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## The Crystal and Molecular Structure of Dicyanotris(phenyldiethoxyphosphine)nickel(II), $\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2)_3$

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The crystal and molecular structure of dicyanotris(phenyldiethoxyphosphine)nickel(II),  $\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2)_3$ , has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques to a final  $R$  factor on  $F$  of 6.9%. The material crystallizes in space group  $\text{C}_2^2\text{-P2}_1$  of the monoclinic system, with two molecules in a cell of dimensions  $a = 19.51$  (3),  $b = 9.90$  (2),  $c = 9.65$  (2) Å, and  $\beta = 96^\circ 29$  (2)'. The calculated density is 1.265 g/cm<sup>3</sup>. The absolute configuration of this crystal was inferred by comparison of intensities of Friedel pairs. The inner coordination about the Ni is intermediate between the two idealized five-coordinate geometries—the trigonal bipyramidal and the tetragonal pyramidal—and is strikingly similar to the geometry about Ni in one of the  $\text{Ni}(\text{CN})_5^{3-}$  ions in  $[\text{Cr}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3][\text{Ni}(\text{CN})_5] \cdot 1.5\text{H}_2\text{O}$ . The Ni and three P atoms are coplanar, with Ni–P bond distances of 2.289 (5), 2.205 (6), and 2.189 (6) Å. The P–Ni–P angle opposite the long Ni–P bond is  $133.5$  (2)°, while the cyanide groups are bent away from this bond with a C–Ni–C angle of  $170.8$  (8)°. The Ni–C distances are 1.87 (2) and 1.89 (2) Å, and the Ni–C–N linkages are linear.

### Introduction

Recently there has been much interest in complexes of the type  $\text{Ni}(\text{CN})_2(\text{PR}_3)_3$ . Five-coordinate complexes have been isolated for  $\text{PR}_3 = \text{P}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2$ ,<sup>1</sup>  $\text{P}(\text{C}_6\text{H}_5)(\text{OCH}_3)_2$  and  $\text{P}(\text{OC}_2\text{H}_5)_3$ ,<sup>2</sup>  $\text{P}(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)_2$ ,<sup>3</sup>  $\text{P}(\text{C}_6\text{H}_5)(\text{CH}_3)_2$ ,<sup>4</sup>  $\text{P}(\text{OCH}_3)_3$ ,  $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ ,  $\text{P}(\text{O}(\text{CH}_2)_3\text{CH}_3)_3$ , and  $\text{P}(\text{OC}_6\text{H}_5)_3$ ,<sup>5</sup> but not for  $\text{PR}_3 = \text{P}(\text{C}_6\text{H}_5)_3$  or  $\text{P}(\text{C}_6\text{H}_5)_2(\text{OC}_2\text{H}_5)$ .<sup>2,5</sup> Molecular orbital calculations<sup>2</sup> have been made for two of these compounds,  $\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2)_3$  and  $\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{OCH}_3)_2)_3$ . For these calculations a trigonal-bipyramidal geometry with axial cyanide groups was assumed, as indicated by the electronic and infrared spectra.<sup>1,2</sup>

The determination of the structure of  $\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2)_3$  is part of a long-range series of studies in this laboratory on the structures of five-coordinate transition metal complexes containing monodentate ligands. The number of such complexes has multiplied rapidly in recent years,<sup>6–8</sup> but it is still difficult to predict which, if either, of the two idealized geometries—trigonal bipyramidal or tetragonal pyramidal—will be utilized in a given complex. Our recent study of the geometry of the two independent  $\text{Ni}(\text{CN})_5^{3-}$  ions in  $[\text{Cr}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3][\text{Ni}(\text{CN})_5] \cdot 1.5\text{H}_2\text{O}$  clearly demonstrates that the two idealized geometries are not always utilized.<sup>9</sup> Whereas one  $\text{Ni}(\text{CN})_5^{3-}$  ion was found to be a nearly perfect tetragonal pyramid, the other was found to be a highly distorted trigonal bipyramid. Whether such a distortion occurs as the result of hydrogen-bonding requirements

among the cations, anions, and water molecules is difficult to assess. For this reason it is of importance to examine closely related systems and this provided additional motivation for the present study of the structure of  $\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2)_3$ .

### Collection and Reduction of the Intensity Data

Crystals of  $\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2)_3$  were kindly supplied by Dr. E. A. Rick and Dr. R. L. Pruett.<sup>1</sup> The material is moderately air sensitive and was handled under a nitrogen atmosphere. Several attempts at recrystallization were made; it was possible to precipitate material that looked crystalline from two solvents—anhydrous diethyl ether and dry hexane—although single crystals were quite difficult to obtain. About two dozen crystals sealed in 0.2–0.3-mm glass capillaries were mounted and examined using Weissenberg or precession techniques before one suitable for data collection was found. A crystal in a properly sealed capillary did not decompose but tended gradually to sublime onto the glass walls. The crystal used for data collection was of approximate dimensions of  $0.16 \times 0.25 \times 0.40$  mm. It was obtained by slow evaporation of a dilute hexane solution.

Precession photographs of zero and upper layers of the reciprocal lattice indicated monoclinic symmetry and exhibited systematic absences only for  $0k0$  when  $k \neq 2n$ , suggesting space groups  $\text{C}_2^2\text{-P2}_1$  or  $\text{C}_{2h}^2\text{-P2}_1/m$ . Preliminary cell constants were obtained from the films, and subsequent refinement of cell parameters from diffractometer measurements using Mo  $\text{K}\alpha_1$  radiation ( $\lambda$  0.7093 Å) gave values of  $a = 19.51$  (3),  $b = 9.90$  (2),  $c = 9.65$  (2) Å, and  $\beta = 96^\circ 29$  (2)' (at  $22^\circ$ ). The calculated density for two molecules per cell is 1.265 g/cm<sup>3</sup>. It was not possible to obtain an accurate experimental density owing to the extreme solubility of this material in organic solvents tested and immediate reaction with aqueous solvent systems. It could be determined only that the density was somewhat greater than 1.0 g/cm<sup>3</sup>.

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The crystal had moderately well-formed faces, and it was carefully measured by means of a micrometer eyepiece. The eight crystal faces of the forms  $\{100\}$ ,  $\{001\}$ , and  $\{110\}$  were identified by optical and X-ray means. Before data collection on the Picker four-circle automatic diffractometer the crystal was deliberately misaligned so that the symmetry axis was not parallel to the spindle axis. This should reduce the possibility of multiple reflections.<sup>10</sup> The cell parameters and orientation angles were determined from a least-squares refinement of the setting angles of 12 centered reflections as previously described.<sup>11</sup>

Mo  $K\alpha$  radiation was used for the data collection. The diffracted beams were filtered through a 3.0-mil Zr foil, and the intensities were collected by the  $\theta$ - $2\theta$  scan technique at a takeoff angle of  $1.3^\circ$ . A symmetrical scan range of  $1.6^\circ$  was found to be sufficient for all reflections. The scan rate was  $1.0^\circ/\text{min}$ . Stationary-crystal, stationary-counter background counts of 10 sec were taken at each end of the scan. The counter was placed 21 cm from the crystal and had an aperture of  $4.0 \times 4.0$  mm.

A unique data set for which  $2\theta \leq 40^\circ$  was initially collected. The intensities of four standard reflections were monitored after 250 reflections had been processed, and they were found to have dropped in intensity by approximately 3%; these standards were subsequently monitored after every 125 reflections and continued to drop slowly in intensity throughout the data collection. A second shell for  $40^\circ < 2\theta \leq 42.5^\circ$  showed little intensity, and, as one of the four standards appeared to be dropping more rapidly than the others, data collection was terminated at this point. The peak and background counts were corrected for this apparent decomposition, the maximum correction being about 9%.

The data were then processed as previously described,<sup>11</sup> a value of  $p = 0.04$  being used in the estimation of  $\sigma(I)$ . The data were also corrected for Lorentz-polarization effects at this time. An absorption correction<sup>12</sup> using  $\mu = 6.96 \text{ cm}^{-1}$  for Mo radiation gave transmission factors ranging from 0.83 to 0.92. Of the 2225 reflections processed, 245 were less than one standard deviation above background. Only the 1612 reflections for which  $F_o^2 \geq 3\sigma(F_o^2)$  were used in the solution and refinement of the structure.

### Solution and Refinement of the Structure

A three-dimensional Patterson function was calculated, and the coordinates of the Ni and two of the three P atoms were determined. Since the Ni and P atoms define a plane that is inclined at an angle of approximately  $45^\circ$  to the  $y$  axis, the noncentric space group  $P2_1$  was established. The fractional  $y$  coordinate of the Ni atom was set at  $1/4$  to fix the origin of the unit cell. The solution of the Patterson function yields

two possible sets of P positions, as reflected across a mirror plane at  $y = 1/4$ ; one set was arbitrarily chosen at this point in the solution of the structure.

Two cycles of least-squares refinement yielded discrepancy factors  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}$  of 36.7 and 45.4%, respectively, where the weights  $w$  were taken as  $4F_o^2 / \sigma^2(F_o^2)$ . In this and succeeding refinements the function minimized was  $\sum w(|F_o| - |F_c|)^2$ . The atomic scattering factors for Ni, P, O, N, and C were those tabulated by Ibers,<sup>13</sup> and those of Stewart, *et al.*,<sup>14</sup> were used for H. The anomalous scattering factors of Cromer<sup>15</sup> were used for both the real and imaginary anomalous scattering by Ni and P.<sup>16</sup> Subsequent difference Fourier maps, interspersed with least-squares refinements, led to the positions of all remaining nonhydrogen atoms. After one cycle of least-squares refinement assigning isotropic temperature factors to all atoms and treating the phenyl rings as rigid groups<sup>17</sup> with a single group temperature factor, the  $R$  factors were reduced to 10.5 and 12.6%. The Ni and three P atoms were then assigned anisotropic thermal parameters, and after three cycles of refinement, the  $R_1$  and  $R_2$  discrepancy factors were 8.0 and 9.4%, respectively. A difference Fourier calculation contained no peak higher than  $0.44 \text{ e}^-/\text{\AA}^3$ , compared with an average value of  $1.9 \text{ e}^-/\text{\AA}^3$  found for the 32 C atoms.

There were at this point two possible structures to consider: enantiomorph A, the structure as heretofore assumed, and enantiomorph B, the mirror image of A as reflected across a plane at  $y = 1/4$ . One cycle of least-squares refinement with  $(\bar{h}\bar{k}\bar{l})$  assumed in place of  $(hkl)$  gave the same  $R$  factor as before, so this could not be used as a criterion for preference of one enantiomorph over the other. The bond lengths and angles were significantly affected by this reversal of configuration;<sup>18</sup> for example, the Ni-P<sub>1</sub> distance increased from 2.261 to 2.289 (5) Å, but neither enantiomorph presented a chemically more "reasonable" model, as both were quite distorted from an idealized five-coordinate geometry. Accordingly, 25 reflections were selected that seemed to show the greatest difference between the values of  $F_o$  for  $(hkl)$  and  $(\bar{h}\bar{k}\bar{l})$ . The original crystal was returned to the diffractometer and recentered, and data were collected under essentially the same conditions as previously described. All four members of  $\{hkl\}$  ( $hkl$ ,  $\bar{h}\bar{k}\bar{l}$ ,  $h\bar{k}l$ , and  $h\bar{k}\bar{l}$ ) were collected for one reflection before moving on to the next; consequently, no standards were monitored. These four members of the form were each collected twice to provide better statistics, as the intensity differences were not large between Friedel pairs (the values of  $\Delta f''$  for Ni and P are only 1.2 and 0.12 electrons, respectively) and most of these

(10) W. H. Zachariasen, *Acta Cryst.*, **18**, 705 (1965).

(11) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(12) Programs used for this analysis included local modifications of Hamilton's GONO9 absorption program, Zalkin's FORDAP Fourier program, the Busing-Levy ORFLS least-squares and ORFFE error function programs, and Johnson's ORTEP plotting program.

(13) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

(14) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(15) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

(16) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

(17) S. J. La Placa and J. A. Ibers, *ibid.*, **18**, 511 (1965); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

(18) T. Ueki, A. Zalkin, and D. H. Templeton, *Acta Cryst.*, **20**, 836 (1966)

reflections were rather weak. The results of this experiment are summarized in Table I; only those reflections for which the final values of  $F_o(hkl)$  and  $F_o(\bar{h}\bar{k}\bar{l})$  differ by 10% or more are listed. It can be seen that enantiomorph B is to be preferred to enantiomorph A in the seven cases for which a definite intensity difference was observed. Thus all  $y$  fractional coordinates were reflected across a plane at  $y = 1/4$ , and refinement was continued on enantiomorph B.

TABLE I  
DETERMINATION OF ABSOLUTE CONFIGURATION OF A CRYSTAL  
OF  $\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2)_3$

Indices <sup>a</sup>			Obsd relations— $\frac{hkl}{hkl} \frac{\bar{h}\bar{k}\bar{l}}{\bar{h}\bar{k}\bar{l}}$	Computed structure factors <sup>b</sup> for enantiomorph B	
$h$	$k$	$l$		$F_o(hkl)$	$F_o(\bar{h}\bar{k}\bar{l})$
1	1	2	>	52.5	41.3
2	2	$\bar{3}$	(?)	14.7	17.6
2	2	2	<	11.7	19.8
3	1	0	>	10.7	6.9
4	2	3	>	27.2	22.3
5	1	3	>	30.5	26.9
7	1	3	(?)	17.1	19.5
8	3	2	>	16.2	14.3
10	4	$\bar{3}$	(?)	12.4	15.2
10	5	$\bar{3}$	(?)	16.7	18.7
15	2	4	>	10.3	9.2

<sup>a</sup> Only reflections for which  $F_o(hkl)$  and  $F_o(\bar{h}\bar{k}\bar{l})$  differ by 10% or more are listed. <sup>b</sup> Based on final structure parameters.

suming C–H = 1.09 Å and H–C–H = 109° 28'. The structure factor contributions for these H atoms and the phenyl group H atoms were added as fixed contributions to the calculated structure factors in subsequent refinements. There was an immediate drop in the values of  $R_1$  and  $R_2$  to 7.2 and 8.3%, and one cycle of least-squares refinement lowered these values even further to 7.0 and 7.8%, respectively.

At this point a careful analysis of the function  $\Sigma w(|F_o| - |F_c|)^2$  over ranges of  $|F_o|$  and  $\lambda^{-1} \sin \theta$  indicated that (a) the absolute weights were too large, (b) the low-order reflections were being overweighted, and (c) the value of 0.04 chosen for  $p$  was satisfactory. The weights were modified so that this function was constant for all ranges of  $\lambda^{-1} \sin \theta$  as well as for ranges of  $|F_o|$ . One last cycle of least-squares refinement using this weighting scheme and assigning anisotropic thermal parameters to the two CN groups (resulting in 180 variables) gave final values of  $R_1$  and  $R_2$  of 6.9 and 8.2%, respectively, and the error of an observation of unit weight of 1.02. As there was no evidence for extinction, no corrections were made.

The final positional, thermal, and group parameters are presented in Table II, along with the corresponding standard deviations in these parameters as estimated from the inverse matrix. Table III presents the positional parameters of the group carbon atoms which may

TABLE II  
FINAL ATOMIC AND GROUP PARAMETERS FOR  $\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2)_3$

Atom	$x$	$y$	$z$	$\beta_{11}^a$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$			
Ni	0.24799 (10) <sup>b</sup>	1/4	0.19001 (18)	0.00345 (6)	0.01069 (22)	0.01094 (21)	0.00027 (13)	0.00066 (9)	0.00035 (25)			
P <sub>1</sub>	0.2879 (2)	0.3951 (5)	0.0326 (4)	0.0032 (1)	0.0120 (6)	0.0128 (5)	-0.0007 (2)	0.0005 (2)	0.0008 (5)			
P <sub>2</sub>	0.3202 (2)	0.0833 (5)	0.2504 (4)	0.0036 (2)	0.0122 (6)	0.0142 (6)	0.0009 (3)	0.0010 (2)	0.0003 (5)			
P <sub>3</sub>	0.1465 (2)	0.3053 (5)	0.2485 (4)	0.0037 (2)	0.0143 (6)	0.0130 (5)	0.0011 (2)	0.0004 (2)	-0.0009 (5)			
C <sub>1</sub>	0.2021 (10)	0.1409 (21)	0.0512 (20)	0.0041 (6)	0.0148 (25)	0.0170 (26)	0.0003 (11)	0.0038 (11)	0.0005 (23)			
C <sub>2</sub>	0.2861 (9)	0.3453 (20)	0.3505 (20)	0.0037 (6)	0.0154 (26)	0.0165 (26)	0.0024 (10)	0.0006 (10)	0.0033 (22)			
N <sub>1</sub>	0.1759 (9)	0.0744 (21)	-0.0370 (17)	0.0057 (7)	0.0209 (27)	0.0198 (24)	0.0003 (12)	-0.0003 (10)	-0.0086 (24)			
N <sub>2</sub>	0.3110 (9)	0.4050 (18)	0.4458 (16)	0.0073 (8)	0.0174 (23)	0.0144 (19)	-0.0005 (11)	-0.0038 (10)	-0.0009 (20)			
Atom	$x$	$y$	$z$	$B_i$ , Å <sup>2</sup>	Atom	$x$	$y$	$z$	$B_i$ , Å <sup>2</sup>			
O <sub>1</sub>	0.3181 (6)	0.3145 (13)	-0.0837 (11)	6.2 (3)	C <sub>6</sub>	0.4455 (20)	0.5642 (43)	0.2260 (39)	15.1 (11)			
O <sub>2</sub>	0.3466 (7)	0.5047 (15)	0.0861 (15)	7.5 (3)	C <sub>7</sub>	0.4519 (13)	0.0619 (28)	0.3614 (25)	9.6 (6)			
O <sub>3</sub>	0.3932 (6)	0.1463 (13)	0.2958 (12)	6.7 (3)	C <sub>8</sub>	0.5143 (19)	0.1363 (42)	0.3747 (35)	14.3 (10)			
O <sub>4</sub>	0.3324 (6)	-0.0332 (12)	0.1421 (12)	5.9 (3)	C <sub>9</sub>	0.3533 (12)	0.0066 (25)	0.0048 (24)	8.5 (6)			
O <sub>5</sub>	0.1369 (7)	0.4468 (14)	0.3265 (13)	7.2 (3)	C <sub>10</sub>	0.3928 (12)	-0.1112 (26)	-0.0437 (23)	9.1 (6)			
O <sub>6</sub>	0.0928 (8)	0.3074 (15)	0.1161 (14)	8.5 (3)	C <sub>11</sub>	0.1620 (11)	0.5694 (26)	0.2790 (22)	8.0 (5)			
C <sub>8</sub>	0.3409 (10)	0.3740 (22)	-0.2128 (20)	7.5 (5)	C <sub>12</sub>	0.1291 (15)	0.6804 (30)	0.3416 (29)	11.0 (8)			
C <sub>4</sub>	0.3996 (11)	0.2948 (22)	-0.2510 (20)	8.2 (5)	C <sub>13</sub>	0.0244 (17)	0.3560 (36)	0.1110 (32)	12.4 (9)			
C <sub>5</sub>	0.4089 (15)	0.4585 (32)	0.1635 (28)	11.0 (7)	C <sub>14</sub>	-0.0086 (21)	0.3434 (42)	-0.0210 (42)	14.8 (10)			
Group	$x_c^c$	$y_c$	$z_c$	$\delta$	$\epsilon$	$\eta$	$B_1$	$B_2$	$B_3$	$B_4$	$B_5$	$B_6$
Ring 1	0.1786 (4)	0.5935 (9)	-0.1339 (8)	2.702 (8)	2.645 (7)	-0.529 (8)	4.6 (3)	5.7 (4)	8.6 (6)	8.6 (6)	8.3 (5)	6.5 (4)
Ring 2	0.2898 (4)	-0.1065 (10)	0.5032 (8)	-2.757 (9)	2.610 (7)	1.199 (9)	5.2 (4)	6.1 (4)	8.0 (4)	8.2 (5)	8.6 (5)	6.0 (4)
Ring 3	0.0877 (4)	0.1106 (11)	0.4668 (10)	2.665 (13)	2.344 (8)	1.545 (13)	5.1 (4)	7.4 (5)	9.8 (6)	8.6 (6)	10.5 (7)	8.7 (5)

<sup>a</sup> The form of the anisotropic thermal ellipsoid is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . <sup>b</sup> The standard deviations of the least significant figures are given in parentheses. <sup>c</sup> The angles  $\delta$ ,  $\epsilon$ , and  $\eta$  (in radians) which bring about alignment (except for translation) of an internal coordinate system within the ring with a fixed external coordinate system have been described in previous papers.<sup>17</sup>  $B_i$  is the isotropic thermal parameter (in Å<sup>2</sup>) of atom  $i$  in a given ring.

The C atoms in the phenyl rings next were given individual thermal parameters, and in one cycle of refinement the values of  $R_1$  and  $R_2$  decreased to 7.7 and 8.9%. A difference Fourier map gave approximate positions for all of the ethylene H atoms and about half of the methyl H atoms with at least one H atom being located for each methyl group. These were idealized for a staggered conformation of ethyl hydrogens, as-

be derived from the data in Table II. The values of  $10|F_o|$  and  $10|F_c|$  (in electrons) are given in Table IV.

The extremely short calculated C–C distance of 1.43 Å and the high thermal parameters for the C atoms (average  $B = 9.5$  Å<sup>2</sup> for C attached to O; 12.1 Å<sup>2</sup> for terminal C) are indicative of a degree of disorder, as has been previously discussed elsewhere.<sup>11</sup> The final difference Fourier map contained no peak higher than 0.58

TABLE III  
DERIVED PARAMETERS FOR GROUP CARBON ATOMS

	x	y	z
Ring 1			
C <sub>1</sub> <sup>a</sup>	0.228 <sup>b</sup>	0.511	-0.059
C <sub>2</sub>	0.180	0.455	-0.161
C <sub>3</sub>	0.131	0.538	-0.237
C <sub>4</sub>	0.130	0.676	-0.209
C <sub>5</sub>	0.178	0.732	-0.107
C <sub>6</sub>	0.227	0.649	-0.031
Ring 2			
C <sub>1</sub>	0.301	-0.026	0.390
C <sub>2</sub>	0.316	-0.164	0.387
C <sub>3</sub>	0.304	-0.245	0.501
C <sub>4</sub>	0.278	-0.188	0.617
C <sub>5</sub>	0.264	-0.049	0.619
C <sub>6</sub>	0.275	0.032	0.505
Ring 3			
C <sub>1</sub>	0.113	0.199	0.372
C <sub>2</sub>	0.080	0.079	0.325
C <sub>3</sub>	0.055	-0.009	0.420
C <sub>4</sub>	0.063	0.023	0.562
C <sub>5</sub>	0.095	0.142	0.609
C <sub>6</sub>	0.120	0.231	0.514

<sup>a</sup> The rings are numbered cyclically so that C<sub>1</sub> is attached to phosphorus. <sup>b</sup> Estimated standard deviations as derived from those of the group parameters are 0.0015 or less. Intra-ring distances are fixed (C-C = 1.397 Å).

e<sup>-</sup>/Å<sup>3</sup>; however, many of the peaks represented alternative positions for those atoms with particularly high temperature factors. These short carbon-carbon distances obviously should not be taken seriously. The uncertainty in the C atom parameters should not have a significant effect on the parameters of the other atoms, which were essentially uncorrelated with those of the ligand carbon atoms. For this reason, no attempt was made to refine the structure using a disordered model.

The root-mean-square amplitudes of vibration of those atoms which were refined anisotropically vary between 0.22 and 0.41 Å. The orientations of the thermal ellipsoids can be seen in Figure 1. The anisotropy is small and is most noticeable for the terminal N atoms as would be expected.

### Description of the Structure

The crystal structure is made up of discrete monomeric units, the closest Ni-Ni distance being 9.65 Å. All intermolecular contacts appear to be normal, with the closest approaches between hydrogen atoms of two adjacent molecules being 2.25 and 2.28 Å, respectively. A stereoscopic view of the molecular structure is given in Figure 2. Interatomic distances and angles and their standard deviations as computed from the final parameters and the correlation matrix are presented in Table V. The inner coordination about nickel is intermediate between a trigonal-bipyramidal and a tetragonal-pyramidal geometry, as is shown in Figure 1; Figure 1 also presents selected bond distances.

The Ni-P bond lengths of 2.205 and 2.189 Å are well within the range of values reported for similar com-

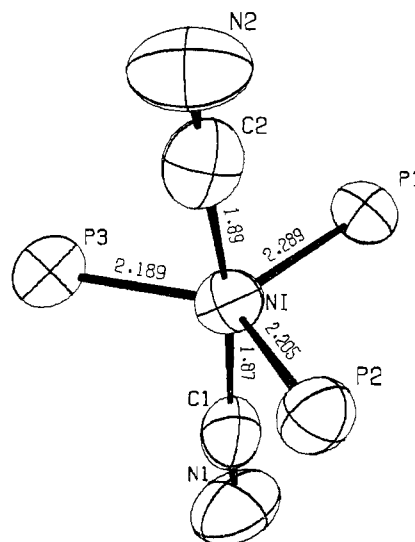


Figure 1.—A perspective drawing of the inner coordination sphere of Ni(CN)<sub>2</sub>(P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)<sub>2</sub>.

pounds, such as 2.22 Å in Ni(P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)<sub>3</sub>(C≡CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>,<sup>19</sup> 2.18 Å in Ni(HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>)<sub>3</sub>I<sub>2</sub>,<sup>20</sup> 2.21 Å in [Ni(TAP)CN]-ClO<sub>4</sub> (TAP = P(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>As(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>),<sup>21</sup> and 2.19 Å (equatorial P) and 2.15 Å (axial P) in the trigonal-bipyramidal Ni(P(OCH)<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>)<sub>5</sub><sup>2+</sup> ion.<sup>22</sup> The Ni-P bond of 2.289 Å is rather long, as would be expected for the apical bond of a tetragonal pyramid. The average distances of 1.88 Å for Ni-C and 1.15 Å for C-N agree with those found for the Ni(CN)<sub>5</sub><sup>3-</sup> ion,<sup>9</sup> average Ni-C = 1.90 Å (excluding the long apical Ni-C bond) and average C-N = 1.15 Å, and for the Ni(TAP)CN<sup>+</sup> ion,<sup>21</sup> Ni-C = 1.87 Å and C-N = 1.12 Å. However, the average axial Ni-C distance in the Ni(CN)<sub>5</sub><sup>3-</sup> ion of corresponding geometry is only 1.84 Å; one might expect the Ni-C bond lengths to be the same in these two structures, in view of their great similarity (see below). This discrepancy can readily be explained on the basis of C-P vs. C-C nonbonded interactions. The shortest nonbonded C-P distance is 2.81 Å, while the shortest C-C distance in the Ni(CN)<sub>5</sub><sup>3-</sup> ion is 2.55 Å; the difference between these values is approximately the same as that between the van der Waals radii of P and C atoms. The Ni-C-N linkages are linear within experimental error.

The average P-O and O-C distances in the P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> ligands are 1.58 and 1.45 Å, respectively. These distances are close to those tabulated by Corbridge in a recent review,<sup>23</sup> in which the average P-O and O-C bond lengths for several organic orthophosphate esters are given as 1.59 ± 0.05 and 1.44 ± 0.04 Å. The P-C distances and O-P-C and C-P-C angles are within the range usually reported for phosphine complexes of transition metals.

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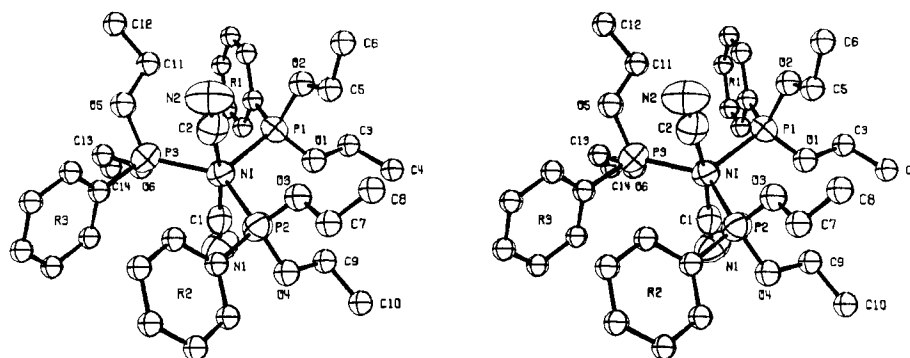
(22) E. F. Riedel, J. G. Verkade, and R. A. Jacobson, to be submitted for publication. See Abstracts, American Crystallographic Association Meeting, Minneapolis, Minn., 1967, No. P-10.

(23) D. E. C. Corbridge, "Topics in Phosphorus Chemistry," Vol. 3, Interscience Publishers, New York, N. Y., 1966, Table III.5.

TABLE IV

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (X10) (IN ELECTRONS) FOR Ni(CN)<sub>2</sub>(P(C<sub>6</sub>H<sub>5</sub>)(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)<sub>2</sub>

Table with columns labeled K, L, FO, FC, K, L, FO, FC, K, L, FO, FC, K, L, FO, FC, K, L, FO, FC, K, L, FO, FC, K, L, FO, FC. It contains a grid of numerical values representing structure amplitudes for various reflections.

Figure 2.—Stereoscopic view of  $\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2)_3$ .TABLE V  
SELECTED DISTANCES (Å) AND ANGLES (DEG)

Atoms	Distance	Atoms	Angle
Ni-P <sub>1</sub>	2.289 (5)	P <sub>1</sub> -Ni-P <sub>2</sub>	113.0 (2)
Ni-P <sub>2</sub>	2.205 (6)	P <sub>1</sub> -Ni-P <sub>3</sub>	113.5 (2)
Ni-P <sub>3</sub>	2.189 (6)	P <sub>2</sub> -Ni-P <sub>3</sub>	133.5 (2)
Ni-C <sub>1</sub>	1.869 (22)	C <sub>1</sub> -Ni-C <sub>2</sub>	170.8 (8)
Ni-C <sub>2</sub>	1.893 (22)	Ni-C <sub>1</sub> -N <sub>1</sub>	177 (2)
C <sub>1</sub> -N <sub>1</sub>	1.150 (22)	Ni-C <sub>2</sub> -N <sub>2</sub>	178 (2)
C <sub>2</sub> -N <sub>2</sub>	1.153 (21)	C <sub>1</sub> -Ni-P <sub>1</sub>	93.4 (5)
P <sub>1</sub> -O <sub>1</sub>	1.546 (12)	C <sub>1</sub> -Ni-P <sub>2</sub>	89.8 (6)
P <sub>1</sub> -O <sub>2</sub>	1.621 (15)	C <sub>1</sub> -Ni-P <sub>3</sub>	87.4 (5)
P <sub>2</sub> -O <sub>3</sub>	1.573 (14)	C <sub>2</sub> -Ni-P <sub>1</sub>	95.7 (6)
P <sub>2</sub> -O <sub>4</sub>	1.593 (13)	C <sub>2</sub> -Ni-P <sub>2</sub>	88.7 (5)
P <sub>3</sub> -O <sub>5</sub>	1.611 (14)	C <sub>2</sub> -Ni-P <sub>3</sub>	87.0 (5)
P <sub>3</sub> -O <sub>6</sub>	1.558 (15)	P <sub>1</sub> -O <sub>1</sub> -C <sub>3</sub>	125 (1)
P <sub>1</sub> -R <sub>1</sub> C <sub>1</sub> <sup>a</sup>	1.800 (12)	P <sub>1</sub> -O <sub>2</sub> -C <sub>6</sub>	118 (2)
P <sub>2</sub> -R <sub>2</sub> C <sub>1</sub>	1.792 (12)	P <sub>2</sub> -O <sub>3</sub> -C <sub>7</sub>	121 (1)
P <sub>3</sub> -R <sub>3</sub> C <sub>1</sub>	1.767 (16)	P <sub>2</sub> -O <sub>4</sub> -C <sub>9</sub>	118 (1)
O <sub>1</sub> -C <sub>3</sub>	1.491 (22)	P <sub>3</sub> -O <sub>5</sub> -C <sub>11</sub>	122 (1)
O <sub>2</sub> -C <sub>6</sub>	1.428 (29)	P <sub>3</sub> -O <sub>6</sub> -C <sub>13</sub>	125 (2)
O <sub>3</sub> -C <sub>7</sub>	1.498 (26)	O <sub>1</sub> -C <sub>3</sub> -C <sub>4</sub>	108 (2)
O <sub>4</sub> -C <sub>9</sub>	1.483 (25)	O <sub>2</sub> -C <sub>6</sub> -C <sub>5</sub>	111 (3)
O <sub>5</sub> -C <sub>11</sub>	1.405 (26)	O <sub>3</sub> -C <sub>7</sub> -C <sub>8</sub>	111 (2)
O <sub>6</sub> -C <sub>13</sub>	1.414 (32)	O <sub>4</sub> -C <sub>9</sub> -C <sub>10</sub>	106 (2)
C <sub>3</sub> -C <sub>4</sub>	1.470 (27) <sup>b</sup>	O <sub>5</sub> -C <sub>11</sub> -C <sub>12</sub>	110 (2)
C <sub>5</sub> -C <sub>6</sub>	1.368 (42)	O <sub>6</sub> -C <sub>13</sub> -C <sub>14</sub>	110 (3)
C <sub>7</sub> -C <sub>8</sub>	1.416 (40)		
C <sub>9</sub> -C <sub>10</sub>	1.501 (31)		
C <sub>11</sub> -C <sub>12</sub>	1.440 (32)		
C <sub>13</sub> -C <sub>14</sub>	1.366 (39)		

## Angles about P

Atoms	Angle	Atoms	Angle
Ni-P <sub>1</sub> -O <sub>1</sub>	110.1 (5)	O <sub>1</sub> -P <sub>1</sub> -O <sub>2</sub>	105.3 (7)
Ni-P <sub>1</sub> -O <sub>2</sub>	119.4 (6)	O <sub>1</sub> -P <sub>1</sub> -R <sub>1</sub> C <sub>1</sub>	104.8 (6)
Ni-P <sub>1</sub> -R <sub>1</sub> C <sub>1</sub>	118.1 (4)	O <sub>2</sub> -P <sub>1</sub> -R <sub>1</sub> C <sub>1</sub>	97.4 (7)
Ni-P <sub>2</sub> -O <sub>3</sub>	108.0 (6)	O <sub>3</sub> -P <sub>2</sub> -O <sub>4</sub>	105.8 (7)
Ni-P <sub>2</sub> -O <sub>4</sub>	120.5 (5)	O <sub>3</sub> -P <sub>2</sub> -R <sub>2</sub> C <sub>1</sub>	106.7 (7)
Ni-P <sub>2</sub> -R <sub>2</sub> C <sub>1</sub>	118.0 (5)	O <sub>4</sub> -P <sub>2</sub> -R <sub>2</sub> C <sub>1</sub>	96.5 (6)
Ni-P <sub>3</sub> -O <sub>5</sub>	119.6 (5)	O <sub>5</sub> -P <sub>3</sub> -O <sub>6</sub>	105.6 (8)
Ni-P <sub>3</sub> -O <sub>6</sub>	109.6 (6)	O <sub>5</sub> -P <sub>3</sub> -R <sub>3</sub> C <sub>1</sub>	97.7 (7)
Ni-P <sub>3</sub> -R <sub>3</sub> C <sub>1</sub>	115.9 (7)	O <sub>6</sub> -P <sub>3</sub> -R <sub>3</sub> C <sub>1</sub>	107.1 (8)

<sup>a</sup> R<sub>i</sub>C<sub>1</sub> refers to carbon atom 1 on phenyl ring *i*. <sup>b</sup> The C-C distances cannot be regarded seriously: see discussion in text.

If the six P-O bond lengths are assumed to be equivalent, the standard deviation of a single distance from the mean is 0.030 Å; this value does not correspond with the computed standard deviations of 0.012–0.015 Å. Similarly, for the six O-C bonds the standard deviation of a given bond length is calculated to be 0.042 Å, while the standard deviations range from 0.022

to 0.032 Å. Thus the standard deviations of these bond distances may have been underestimated by perhaps a factor of 2. Again this could be the result of the partial disordering of the ethoxy groups. Nevertheless, the distortions of this molecule discussed in the following paragraph remain highly significant even if the calculated standard deviations are doubled.

If the structure is considered to be a trigonal bipyramid, then all distortions from this idealized geometry are in the direction of a tetragonal-pyramidal configuration: the Ni-P<sub>1</sub> bond length of 2.289 (5) Å is much longer than the other two Ni-P bonds of 2.205 (6) and 2.189 (6) Å, as would be the case for the apical bond in a tetragonal pyramid, and the angle opposite this long bond is expanded to 133.5 (2)° from the expected 120°. The two cyanide groups are bent away from the Ni-P<sub>1</sub> bond, with a C-Ni-C angle of 170.8 (8)°. The Ni and three P atoms are coplanar, with no atom more than 0.001 (5) Å out of the best weighted least-squares plane, as would be expected for either of the idealized five-coordinate configurations. The inner coordination geometry found here is remarkably similar to the distorted trigonal-bipyramidal geometry reported for one of the Ni(CN)<sub>5</sub><sup>3-</sup> ions in [Cr(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-NH<sub>2</sub>)<sub>3</sub>][Ni(CN)<sub>5</sub>].1.5H<sub>2</sub>O; the angular distortions of Ni(CN)<sub>2</sub>(P(C<sub>6</sub>H<sub>5</sub>)(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)<sub>3</sub> and the Ni(CN)<sub>5</sub><sup>3-</sup> ion from the two idealized five-coordinate geometries are summarized in Table VI. In most cases, the bond angles for these two complexes lie about halfway between the angles for the two idealized configurations.

Whereas one might be tempted to invoke steric effects in the present structure and hydrogen bonding in the Ni(CN)<sub>5</sub><sup>3-</sup> structure as primary causes of the distortion, the structures are too similar to make this probable. It might be argued that the configuration of Ni(CN)<sub>2</sub>(P(C<sub>6</sub>H<sub>5</sub>)(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)<sub>3</sub> is determined by the steric interactions of the bulky phosphine groups. Admittedly, many five-coordinate transition metal complexes with at least three large or complex ligands exhibit distortions which may be sterically controlled, for example, Ru(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>,<sup>24</sup> Ni(HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>)<sub>3</sub>I<sub>2</sub>,<sup>20</sup> and Co(HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>)<sub>3</sub>Br<sub>2</sub>.<sup>20</sup> However, the corresponding complex with P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, probably a more sterically hindered ligand, in place of P(C<sub>6</sub>H<sub>5</sub>)(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> has been reported,<sup>5</sup>

TABLE VI  
ANGULAR DISTORTIONS OF  $\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2)_3$  AND  
 $\text{Ni}(\text{CN})_5^{3-}$  FROM IDEALIZED FIVE-COORDINATE GEOMETRIES

Atoms	Angles, deg			
	Trigonal bipyramid	$\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2)_3$	$\text{Ni}(\text{CN})_5^{3-}$	Tetragonal <sup>a</sup> pyramid
$\text{P}_1\text{-Ni-P}_2^b$	120	113.0 <sup>c</sup>	107.4	100
$\text{P}_1\text{-Ni-P}_3$	120	113.5	111.5	100
$\text{P}_2\text{-Ni-P}_3$	120	133.5	141.2	160
$\text{C}_1\text{-Ni-C}_2$	180	170.8	172.8	180
$\text{P}_1\text{-Ni-C}_1$	90	93.4	92.3	100
$\text{P}_1\text{-Ni-C}_2$	90	95.7	94.4	100
$\text{P}_2\text{-Ni-C}_1$	90	89.8	89.3	88
$\text{P}_2\text{-Ni-C}_2$	90	88.7	91.3	88
$\text{P}_3\text{-Ni-C}_1$	90	87.4	89.5	88
$\text{P}_3\text{-Ni-C}_2$	90	87.0	85.6	88

<sup>a</sup> These angles represent the average values for the tetragonal pyramid formed by  $\text{Ni}(\text{CN})_5^{3-}$ , in which the Ni atom lies 0.34 Å above the plane of the four C atoms and 0.55 Å above the plane of the four N atoms.<sup>9</sup> These values appear to be normal for tetragonal pyramids involving first-row transition metals, in which the metal atom has been found to lie 0.3–0.6 Å above the tetragonal plane: see, for example, B. F. Hoskins, R. L. Martin, and A. H. White, *Nature*, **211**, 627 (1966). A purely electrostatic model with five equivalent ligands gives an L(apical)–M–L (basal) angle of 104°: J. Zemann, *Z. Anorg. Allgem. Chem.*, **324**, 241 (1963). <sup>b</sup> Or the corresponding C–Ni–C angle for the  $\text{Ni}(\text{CN})_5^{3-}$  ion. <sup>c</sup> The standard deviations of these angles range from 0.2 to 0.8°.

and the indirect evidence again indicates a trigonal-bipyramidal structure with axial cyanide groups. We feel that this fact, coupled with the close similarities be-

tween this compound and the  $\text{Ni}(\text{CN})_5^{3-}$  ion, tend to preclude such an argument based on steric grounds alone.

It is of interest to view this intermediate structure in relation to the infrared evidence and other similar structures. Although the symmetry of the inner coordination sphere in this case is halfway between the  $D_{3h}$  of a trigonal bipyramid and  $C_{2v}$  of a tetragonal pyramid, the infrared spectrum of the crystalline solid still exhibits a single C–N stretching frequency. This is, of course, one of the many examples of the ineffectiveness of band counting in the determination of important deviations from idealized symmetries. Moreover, it is just these small differences, inaccessible by nondiffraction means, that often present the clues to changes in chemical bonding on change of ligands. Clearly it is necessary to examine other  $\text{Ni}(\text{CN})_2(\text{PR}_3)_3$  structures in an attempt to understand possible causes for the distortion from idealized geometry observed here. The following paper discusses the structure of  $\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{CH}_3)_2)_3$ .

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## The Crystal and Molecular Structure of Dicyanotris(phenyldimethylphosphine)nickel(II), $\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{CH}_3)_2)_3$

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The crystal and molecular structure of dicyanotris(phenyldimethylphosphine)nickel(II),  $\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{CH}_3)_2)_3$ , has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques to a final *R* factor on *F* of 4.9%. The material crystallizes in space group  $C_1^1\text{-P}\bar{1}$  of the triclinic system, with two molecules in a cell of dimensions  $a = 8.907$  (8),  $b = 16.292$  (15),  $c = 9.876$  (9) Å,  $\alpha = 97^\circ 58' (1)'$ ,  $\beta = 102^\circ 40' (1)'$ , and  $\gamma = 86^\circ 40' (1)'$ . (Reduced cell:  $a = 8.907$ ,  $b = 16.292$ ,  $c = 17.842$  Å,  $\alpha = 146^\circ 46'$ ,  $\beta = 93^\circ 55'$ , and  $\gamma = 93^\circ 20'$ .) The observed and calculated densities are  $1.26 \pm 0.01$  and  $1.260$  g/cm<sup>3</sup>, respectively. The inner coordination about the Ni is trigonal bipyramidal with the two cyanides at the apices and the three phosphines in the basal plane. There is a slight but significant distortion toward a tetragonal-pyramidal geometry, which is discussed in relation to the far more distorted structure of  $\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2)_3$ . The Ni–P bond lengths are 2.261 (3), 2.223 (3), and 2.223 (3) Å, and the Ni–C distances are 1.84 (1) and 1.86 (1) Å.

### Introduction

In the preceding paper<sup>1</sup> the structure of  $\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2)_3$  was described. It was found that the geometry about the Ni atom is a highly distorted trigonal bipyramid, with a distortion remarkably similar to that found for one of the  $\text{Ni}(\text{CN})_5^{3-}$  ions in

$[\text{Cr}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3][\text{Ni}(\text{CN})_5] \cdot 1.5\text{H}_2\text{O}$ .<sup>2</sup> This paper describes the structure of  $\text{Ni}(\text{CN})_2(\text{P}(\text{C}_6\text{H}_5)(\text{CH}_3)_2)_3$ . Both  $\text{P}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2$  and  $\text{P}(\text{C}_6\text{H}_5)(\text{CH}_3)_2$  should have similar steric requirements, but the latter phosphine is more basic and hence capable of transferring more electrons to the  $\text{Ni}(\text{CN})_2$  system. Thus any differences be-

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