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The Crystal and Molecular Structure of Bis(9-phenyl-9-phosphabicyclo[3.3.1]nonane)nickel Chloride, $(C_8H_{14}PC_6H_5)_2NiCl_2$

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The structure and molecular configuration of a 9-phenyl-9-phosphabicyclononane ($C_8H_{14}PC_6H_5$) of unknown configuration has been established by the determination of the crystal structure of the metal complex $(C_8H_{14}PC_6H_5)_2NiCl_2$ by X-rays. The question of which of the two isomers formed during synthesis was the symmetric and which was the asymmetric isomer could not be determined by the usual chemical and physical methods. The X-ray crystal structure determination unambiguously established the configuration of the more readily crystallizable component as that of the symmetric isomer. Three-dimensional diffractometer data were collected by counter methods using Ni-filtered Cu Kα radiation. The unit cell of the complex is triclinic, space group $P\bar{1}$, $a = 9.497$ (4) Å, $b = 9.825$ (5) Å, $c = 8.581$ (5) Å, $\alpha = 84.49$ (2)°, $\beta = 100.21$ (2)°, $\gamma = 121.95$ (3)°, with one molecule of $(C_8H_{14}PC_6H_5)_2NiCl_2$ per unit cell. The calculated and observed densities are 1.408 and 1.40 ± 0.03 g/cm^3, respectively. A spherical crystal 0.24 mm in diameter was used for the collection of the data, and absorption corrections were applied. The structure was refined by full-matrix least squares to a conventional R factor, on F, of 0.039 (2900 reflections) and a weighted R factor of 0.048. The nickel atom occupies a site of inversion symmetry requiring the Cl and P atoms to be in a trans-square-planar configuration. The phosphorus is tetrahedrally coordinated with two of the bonds symmetrically bridging the cyclooctane molecule [P–C bonds = 1.834 (3) and 1.831 (3) Å, respectively].

Introduction

A 9-phenyl-9-phosphabicyclononane ($C_8H_{14}PC_6H_5$) of unknown configuration was synthesized by Mason.[2] The question of which of the two isomers formed during synthesis was the symmetric (Figure 1a) and which was the asymmetric isomer (Figure 1b) could not be established by the usual chemical and physical methods. An X-ray structure investigation of the nickel complex, $(C_8H_{14}PC_6H_5)_2NiCl_2$ was, therefore, undertaken to determine which isomer was the symmetric one and to establish its molecular configuration.

Collection and Reduction of the Data

Crystals suitable for X-ray structure determination were grown by the slow evaporation of a toluene solution in a stream of dry nitrogen. Crystals were ground into spheres in a stream of nitrogen and mounted in thin-walled Lindemann glass capillaries. The spherical crystal selected for the collection of the X-ray data was 0.240 ± 0.006 mm in diameter.

A series of precession and Weissenberg photographs taken with Ni-filtered Cu Kα radiation showed there were no systematic extinctions suggesting space groups C_1^1-$P1$ or C_i^1-$P\bar{1}$. A triclinic cell was assigned and a subsequent Delaunay reduction of the cell parameters failed to indicate any hidden symmetry. The unit cell parameters measured on a Picker diffractometer using Ni-filtered Cu Kα radiation (λ 1.5418 Å) are $a = 9.497$ (4) Å, $b = 9.825$ (5) Å, $c = 8.581$ (5) Å, $\alpha = 84.49$ (2)°, $\beta = 100.21$ (2)°, and $\gamma = 121.95$ (2)°. The observed density of 1.40 g/cm^3, obtained by flotation in a series of liquids of varying density, agrees well with the calculated value of 1.408 g/cm^3 for one molecule of $(C_8H_{14}PC_6H_5)_2NiCl_2$ per unit cell ($V = 668.63$ Å^3). The Delaunay reduced cell[3] has dimensions $a = 11.616$ Å, $b = 9.825$ Å, $c = 8.5810$ Å, $\alpha = 95.50°$, $\beta = 126.43°$, and $\gamma = 111.21°$.

The spherical crystal used for collecting the data was mounted in a thin-walled capillary with the b axis of the crystal along the ϕ axis of the diffractometer to minimize the possibility of multiple reflections. The data were collected with a Picker four-circle card-controlled automatic diffractometer using Cu Kα radiation. The diffracted beam was filtered through a 1.0-mil nickel foil. The mosaic character of the crystal was checked by performing ω scans with several reflections. The ω scan peak width at half maximum height was approximately 0.08°.

The intensities were collected by the θ–2θ scan technique at a scan rate of 0.5°/min using a takeoff angle of 1.8°. The scan range was $-1.20°$ from Kα_1 to $+1.20°$ from the 2θ value calculated for Kα_2. Stationary-counter, stationary-crystal background counts of 20 sec were taken at each end of the scan range. The scintillation counter was 28 cm from the crystal and had an aperture of 6 × 7 mm. Aluminum-foil attenuators were inserted automatically when the intensity exceeded about 7000 counts/sec. Several standard reflections were monitored every 3–4 hr. There were no variations in intensity beyond that expected from counting statistics. The mean values of F_o and their standard deviations for the different reflections used as standards are given in Table I where N is the number of times the reflection was measured.

TABLE I

REFERENCE REFLECTIONS MEAN F_o VALUES AND THEIR STANDARD DEVIATIONS

hkl	*F* mean	σF	*N*
(00$\bar{3}$)	30.67	0.101	42
(011)	27.41	0.094	21
(302)	35.97	0.044	6
($\bar{5}$00)	25.72	0.037	5

Data were collected up to $2\theta = 125°$, however, there were very few reflections above background beyond $2\theta = 122°$. The data used for the structure determination were, therefore, restricted to $2\theta \leq 122°$. A fairly large number of very faint reflections were still present at this 2θ range, therefore, those with $I \leq 3\sigma(I)$ were given zero weight during the least-squares refinement. The data were corrected for Lorentz and polarization effects and for absorption. The linear absorption coefficient μ for this complex for Cu Kα radiation is 40.56 cm^{-1} and $\mu R = 0.989$ for the crystal. An analytical expression of the form

$$\sum_{n=0}^{3} An(\sin\theta)^n$$

was fitted by least-squares to the interpolated value of μr for the absorption correction factor A^* for a sphere.[4] This was used to correct for absorption during the Lorentz-polarization corrections. A weighting scheme similar to that of Busing and Levy[5a] and

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[2] R. F. Mason, U. S. Patent No. 3,400,163, Sept 1968.

[3] "International Tables for X-ray Crystallography," Vol. I, 2nd ed, Kynoch Press, Birmingham, England, 1965, p 530.

[4] "International Tables for X-ray Crystallography," Vol. II, Kynoch Press, Birmingham, England, 1959, Table 5.3.6B, p 302.

[5] (a) W. R. Busing and H. Levy, *J. Chem. Phys.*, **26**, 563 (1957); (b) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

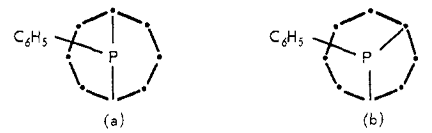

Figure 1.—$(C_8H_{14}PC_6H_5)_2NiCl_2$: (a) symmetric isomer, and (b) asymmetric isomer.

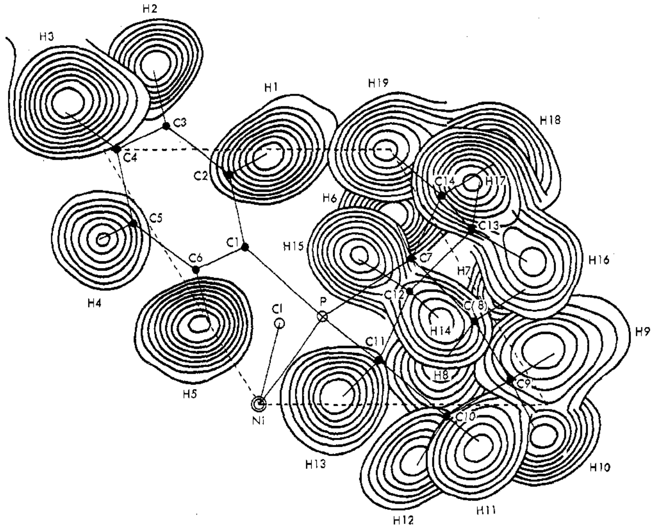

Figure 2.—Composite sections of a difference map indicating locations of hydrogen atoms. The contours are evenly spaced on an arbitrary scale.

that of Corfield, *et al.*,[5b] was used with $p = 0.01$. The standard deviation in F, $\sigma(F)$ was taken as

$$\sigma(F) = \frac{[S\sigma(F_o)^2]^{1/2}}{2F_o}$$

where S is a scale factor. Of the 2900 reflections collected, 2813 with $I \geq 3\sigma(I)$ were given $\omega(F) > 0$. The final values of R and Rw were 0.039 and 0.048, respectively.

Structure Determination

The Ni, P, and Cl atoms were located from a three-dimensional Patterson synthesis. A structure factor calculation followed by three-dimensional Fourier and difference Fourier syntheses phased by the Ni, P, and Cl atoms revealed the positions of all the carbon atoms. Full-matrix least-squares refinement was begun and the R factor decreased from 0.38 to 0.089 in three cycles. The function minimized was $\Sigma w\Delta^2$, where $w = 1/\sigma^2(F_o)$ and $\Delta = |F_o| - |F_c|$, $|F_o|$ and $|F_c|$ being the observed and calculated structure amplitudes, respectively. The atomic scattering factors were taken from Cromer and Waber's[6] values with the exception that Stewart, *et al.*,[7] values were used for hydrogen. The anomalous scattering factors for Ni, Cl, and P were included throughout the refinement. Cromer's[8] values for $\Delta f'$ and $\Delta f''$ for Ni, P, and Cl were used.

A difference Fourier synthesis was then calculated and all the hydrogen atoms readily located quite close to the calculated theoretical positions. A composite difference Fourier map of the hydrogen atoms is shown in Figure 2. The hydrogen atoms were added to the structure factors using the calculated coordinates but they were not varied during the least-squares refinement. Isotropic temperature factors were used for the hydrogen atoms; the B values ranged from 3.5 to 4.5 Å^2 depending upon the magnitude of the thermal vibration of the carbon atom to which it was attached. Individual anistropic temperature factors were used for all 14 carbon atoms and for the Ni, P, and Cl atoms. The refinement converged with $R = 0.039$ (2900 reflections), $R_o = 0.038$ (2813 reflections of nonzero weight), and $Rw = 0.048$ after three more cycles. No parameter of the Ni, Cl, or P atoms shifted by more than about one-tenth of the estimated standard deviations and no parameter of the carbon atoms shifted more than about one-third of their estimated σ's. The standard deviation of unit weight was 0.939, close to the expected value of unity.[9]

The positional and thermal parameters derived from the last cycle of least-squares are presented in Tables II and III along with the associated standard deviations in these parameters estimated from the inverse error matrix. The final values of $10|F_o|$ and $10|F_c|$ are given in Table IV for the 2900 reflections used in the refinement.[10]

TABLE II

ATOMIC COORDINATES OF $(C_8H_{14}PC_6H_5)_2NiCl$[a]

ATOM	X	Y	Z
NI	0.00000	0.00000	0.00000
CL	0.12519(9)	0.16003(8)	-0.18761(8)
P	0.20625(8)	0.17116(7)	0.17862(7)
C(1)	0.1468(3)	0.3089(3)	0.2219(3)
C(2)	0.1991(4)	0.4533(3)	0.1403(3)
C(3)	0.1402(4)	0.5506(4)	0.1645(4)
C(4)	0.0278(4)	0.5061(4)	0.2669(4)
C(5)	-0.0240(4)	0.3650(4)	0.3477(4)
C(6)	0.0333(4)	0.2643(4)	0.3268(4)
C(7)	0.4208(3)	0.2886(3)	0.1312(3)
C(8)	0.4660(4)	0.1668(4)	0.0978(4)
C(9)	0.4607(5)	0.0497(4)	0.2327(4)
C(10)	0.3118(4)	-0.0228(3)	0.3220(4)
C(11)	0.2581(3)	0.0905(3)	0.3664(3)
C(12)	0.3857(3)	0.2237(3)	0.4841(3)
C(13)	0.5544(3)	0.3450(3)	0.4287(3)
C(14)	0.5413(3)	0.4116(3)	0.2621(3)
H(1)	0.2832	0.4894	0.0610
H(2)	0.1736	0.6566	0.1043
H(3)	-0.0235	0.5728	0.2884
H(4)	-0.1070	0.3252	0.4333
H(5)	-0.0084	0.1540	0.3891
H(6)	0.4320	0.3566	0.0258
H(7)	0.5859	0.2280	0.0659
H(8)	0.3809	0.0964	-0.0026
H(9)	0.5703	0.1065	0.3086
H(10)	0.4550	-0.0489	0.1795
H(11)	0.3448	-0.0702	0.4282
H(12)	0.2090	-0.1171	0.2560
H(13)	0.1561	0.0177	0.4295
H(14)	0.4062	0.1706	0.5889
H(15)	0.3294	0.2861	0.5034
H(16)	0.6191	0.2842	0.4325
H(17)	0.6189	0.4371	0.5090
H(18)	0.6618	0.4722	0.2312
H(19)	0.5022	0.4900	0.2673

[a] The standard deviation of the least significant figure is given in parentheses.

TABLE III

THERMAL PARAMETERS ($\times 10^3$) OF $(C_8H_{14}PC_6H_5)_2NiCl_2$[a]

ATOM	B11	B22	B33	B12	B13	B23
NI	2.81(3)	2.10(4)	2.49(3)	0.53(2)	0.63(2)	-0.14(2)
CL	3.98(3)	3.75(3)	3.00(3)	0.06(3)	0.84(2)	0.53(2)
P	2.57(3)	2.21(3)	2.44(3)	0.75(2)	0.59(2)	-0.14(2)
C(1)	2.58(10)	3.13(12)	2.93(11)	1.14(9)	0.20(8)	-0.49(9)
C(2)	4.60(13)	3.63(14)	3.78(13)	2.31(12)	0.88(10)	0.27(10)
C(3)	5.81(17)	4.26(16)	5.30(14)	3.17(13)	0.28(13)	-0.33(12)
C(4)	4.72(16)	5.15(19)	6.52(18)	3.24(14)	-0.14(14)	-1.80(15)
C(5)	3.96(15)	5.91(20)	7.41(20)	2.18(14)	2.01(14)	-1.73(16)
C(6)	4.02(14)	3.97(14)	5.39(16)	1.79(12)	1.87(12)	-0.05(12)
C(7)	2.85(11)	2.73(12)	3.35(11)	1.09(9)	0.91(8)	0.04(9)
C(8)	4.53(15)	5.16(16)	4.55(14)	2.84(13)	1.38(11)	-0.39(12)
C(9)	6.98(21)	5.51(19)	6.57(20)	4.23(17)	1.23(16)	-0.63(15)
C(10)	5.44(16)	2.98(14)	4.78(14)	2.20(12)	0.15(12)	0.19(11)
C(11)	3.84(12)	2.65(12)	3.03(11)	1.25(10)	0.74(9)	0.25(9)
C(12)	4.25(13)	4.08(14)	2.93(11)	1.99(11)	0.09(9)	-0.29(9)
C(13)	3.50(13)	3.71(13)	4.13(14)	1.59(13)	-0.36(11)	-0.91(10)
C(14)	2.72(11)	3.50(13)	4.27(13)	0.98(10)	0.48(9)	-0.41(10)

[a] Anisotropic thermal parameters are in the form $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2\,hlB_{13} + 2klB_{23})]$.

Description of the Structure

The crystal structure of $(C_8H_{14}PCH_5)_2NiCl_2$ consists of discretely packed molecules. An inspection of the

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(6) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(7) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3172 (1965).

(8) (a) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965); (b) D. T. Cromer, Personal Communication.

(9) In addition to various local programs, the programs used in refinement were Busing and Levy's ORFLS program, Zalkin's FORDAP Fourier, LSLONG least-squares, and DISTAN distance and angle programs, and Johnson's ORTEP thermal ellipsoid program. Hope's program HPOSN was used to calculate the hydrogen positions.

(10) Table IV, listing structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-3017. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

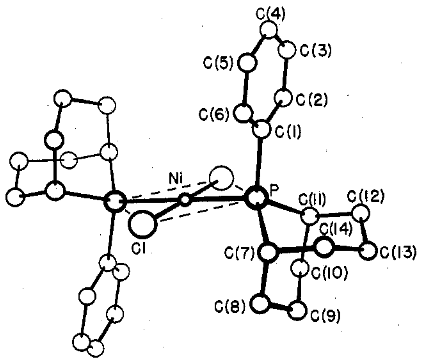

Figure 3.—Perspective view of molecular complex $(C_8H_{14}PC_6H_5)_2$-$NiCl_2$.

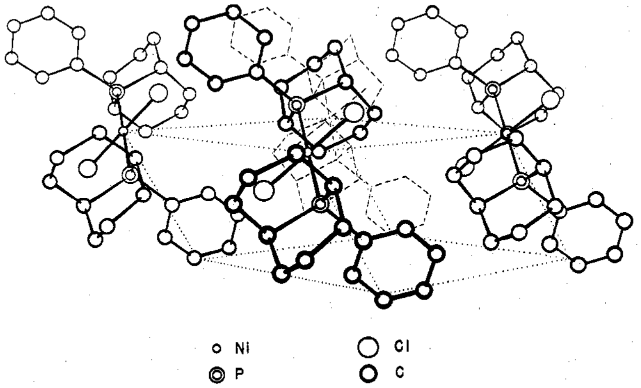

Figure 4.—Schematic drawing of molecules of $(C_8H_{14}PC_6H_5)_2NiCl_2$ in $^1/_2$ unit cell. Unit cell outlined with dotted lines.

intermolecular contacts shows that there are none appreciably smaller than the sum of the corresponding van der Waals radii. The coordination of the Cl and P around the Ni is square planar. The Ni–Cl distance is 2.166 (1) Å and the Ni–P distance 2.227 (1) Å. The phosphorus is tetrahedrally coordinated with two of the bonds symmetrically bridging the cyclooctane molecule (*i.e.*, the symmetrical isomer). The phosphorus–carbon bonds to the cyclooctane molecule are 1.834 (3) and 1.831 (3) Å. The phosphorus–benzene carbon distance is 1.807 (3) Å. A perspective view of the molecule is shown in Figure 3. The packing arrangement of the molecule in the unit cell is shown schematically in perspective in Figure 4. The principal interatomic distances and angles and their standard deviations computed from the inverse correlation matrix are given in Tables V and VI. The root-mean-square amplitudes of vibration of the atoms are listed in Table VII. The orientations of the thermal ellipsoids are indicated in ORTEP Figures 5 and 6.

Table V

Principal Interatomic Distances of $(C_8H_{14}PC_6H_5)_2NiCl_2$[a]

ATOMS	DIST.
NI-CL	2.166(1)
NI-P	2.227(1)
P-C(1)	1.807(3)
P-C(7)	1.834(3)
P-C(11)	1.831(3)
C(1)-C(2)	1.392(4)
C(1)-C(6)	1.391(4)
C(2)-C(3)	1.383(4)
C(3)-C(4)	1.366(5)
C(4)-C(5)	1.366(5)
C(5)-C(6)	1.395(5)
C(7)-C(8)	1.533(4)
C(7)-C(14)	1.541(4)
C(8)-C(9)	1.540(5)
C(9)-C(10)	1.519(5)
C(10)-C(11)	1.548(4)
C(11)-C(12)	1.530(4)
C(12)-C(13)	1.534(4)
C(13)-C(14)	1.526(4)

[a] The standard deviation of the least significant figure is given in parentheses.

Table VI

Principal Bond Angles of $(C_8H_{14}PC_6H_5)_2NiCl_2$[a]

ATOMS	ANGLE DEG.
CL-NI-P	90.29(2)
NI-P-C(1)	106.19(8)
NI-P-C(7)	119.16(8)
NI-P-C(11)	118.34(8)
C(1)-P-C(7))	108.29(11)
C(1)-P-C(11)	108.14(11)
C(7)-P-C(11)	96.00(11)
P-C(1)-C(2)	121.3(2)
P-C(1)-C(6)	119.9(2)
P-C(7)-C(8)	106.3(2)
P-C(7)-C(14)	111.2(2)
P-C(11)-C(10)	105.7(2)
P-C(11)-C(12)	111.9(2)
C(1)-C(2)-C(3)	120.6(3)
C(2)-C(3)-C(4)	120.9(3)
C(3)-C(4)-C(5)	119.1(3)
C(4)-C(5)-C(6)	121.6(3)
C(6)-C(1)-C(2)	118.4(3)
C(7)-C(8)-C(9)	116.8(3)
C(7)-C(14)-C(13)	116.7(2)
C(8)-C(7)-C(14)	115.5(2)
C(8)-C(9)-C(10)	116.1(3)
C(9)-C(10)-C(11)	117.4(3)
C(10)-C(11)-C(12)	115.7(2)
C(11)-C(12)-C(13)	115.7(2)
C(12)-C(13)-C(14)	114.9(2)

[a] The standard deviation of the least significant figure is given in parentheses.

Table VII

Root-Mean-Square Amplitudes of Vibration (Å)[a] of $(C_8H_{14}PC_6H_5)_2NiCl_2$

ATOM	MAX.	MED.	MIN.
NI	0.189(4)	0.177(4)	0.163(4)
CL	0.225(6)	0.218(6)	0.195(6)
P	0.180(7)	0.176(8)	0.163(7)
C(1)	0.20(1)	0.19(1)	0.18(1)
C(2)	0.24(1)	0.22(1)	0.21(1)
C(3)	0.27(1)	0.26(1)	0.23(1)
C(4)	0.29(1)	0.26(1)	0.24(1)
C(5)	0.31(1)	0.27(1)	0.22(1)
C(6)	0.26(1)	0.23(1)	0.22(1)
C(7)	0.21(1)	0.19(1)	0.19(1)
C(8)	0.25(1)	0.24(1)	0.24(1)
C(9)	0.29(1)	0.29(1)	0.26(1)
C(10)	0.26(1)	0.25(1)	0.19(1)
C(11)	0.22(1)	0.20(1)	0.18(1)
C(12)	0.23(1)	0.23(1)	0.19(1)
C(13)	0.23(1)	0.22(1)	0.21(1)
C(14)	0.23(1)	0.21(1)	0.18(1)

[a] Corresponding to the principal area of the anisotropic ellipse. The standard deviation of the least significant figure is given in parentheses.

The Ni–P distance 2.227 (1) Å is significantly shorter than the values 2.251 (3)[11] and 2.26 Å[12,13] reported for the diamagnetic trans planar $NiBr_2(PR_3)_2$ complexes. It is also shorter than the values 2.257 (2) and 2.306 (2) Å found in the pseudotetrahedral $Ni(N_3)(NO)(P(C_6H_5)_3)_2$[14] complex and the values 2.315 (8)[13] and 2.31 Å[15] found in the paramagnetic tetrahedral $NiBr_2(PR_3)_2$ complexes. The phosphorus–benzene carbon distance 1.807 (3) Å is similar to the values reported for $P-C_6H_5$ distances, 1.800 (11)–1.802 (10) Å for $NiBr_3[P(C_6H_5)(CH_3)]_2 \cdot 0.5NiBr_2$ and $[P(C_6H_5)(CH_3)_2]_2C_6H_6$,[11] 1.815 (9)–1.824 (10) Å for $ReCl_3(NC_6H_4OCH_3)[P(C_2H_5)_2C_6H_5]_2$,[16] but shorter than those (1.827 (5)–1.842 (5) Å) reported for $Ni(N)_3(NO)[P(C_6H_5)_3]_2$.[14]

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(16) D. Bright and J. A. Ibers, *Inorg. Chem.*, **7**, 1099 (1968).

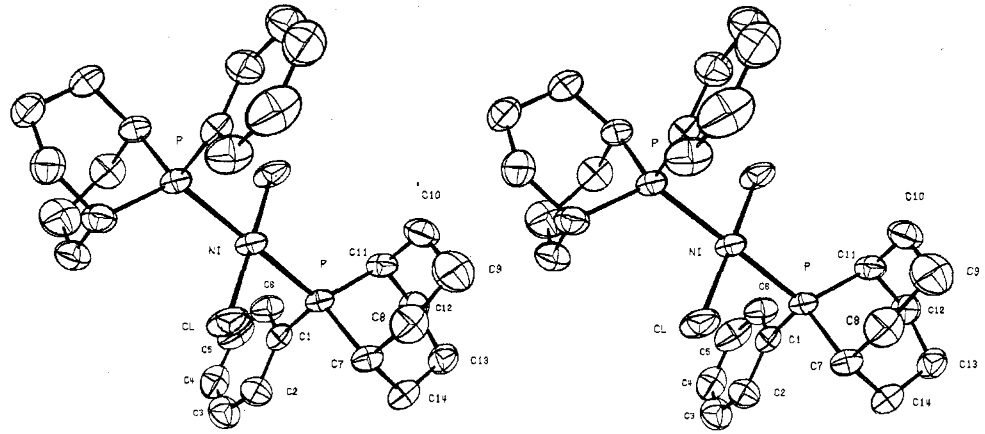

Figure 5.—ORTEP stereoscopic drawing of $(C_8H_{14}PC_6H_5)_2NiCl_2$ 50% probability ellipsoids. For clarity, no hydrogen atoms are included.

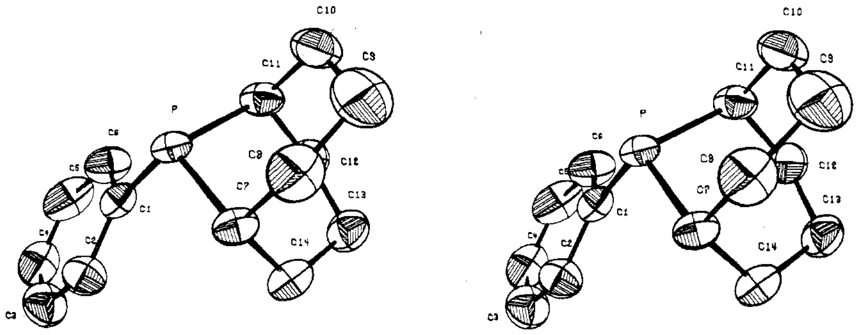

Figure 6.—ORTEP stereoscopic drawing of phenylphosphorobicyclononane molecule; 50% probability ellipsoids. For clarity, no hydrogen atoms are included.

The phosphorus–cyclooctane carbon distances, P–C(7) = 1.834 (3) and P–C(11) = 1.831 (3) Å, are significantly longer than the P–C_6H_5 distance. Evidence that P–C_6H_5 distances are somewhat shorter than P–C alkyl distances has been reported.[4,16]

In compounds containing $>P(C_6H_5)$ or $P(C_6H_5)_3$ groups the possibility arises that the d orbitals of the phosphorus atom may have a significant overlap with the π clouds of the phenyl groups.[17] Assuming sp^3 tetrahedral hybrid σ bonds from the P to Ni, alkyl C, and phenyl C atoms, the d_{xz} and d_{yz} π orbitals of P could overlap with the π clouds of the phenyl group. This would reduce the length of the P–phenyl carbon distance relative to that of the P–C cyclooctane distances in agreement with the observed results, and also lengthen the phenyl C–C distances adjacent to the phosphorus atom. The coordinate axes are chosen with the P atom at the origin and the X, Y, Z axes through the faces of a cube with the coordinates of Ni, C(11), C(7), and C(1) given by $(-1,-1,-1)$, $(1, 1, -1)$, $(-1, 1, 1)$, and $(1, -1, 1)$, respectively. The C–C distances in the C_6H_5 group show an apparent decrease in bond length with distance from the carbon atom attached to the phosphorus atom. The bond lengths, however, have not been corrected for thermal motion. Comparison of Tables III and VII and ORTEP Figures 5 and 6 shows that the thermal oscillations of the carbon atoms in the C_6H_5 ring most distant from the phosphorus atoms are larger, which would tend to decrease the apparent bond lengths between these atoms.

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[17] J. J. Daly, *Perspect. Struct. Chem.*, **3**, 169 (1971).