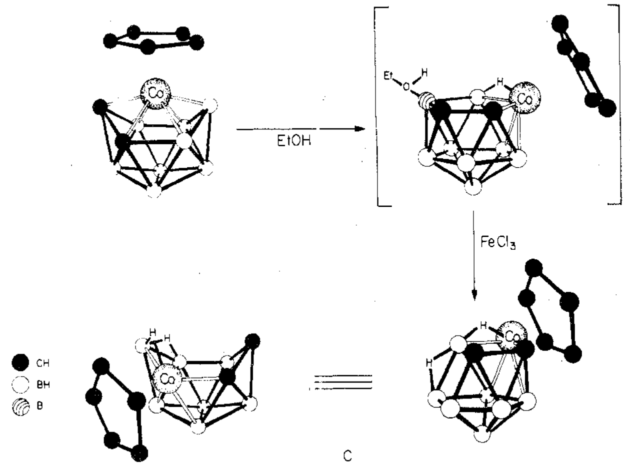

Figure 5. Proposed mechanism of formation of 8-η-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$.

in ethanol led to the conclusion that 6-η-C_5H_5-6-Co-2,3-$C_2B_7H_9$ was produced upon dehydrogenation of $C_5H_5CoC_2B_7H_{11}$, and the structure proposed for this latter compound was that which would readily close to produce the observed isomer of closo geometry. To rationalize the structure of $C_5H_5CoC_2B_7H_{11}$ thus generated, an alternate site of ligand attack in the reaction of 1-η-C_5H_5-1-Co-2,4-$C_2B_8H_{10}$ with ethanol and $FeCl_3$ was proposed. This proposed reaction sequence is shown in Figure 4b.

The structural results presented here indicate that there is no evidence to support a mode of attachment of ethanol to 1-η-C_5H_5-1-Co-2,4-$C_2B_8H_{10}$ different from that observed for pyridine. Instead, we envision the reaction to proceed in a manner similar to that observed with pyridine. Ferric chloride oxidation would remove the ligand-substituted boron atom from the polyhedron and thus generate the *nido*-8-η-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$ geometry found here (Figure 5c).

Dehydrogenation of this compound would not produce 6-η-C_5H_5-6-Co-2,3-$C_2B_7H_9$, however. Closure would instead produce the presently unknown species 3-η-C_5H_5-3-Co-1,2-$C_2B_7H_9$. This compound would be expected to undergo rapid thermal polyhedral rearrangement[26] to produce, in turn, the 1,6 and 1,10 isomers (carbon positions numbered only), and, in fact, 2-η-C_5H_5-2-Co-1,10-$C_2B_7H_9$ is the major product isolated from the reaction of 8-η-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$ with ethanolic ferric chloride (only traces of 6-η-C_5H_5-6-Co-2,3-$C_2B_7H_9$ were noticed in the reaction mixture). It therefore appears that the side product, 6-η-C_5H_5-6-Co-2,3-$C_2B_7H_9$, is not an intermediate in the reaction sequence 1-η-C_5H_5-1-Co-2,4-$C_2B_8H_{10}$ $\rightarrow$ $C_5H_5CoC_2B_7H_{11}$ $\rightarrow$ 2-η-C_5H_5-2-Co-1,10-$C_2B_7H_9$. The origin of this side product still remains obscure. It could arise in the initial reaction solution by oxidative removal of boron atom 8 from 1-η-C_5H_5-1-Co-2,4-$C_2B_8H_{10}$ followed by polyhedral closure, but its production from $C_5H_5CoC_2B_7H_{11}$ must involve substantial polyhedral rearrangement.

Acknowledgments. This work was supported, in part, by a grant from the Office of Naval Research and the Army Research Office (Durham), to whom we express our thanks. The UCLA Campus Computing Network provided a generous amount of computer time for the requisite calculations, which is greatly appreciated. We thank Professor D. F. Gaines for results prior to publication.

Registry No. 8-η-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$, 52760-69-7.

Supplementary Material Available. Observed and calculated structure factors for 8-η-C_5H_5-8-Co-6,7-$C_2B_7H_{11}$ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2842.

(26) M. F. Hawthorne, K. P. Callahan, and R. J. Wiersema, *Tetrahedon*, **30**, 1795 (1974), and references therein.

Contribution from the Laboratorio CNR and Istituto di Chimica
Generale e Inorganica, Universita di Firenze, Florence, Italy

Description of a Monovalent Nickel Complex. Crystal and Molecular Structure of Iodo[1,1,1-tris(diphenylphosphinomethyl)ethane]nickel(I)

P. DAPPORTO, G. FALLANI, and L. SACCONI*

Received May 22, 1974 AIC403298

The complex of nickel(I) with the terdentate ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (p_3), having the formula $Ni(p_3)I$, has been studied by X-ray analysis using diffractometric data. The crystals are orthorhombic, space group $Pn2_1a$, with cell dimensions $a = 20.439$ (6), $b = 17.143$ (7), and $c = 10.359$ (3) Å. The structure has been solved by three-dimensional Patterson and Fourier syntheses and refined by least-squares techniques to a final conventional R factor of 0.051, for the 2357 independent observed reflections. The structure consists of discrete $Ni(p_3)I$ molecules. The nickel atoms are four-coordinate, linked to the three phosphorus atoms of the p_3 ligand and to the iodine atom. The coordination polyhedron can be described as a distorted tetrahedron. Bond lengths and angles in the coordination polyhedron are Ni–I = 2.546 (2), Ni–P(1) = 2.222 (4), Ni–P(2) = 2.224 (4), Ni–P(3) = 2.217 (4) Å; I–Ni–P(1) = 125.0 (1), I–Ni–P(2) = 125.3 (1), I–Ni–P(3) = 116.2 (1), P(1)–Ni–P(2) = 91.8 (1), P(1)–Ni–P(3) = 94.1 (1), P(2)–Ni–P(3) = 96.9 (1)°.

Introduction

By reaction of the potentially terdentate tripod ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, $CH_3C(CH_2PPh_2)_3$ (p_3), with NiI_2 and CoI_2 in alcoholic solution, nickel(I) and cobalt(I) complexes having the general formula $M(p_3)I$ are formed.[1] This reaction can be attributed to the reducing

(1) L. Sacconi and S. Midollini, *J. Chem. Soc., Dalton Trans.*, 1213 (1972).

Table I. Positional Parameters ($\times 10^5$), Anisotropic Temperature Factors[a] ($\times 10^5$), and Estimated Standard Deviations in Parentheses

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I	−12,845 (6)	−25,000	−855 (8)	445 (4)	350 (4)	925 (9)	−167 (3)	9 (5)	−106 (6)
Ni	−6,662 (8)	−13,206 (13)	7,747 (14)	215 (4)	245 (5)	702 (14)	−21 (5)	8 (6)	−5 (8)
P(1)	3,895 (17)	−13,079 (24)	12,885 (31)	233 (8)	250 (11)	761 (30)	13 (10)	−13 (13)	6 (18)
P(2)	−5,880 (18)	−1,715 (23)	−2,099 (31)	211 (8)	266 (11)	666 (29)	−37 (8)	−5 (13)	41 (16)
P(3)	−9,881 (17)	−8,697 (23)	26,779 (32)	212 (9)	258 (11)	697 (29)	5 (9)	20 (13)	0 (16)

[a] Anisotropic thermal factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

power of the triphosphine which acts as an acceptor of iodine from the metal(II) iodide to form iodo derivatives of pentavalent phosphorus. The corresponding chloro- and bromo-metal complexes can be obtained only by using a specific reducing agent such as $NaBH_4$. Magnetic measurements show that these complexes contain d^9 nickel and high-spin d^8 cobalt species.

The X-ray powder patterns (which are all practically identical) of these complexes indicate that their coordination geometries are similar.[1]

Since complexes of cobalt and nickel in the monovalent state are very few and structure determinations even fewer, it seemed interesting to undertake the structure analysis on the $Ni(p_3)I$ complex. A preliminary account of this work has already appeared.[2]

Experimental Section

The preparation and characterization of all the $M(p_3)X$ complexes have been reported elsewhere.[1] The yellow crystals of $Ni(p_3)I$ used for the data collection were grown from a methylene chloride solution.

Collection of X-Ray Data. The unit cell of $Ni(p_3)I$ is orthorhombic, space group $Pn2_1a$, with $a = 20.439$ (6) Å, $b = 17.143$ (7) Å, $c = 10.359$ (3) Å, $V = 3629.6$ Å^3, $d_m = 1.49$ g cm^{-3}, $Z = 4$, $M = 810.63$, and $d_c = 1.49$ g cm^{-3}. Cell parameters were determined by least-squares refinement of 20 selected 2θ values. The crystal used for the collection of the intensities was a parallelepiped of dimensions 0.17 × 0.60 × 0.33 mm, for the [100], [010], and [001] directions, respectively. The radiation used was zirconium-filtered Mo Kα (λ 0.7107 Å), and the linear absorption coefficient was calculated to be 15.51 cm^{-1}. Intensities were collected on a four-circle Hilger automatic diffractometer, using a θ–ω scan technique. A total of 2357 reflections having $I \geqslant 3\sigma(I)$ were measured in the range $0° < 2\theta \leqslant 50°$. Scans of 70 sec, with steps of 0.01° and a count of 1 sec for each step, were taken across the peaks; backgrounds were counted for 35 sec on each side of the peak. Three standard reflections were monitored every 50 measurements. No differences larger than 5% were found in these measurements. The intensities were calculated according to the expression $I = P - 0.5 \cdot (T_p/T_b)(B_1 + B_2)$, where P is the peak count, B_1 and B_2 are the background counts, and T_p and T_b are the count times on the peak and background, respectively. The standard deviations on the intensities were calculated by use of the expression $\sigma = [P + 0.25(B_1 + B_2)(T_p/T_b)^2 + (0.02I)^2]^{1/2}$.[3] The intensities were corrected for Lorentz and polarization effects. An absorption correction was applied by numerical methods;[4] transmission factors varied between 0.60 and 0.82. Atomic scattering factors were taken from ref 5 for neutral iodine, nickel, phosphorus, and carbon atoms and from ref 6 for hydrogen atoms. The effects of the anomalous dispersion of iodine, nickel, and phosphorus atoms were considered[7] in the final stage of refinement.

Structure Determination

A three-dimensional Patterson synthesis yielded the positional parameters of the nickel and the iodine atoms. The other nonhydrogen atoms were located from successive three-dimensional Fourier maps. These calculations were performed on an IBM 1130 computer.[8] Refinement was then undertaken by use of a full-matrix least-squares program.[9] The weighting scheme used was $w = 1$ for reflections with $F_o \leqslant 25$ and $\sqrt{w} = 25/F_o$ for reflections with $F_o > 25$. Several cycles with isotropic temperature factors for carbon atoms and anisotropic parameters for the heavier atoms gave an R factor of 5.5%. At this point the absolute configuration was determined by application of the anomalous dispersion corrections on iodine, nickel, and phosphorus atoms. The correct configuration was obtained by changing the signs of the three atomic coordinates of all the atoms, since this configuration gave an R factor of 5.4%, *vs.* 5.6% for the other configuration, and the standard deviations on the atomic parameters were remarkably lower. The high significance of this choice was confirmed by the Hamilton test.[10] A difference Fourier synthesis calculated at this point showed the positions of 22 of the 39 hydrogen atoms. These 22 hydrogen atoms were intro-

Table II. Positional Parameters ($\times 10^4$), Isotropic Temperature Factors, and Estimated Standard Deviations in Parentheses

Atom	x/a	y/b	z/c	B, Å^2
C(1)	355 (7)	951 (9)	2824 (14)	4.1 (0.3)
C(2)	42 (7)	223 (9)	2184 (14)	3.9 (0.3)
C(3)	610 (6)	−290 (8)	1723 (12)	3.1 (0.2)
C(4)	−370 (7)	536 (8)	1087 (13)	3.5 (0.2)
C(5)	−341 (7)	−205 (9)	3270 (13)	3.8 (0.2)
C(6)	646 (7)	−1884 (9)	2678 (15)	4.2 (0.3)
C(7)	266 (7)	−2488 (11)	3056 (13)	4.3 (0.3)
C(8)	445 (11)	−3004 (14)	4071 (22)	6.4 (0.4)
C(9)	1008 (12)	−2842 (16)	4672 (24)	7.6 (0.5)
C(10)	1423 (10)	−2222 (12)	4405 (21)	6.1 (0.4)
C(11)	1239 (8)	−1740 (10)	3366 (16)	4.7 (0.3)
C(12)	1015 (7)	−1607 (10)	124 (13)	3.9 (0.3)
C(13)	1637 (7)	−1286 (10)	78 (12)	4.1 (0.3)
C(14)	2063 (8)	−1522 (11)	−829 (16)	5.1 (0.3)
C(15)	1929 (10)	−2124 (14)	−1675 (21)	6.7 (0.4)
C(16)	1299 (9)	−2437 (14)	−1615 (18)	5.8 (0.3)
C(17)	861 (9)	−2190 (11)	−718 (18)	5.4 (0.4)
C(18)	45 (7)	−57 (8)	−1432 (13)	3.5 (0.2)
C(19)	399 (9)	645 (12)	−1597 (19)	6.3 (0.4)
C(20)	836 (10)	708 (14)	−2610 (22)	6.3 (0.4)
C(21)	940 (11)	95 (15)	−3415 (23)	7.5 (0.5)
C(22)	619 (10)	−639 (13)	−3221 (19)	6.2 (0.4)
C(23)	178 (7)	−689 (10)	−2249 (15)	4.7 (0.3)
C(24)	−1266 (7)	285 (9)	−1029 (15)	4.0 (0.3)
C(25)	−1337 (8)	1116 (10)	−1089 (17)	4.7 (0.3)
C(26)	−1864 (9)	1445 (11)	−1750 (17)	5.4 (0.3)
C(27)	−2312 (10)	968 (12)	−2372 (19)	5.9 (0.4)
C(28)	−2260 (9)	198 (12)	−2343 (19)	5.8 (0.4)
C(29)	−1750 (8)	−171 (11)	−1651 (16)	5.0 (0.3)
C(30)	−1136 (6)	−1532 (8)	4016 (13)	3.4 (0.2)
C(31)	−1493 (7)	−2197 (9)	3779 (14)	4.3 (0.3)
C(32)	−1639 (9)	−2708 (11)	4748 (17)	4.8 (0.4)
C(33)	−1412 (8)	−2566 (11)	6009 (15)	4.5 (0.3)
C(34)	−1055 (8)	−1905 (11)	6275 (17)	4.8 (0.3)
C(35)	−921 (7)	−1363 (10)	5282 (13)	4.4 (0.2)
C(36)	−1726 (6)	−242 (8)	2802 (13)	3.6 (0.2)
C(37)	−1865 (8)	182 (11)	3903 (16)	5.4 (0.3)
C(38)	−2412 (9)	655 (11)	3947 (17)	5.7 (0.4)
C(39)	−2793 (11)	728 (14)	2921 (21)	6.4 (0.4)
C(40)	−2683 (10)	290 (13)	1811 (20)	6.4 (0.4)
C(41)	−2132 (8)	−203 (11)	1750 (17)	5.2 (0.3)

---

(2) P. Dapporto, G. Fallani, S. Midollini, and L. Sacconi, *J. Chem. Soc., Chem. Commun.*, 1161 (1972).

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

(4) Hamilton's GONO9 program for absorption correction, with local modification.

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

(6) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, 1962, p 202.

(7) D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

(8) Series of programs from the A.R.C., Unit of Structural Chemistry, University College London, for the IBM 1130 Computer.

(9) The program used is a modification of Martin, Busing, and Levy's ORFLS to include the real and imaginary parts of the anomalous dispersion by E. Cannillo.

(10) W. C. Hamilton, *Acta Crystallogr.*, 18, 502 (1965).

Table III. Positional Parameters ($\times 10^3$) of the Hydrogen Atoms[a]

Atom	x/a	y/b	z/c
H(1')	0	141	304
H(1'')	65	83	360
H(3')	81	−2	104
H(4')	−28	108	44
H(5')	−49	25	388
H(7)	−10	−262	264
H(9)	115	−342	530
H(10)	200	−205	460
H(11)	160	−140	324
H(13)	160	−80	76
H(14)	252	−137	−70
H(16)	125	−300	−224
H(17)	40	−223	−78
H(23)	−20	−125	−200
H(25)	−80	130	−90
H(29)	−163	−85	−166
H(31)	−165	−250	310
H(32)	−195	−315	456
H(33)	−138	−277	680
H(35)	−73	−80	580
H(37)	−154	26	456
H(39)	−324	107	260

[a] These atoms are numbered according to the atom to which they are attached.

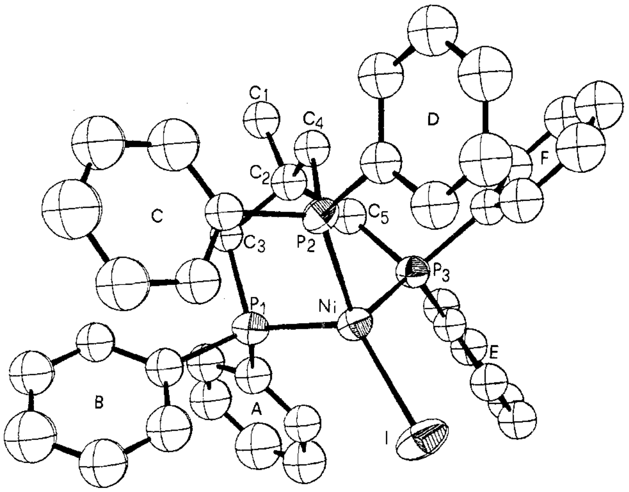

Figure 1. A perspective view of the Ni(p_3)I molecule (ORTEP diagram, showing 30% probability ellipsoids).

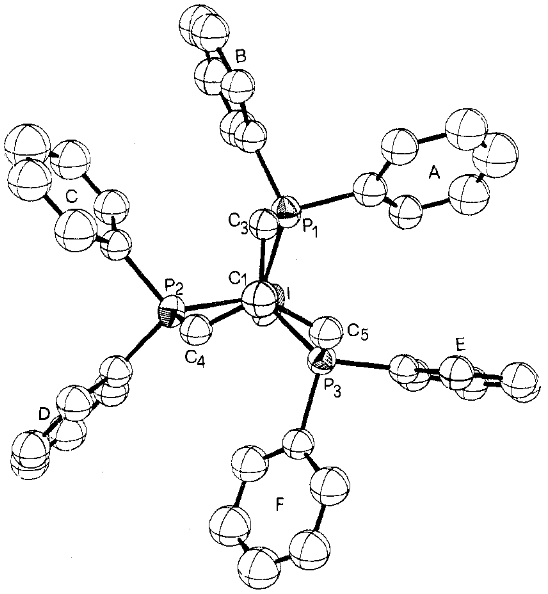

Figure 2. View of the Ni(p_3)I molecule along the pseudo-C_3 axis.

Table IV. Interatomic Distances (Å), Angles (deg), and Their Respective Standard Deviations

(a) Bond Lengths

Ni-I	2.546 (2)	P(2)-C(18)	1.82 (1)
Ni-P(1)	2.222 (4)	P(2)-C(24)	1.80 (1)
Ni-P(2)	2.224 (4)	P(3)-C(5)	1.85 (1)
Ni-P(3)	2.217 (4)	P(3)-C(30)	1.82 (1)
		P(3)-C(36)	1.86 (1)
P(1)-C(3)	1.86 (1)	C(1)-C(2)	1.55 (2)
P(1)-C(6)	1.82 (2)	C(2)-C(3)	1.53 (2)
P(1)-C(12)	1.83 (2)	C(2)-C(4)	1.51 (2)
P(2)-C(4)	1.86 (1)	C(2)-C(5)	1.55 (2)

(b) Bond Angles

I-Ni-P(1)	125.0 (0.1)	C(5)-P(3)-C(36)	101.6 (0.6)
I-Ni-P(2)	125.3 (0.1)	C(30)-P(3)-C(36)	100.0 (0.6)
I-Ni-P(3)	116.2 (0.1)	C(1)-C(2)-C(3)	106.4 (1.1)
P(1)-Ni-P(2)	91.8 (0.1)	C(1)-C(2)-C(4)	105.3 (1.2)
P(1)-Ni-P(3)	94.1 (0.1)	C(1)-C(2)-C(5)	106.2 (1.1)
P(2)-Ni-P(3)	96.9 (0.1)	C(3)-C(2)-C(4)	113.1 (1.1)
		C(3)-C(2)-C(5)	109.7 (1.2)
Ni-P(1)-C(3)	107.6 (0.4)	C(4)-C(2)-C(5)	115.5 (1.5)
Ni-P(1)-C(6)	117.6 (0.5)	P(1)-C(3)-C(2)	115.5 (0.9)
Ni-P(1)-C(12)	121.2 (0.5)	P(2)-C(4)-C(2)	116.3 (1.0)
C(3)-P(1)-C(6)	104.4 (0.7)	P(3)-C(5)-C(2)	114.3 (0.9)
C(3)-P(1)-C(12)	104.6 (0.7)	P(1)-C(6)-C(7)	118.6 (1.1)
C(6)-P(1)-C(12)	99.6 (0.7)	P(1)-C(6)-C(11)	123.0 (1.2)
Ni-P(2)-C(4)	105.3 (0.5)	P(1)-C(12)-C(13)	123.6 (1.2)
Ni-P(2)-C(18)	117.7 (0.5)	P(1)-C(12)-C(17)	117.7 (1.2)
Ni-P(2)-C(24)	123.0 (0.5)	P(2)-C(18)-C(19)	122.6 (1.2)
C(4)-P(2)-C(18)	105.2 (0.6)	P(2)-C(18)-C(23)	118.4 (1.1)
C(4)-P(2)-C(24)	103.9 (0.7)	P(2)-C(24)-C(25)	122.0 (1.1)
C(18)-P(2)-C(24)	99.9 (0.7)	P(2)-C(24)-C(29)	120.7 (1.2)
Ni-P(3)-C(5)	107.3 (0.5)	P(3)-C(30)-C(31)	118.0 (1.0)
Ni-P(3)-C(30)	120.6 (0.5)	P(3)-C(30)-C(35)	121.9 (1.1)
Ni-P(3)-C(36)	120.3 (0.4)	P(3)-C(36)-C(37)	121.9 (1.1)
C(5)-P(3)-C(30)	104.5 (0.6)	P(3)-C(36)-C(41)	117.7 (1.1)

(c) Phenyl Rings

Ring	Mean	Mean dev	Max dev
	(i) Bond Lengths		
A	1.39	0.02	0.05
B	1.37	0.02	0.05
C	1.39	0.03	0.04
D	1.39	0.03	0.06
E	1.39	0.02	0.03
F	1.38	0.02	0.06
	(ii) Bond Angles		
A	120.0	3.3	6.4
B	120.0	1.7	3.8
C	120.0	1.3	2.3
D	120.0	0.9	2.7
E	120.0	0.4	1.3
F	120.0	0.7	1.6

duced in the calculations in the positions obtained from this ΔF map, with an overall isotropic B thermal parameter of 5 Å^2, and were not refined. The final R was 5.1%. A final difference Fourier showed no remarkable features. The final values of the parameters and their standard deviations, as estimated from the inverse matrix, are reported in Tables I–III.

Description and Discussion of the Structure

The structure consists of Ni(p_3)I molecules. The nickel atom is tetracoordinate, linked to the three phosphorus atoms of the p_3 ligand and to the iodine atom. The geometry of the coordination polyhedron can be described in terms of a distorted tetrahedron. Perspective views of the configuration of the molecule are shown in Figures 1 and 2. Table IV lists intramolecular distances and angles with their estimated standard deviations. The intermolecular distances did not show remarkable features. The distortion from a regular tetrahedron is very remarkable, as can be noted from the values of the angles in the coordination polyhedron. In fact, the three P-Ni-P angles (91.8, 94.1, and 96.9°) have values much lower than the regular tetrahedral angle, while the three I-Ni-P angular values are very much larger (125.0, 125.3, and 116.2°).

The P-Ni-P angles in the present structure can be compared with the analogous P-Fe-P angles found in the $[Fe_2H_3(p_3)_2]PF_6 \cdot 1.5CH_2Cl_2$ complex,[11] whose coordination polyhedron was described in terms of two octahedra sharing a face (confacial bioctahedral geometry). These P-Fe-P angles have values ranging from 87.0 to 89.6°, therefore remarkably lower than those found for the P-Ni-P angles in the $Ni(p_3)I$ complex (the average value is 94.3°). This fact means that in the nickel complex the ligand molecule "stretches" allowing P-Ni-P angles to become closer to tetrahedral values. Ideal tetrahedral values are not achieved probably because of the shortness of the aliphatic chains of the ligand molecule.

Berglund and Meek, using the same p_3 ligand and another similar tripod ligand, the 1,1,1-tris(diethylphosphinomethyl)ethane (tep), which is different from p_3 only because there are ethyl groups linked to the phosphorus atoms, obtained nitrosyl nickel(0) tetrahedral complexes.[12] The molecular structure of the $[Ni(tep)NO]BF_4$ complex has been reported.[12,13] The P-Ni-P angular values found in this structure, which are all 93.5° because the $[Ni(tep)NO]^+$ ions have threefold crystallographic symmetry, are very close to those found in the $Ni(p_3)I$ structure; *i.e.*, also in this case these angles are very different from the ideal tetrahedral angular value. This fact confirms that these distortions from a tetrahedron are due to the particular steric requirements of these ligands which prevent the three phosphorus atoms moving apart. Also the Ni-P distances in these two complexes are very close: 2.208 Å in $[Ni(tep)NO]BF_4$ *vs.* 2.22 Å (average) in $Ni(p_3)I$.

This distortion from a regular tetrahedral geometry in the complexes of the $M(p_3)X$ series can account for the differences found between the spectra of the $Co(p_3)X$ complexes,[1] which are all isomorphous with $Ni(p_3)I$, and the spectra of the analogous cobalt(I) complexes with triphenylphosphine, $Co(PPh_3)_3X$, which have the same donor set and have been described as pseudotetrahedral.[14] In the latter case, in fact, the three phosphorus atoms are not constrained by the aliphatic chains and may form P-Co-P angles closer to tetrahedral.

Registry No. $Ni(p_3)I$, 37726-33-3.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2847.

(11) P. Dapporto, G. Fallani, S. Midollini, and L. Sacconi, *J. Amer. Chem. Soc.*, 95, 2021 (1973).

(12) D. Berglund and D. W. Meek, *Inorg. Chem.*, 11, 1493 (1972).

(13) P. G. Eller and P. W. R. Corfield, Abstracts, American Crystallographic Association Summer Meeting, Ottawa, Canada, Aug 1970, p 85; P. G. Eller, Ph.D. Dissertation, The Ohio State University, Dec 1971.

(14) M. Aresta, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, 3, 227 (1969).

Contribution from the Laboratorio CNR and Istituto di Chimica Generale e Inorganica, Universita di Firenze, Florence, Italy

Synthesis, Properties, and Structural Characterizations of Nonstoichiometric Hydrido Complexes of Nickel with the Tetradentate Ligand Tris(2-diphenylphosphinoethyl)amine

L. SACCONI,* A. ORLANDINI, and S. MIDOLLINI

Received July 11, 1974 AIC404620

Reaction of the tetradentate tripod ligand $N(CH_2CH_2PPh_2)_3$ (np_3) with $Ni(BF_4)_2$, in the presence or absence of $NaBH_4$, yields nonstoichiometric hydrido complexes of the general formula $[NiH_x(np_3)]BF_4$ which contain nickel in a range of formal oxidation states intermediate between +1 and +2. The most hydrogen-rich compounds are obtained by protonation of the trigonal-pyramidal nickel (0) complex of the same ligand, $[Ni(np_3)]$, with HBF_4. The values of the amount of hydride, x, range from 0.83 to 0.04, while the magnetic moments for the corresponding compounds range from 0.88 to 2.08 BM. The presence of nonstoichiometric hydridic hydrogen bound to the nickel has been ascertained by volumetric gas analysis and by the existence of an infrared Ni-H band at *ca.* 595 cm^{-1} whose intensity increases with decreasing magnetic moment. All the complexes are isomorphous. An X-ray analysis of the compound with the formula $[NiH_{0.5}(np_3)]BF_4$ shows the presence of only one crystallographic type of cation. However, due to the nonstoichiometric amounts of hydrogen in these compounds, a percentage of these cations are trigonal bipyramidal with nitrogen and hydrogen atoms in the axial positions, while those remaining cations lacking hydride are trigonal pyramidal in structure. The missing hydrogen in a percentage of cations causes vacant sites to appear both in the $[Ni(np_3)]BF_4$ unit and in the crystal lattice as a whole. This is supported by the X-ray analysis of the isomorphous compound $[Co(np_3)]BF_4$ whose structure was found to be practically equal to that of the nickel complex but lacking the hydride ligand.

Introduction

We have previously shown that the tripod-shaped ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, $CH_3C(CH_2PPh_2)_3$ (p_3), can form complexes from nickel(I) and cobalt(I) of the general type $Ni(p_3)X$ (X = halogen).[1] In some cases, such as with the iodide derivative, the reduction of the bivalent ions occurs even in the absence of specific reducing agents. The complex $Ni(p_3)I$ was shown by X-ray methods to have a pseudotetrahedral structure;[2] a similar structure can be attributed to the other nickel and cobalt

(1) L. Sacconi and S. Midollini, *J. Chem. Soc., Dalton Trans.*, 1213 (1972).

(2) P. Dapporto, G. Fallani, S. Midollini, and L. Sacconi, *J. Chem. Soc., Chem. Commun.*, 1161 (1972).