*). In this case the forms obtained are (*c*) or (*d*) which give the next largest X $\cdots$ X separation; for (*c*) the separation is increased relative to those in (*e*) and (*f*) by the elongation (*ca.* 0.5 Å) of the apical bond and the relatively large X–M–X angle. The steric difficulty between X and L does not disfavour either (*c*) or (*d*) relative to the other. The minimum observed C $\cdots$ Br separation in $[PdL_3Br_2]$ [L = (I), R = Et], form (*c*), is 3.80 Å. A hypothetical form (*d*) for this compound with the valency angles observed for $[NiL_3Cl_2]$ (the title complex) has minimum C $\cdots$ Br 3.72 Å. This is slightly less than in the (*c*) form but larger than the observed C $\cdots$ Br in the analogous compound with R = Me, and therefore cannot be regarded as excluding form (*d*).

TABLE 5

Non-bonded distances (Å) in observed and hypothetical forms of $[PdL_3Br_2]$ (R = Et)

	P(I) $\cdots$ P(II)	P(II) $\cdots$ P(III)	P(I) $\cdots$ P(III)	Br(2) $\cdots$ P(I)	Br(2) $\cdots$ P(II)
(1) Real form (*c*)	3.508	3.329	4.635	3.673	4.266
(2) Hypothetical form (*d*)	3.514	3.384	4.628	3.348	4.184
Difference (1) − (2)	−0.006	−0.055	+0.007	+0.325	+0.082

	Br(2) $\cdots$ P(III)	Br(1) $\cdots$ P(I)	Br(1) $\cdots$ P(III)	Br(1) $\cdots$ P(II)	Br(1) $\cdots$ Br(2)
(1) Real form (*c*)	3.601	3.355	3.341	4.659	4.317
(2) Hypothetical form (*d*)	3.341	3.351	3.353	4.349	4.271
Difference (1) − (2)	+0.260	+0.004	−0.012	+0.310	+0.046

Non-bonded separations between the five atoms directly attached to the metal atom may not go much below a value which can be estimated. This factor accounted for tetrahedral-type distortion of the basal bonds in form (*c*). It can also explain the choice of stereochemistry (*c*) or (*d*). Tables 3 and 5 give all non-bonded distances between the five-co-ordinated atoms in $[NiL_3Cl_2]$ and $[PdL_3Br_2]$, respectively, in forms (*d*) and (*c*). For each molecule the observed distances are accompanied by calculated values for a hypothetical molecule which has the stereochemistry of the other. Four of the distances differ insignificantly between (*c*) and (*d*). All others are greater for (*c*) except P(II) $\cdots$ P(III) which is *ca.* 0.05 Å greater for (*d*). Only this last distance could provide a steric explanation of the preference for form (*d*). In $[PtL_3Br_2]$ and $[PdL_3Br_2]$ this distance in both observed and hypothetical forms is well above the empirical shortest P $\cdots$ P in the series. Stereochemistry (*c*) is therefore expected since this gives five significantly larger non-bonded distances including the important X $\cdots$ X distance. For $[NiL_3X_2]$, however, P(II) $\cdots$ P(III) in the hypothetical (*c*) form is considerably less than the estimated minimum and also less than the shortest observed P $\cdots$ P value in the series of compounds. It is concluded therefore that in this case (*c*) is excluded by this particular steric difficulty. Those other non-bonded distances which are favourable for (*c*) are not short enough to exclude (*d*). Though the ligand–ligand interaction has a shortening effect on P(II) $\cdots$ P(III) it cannot be claimed as the sole reason for the adoption of stereochemistry (*d*) since, without it, the distance P(II) $\cdots$ P(III) would still favour (*d*).

The isomers (*e*) and (*f*) do not occur. In form (*e*) where the P–M–P angles should not greatly exceed 90° there are special steric difficulties in attaching the three phosphole ligands. It is assumed that, as in all other members of the series, two ligands will interact and have their aromatic ring systems plane-to-plane. The planes of these rings will be very steeply inclined to the plane containing their two phosphorus atoms and the metal atom. A third ligand approaching for attachment through a bond roughly perpendicular to this plane will be impeded sterically. Whatever its disposition with respect to rotation about the phosphorus–metal bond some of its carbon atoms will be close to some or other of the carbon atoms of the protruding rings of the other two ligands. This consideration precludes the occurrence of form (*e*). When the third ligand is *trans* to one of the others (P–M–P *ca.* 180°) the difficulty does not arise. Angles of *ca.* 120° between all three M–P bonds are also sterically possible, as in form (*b*), if the size of the ligand X permits. In form (*f*) the third ligand should have two angles P–M–P slightly greater than 90° and the other roughly 120°. The steric difficulty in adding the third ligand is less than for form (*e*). It is concluded that the steric difficulty of attaching three ligands L by bonds which depart seriously from the co-planar excludes form (*e*) and strongly disfavours (*f*).

Valency Angles in ML_3X_2.—In the whole series the minimum P $\cdots$ P separation makes the angle P–M–P always greater than 90° and so modifies some of the idealized angles. This leads to the tetrahedral distortion in form (*c*) and to the off-axial directions of M–P bonds in form (*d*). Interaction between the aromatic systems of L(II) and L(III) causes the angle P(II)–M–P(III) to be a few degrees less than the otherwise stereochemically equivalent angle P(II)–M–P(I).

EXPERIMENTAL

Crystal Preparation.—The green powdery material was recrystallized by evaporation of a solution in acetone.

Data Collection.—A green crystal (0.14 × 0.34 × 0.79 mm) was mounted about its needle axis (*a*) and diffraction data collected with Cu radiation on a Hilger and Watts

TABLE 6

Atomic (fractional) co-ordinates for [NiL_3Cl_2], with estimated standard deviations in parentheses

	x/a	y/b	z/c
Ni	−0.131 2(1)	0.278 9(1)	0.270 0(1)
Cl(1)	−0.264 2(2)	0.160 9(1)	0.203 1(1)
Cl(2)	−0.182 7(2)	0.271 7(1)	0.407 7(1)
P(I)	−0.290 7(1)	0.287 2(1)	0.247 6(1)
P(II)	0.030 4(2)	0.389 5(1)	0.218 7(1)
P(III)	−0.007 2(2)	0.246 6(1)	0.306 7(1)
C(α,I)	−0.284 1(6)	0.367 6(3)	0.281 5(4)
C(4,I)	−0.258 7(6)	0.398 1(4)	0.358 7(4)
C(3,I)	−0.260 3(7)	0.460 4(4)	0.372 0(5)
C(2,I)	−0.287 2(7)	0.489 8(4)	0.308 9(5)
C(1,I)	−0.316 0(6)	0.458 3(4)	0.230 9(5)
C(9,I)	−0.369 1(7)	0.373 8(4)	0.066 5(4)
C(8,I)	−0.389 0(8)	0.330 4(5)	−0.001 8(5)
C(7,I)	−0.376 9(8)	0.271 5(5)	0.003 6(5)
C(6,I)	−0.348 4(7)	0.254 8(4)	0.076 8(4)
C(α′,I)	−0.330 9(6)	0.296 8(3)	0.144 6(4)
C(β′,I)	−0.339 8(6)	0.356 5(3)	0.140 3(4)
C(β,I)	−0.314 3(6)	0.396 3(3)	0.217 5(4)
C(γ,I)	−0.444 3(6)	0.204 4(4)	0.292 0(4)
C(δ,I)	−0.562 4(7)	0.203 4(4)	0.277 0(5)
C(α,II)	0.173 3(6)	0.406 3(4)	0.171 0(4)
C(4,II)	0.176 1(7)	0.375 0(4)	0.099 1(4)
C(3,II)	0.298 4(8)	0.402 0(5)	0.067 1(5)
C(2,II)	0.414 3(7)	0.458 9(5)	0.109 9(5)
C(1,II)	0.408 9(6)	0.488 3(4)	0.181 1(4)
C(9,II)	0.358 1(7)	0.544 0(4)	0.342 0(4)
C(8,II)	0.318 6(7)	0.568 3(4)	0.404 3(5)
C(7,II)	0.188 2(8)	0.540 1(4)	0.412 1(5)
C(6,II)	0.092 9(7)	0.484 4(4)	0.357 3(4)
C(α′,II)	0.133 9(6)	0.461 7(3)	0.294 9(4)
C(β′,II)	0.265 2(6)	0.491 0(3)	0.285 1(4)
C(β,II)	0.289 1(6)	0.462 9(3)	0.214 1(4)
C(γ,II)	−0.010 4(7)	0.435 1(4)	0.146 4(5)
C(δ,II)	0.109 1(8)	0.514 2(4)	0.113 6(6)
C(α,III)	0.080 6(6)	0.235 3(4)	0.231 7(4)
C(4,III)	0.030 9(7)	0.188 4(4)	0.162 8(4)
C(3,III)	0.118 5(8)	0.189 4(5)	0.112 4(5)
C(2,III)	0.250 2(8)	0.235 2(5)	0.129 0(5)
C(1,III)	0.300 9(7)	0.281 8(4)	0.196 8(5)
C(9,III)	0.372 0(7)	0.369 3(4)	0.363 3(5)
C(8,III)	0.384 5(8)	0.401 6(5)	0.438 8(5)
C(7,III)	0.275 7(8)	0.389 5(5)	0.477 2(5)
C(6,III)	0.152 4(7)	0.343 4(4)	0.441 3(6)
C(α′,III)	0.140 6(6)	0.310 6(4)	0.365 2(4)
C(β′,III)	0.247 7(6)	0.323 5(4)	0.326 1(4)
C(β,III)	0.214 2(6)	0.280 5(4)	0.250 0(4)
C(γ,III)	−0.103 2(7)	0.157 0(4)	0.364 9(5)
C(δ,III)	−0.025 8(9)	0.127 4(5)	0.387 6(6)

four-circle diffractometer. The ω–θ scan technique [5] was used. Intensities were recorded in the reciprocal regions *hkl* and *h$\bar{k}$l* for θ values up to 62°. Balanced filters were used in the θ range 0—25°. The three monitoring reflexions were 7,0,0, 0,$\bar{3}$,8, and 0,10,$\bar{1}$. Absorption was corrected by use of the intensity curve (I *vs.* ϕ) of the scattering vector 6,$\bar{6}$,0. Altogether 4 711 independent reflexions with $I > 3\sigma(I)$ were collected.

Solution of the Structure.—The direct method for a centrosymmetric structure was used. A set of E values with $|E| > 1.1$ were generated, and were used for a Wilson plot which gave an overall temperature factor B 3.00 Å^2. Only the 662 E values with $|E| > 1.5$ were used for phase determination. The signs were determined in terms of one symbol, *i.e.* two alternative solutions. The more probable solution gave an E map which showed the position of the six heavy atoms. An electron-density map phased on the six heavy atoms gave a solution for the whole complex molecule (hydrogen atoms excluded), and this solution was refined by least-squares methods. Anisotropic refinement terminated at R 0.081 with the root-mean-square (shift to estimated standard deviation) < 0.02. The weighting scheme used was: $w^{\frac{1}{2}} = \{1 + [(|F_0| - P_2)^2/P_1]\}^{-1/2}$, with $P_1 = 30.9$ and $P_2 = 15.4$. Final positional parameters are listed in Table 6; thermal parameters and structure factors have been deposited as Supplementary Publication No. SUP 21634 (27 pp., 1 microfiche).*

Crystal Data.—[$(C_{14}H_{13}P)_3NiCl_2$], $M = 766.00$, Monoclinic, $a = 12.94 \pm 0.02$, $b = 22.14 \pm 0.04$, $c = 16.53 \pm 0.03$ Å, $\gamma = 127.84 \pm 0.02°$, $U = 3\,745$ Å^3; $D_m = 1.37 \pm 0.01$ g cm^{-3}, $Z = 4$, $D_c = 1.36 \pm 0.01$ g cm^{-3}, $F(000) = 3\,184$. Space group $P2_1/b$. Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) 32.95 cm^{-1}.

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, Index issue, 1975.

[5] U. W. Arndt and B. T. M. Willis, ' Single Crystal Diffractometry,' Cambridge University Press, 1966.