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.

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

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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

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Table I. Analytical Magnetic and Infrared Data for the $[NiH_x(np_3)](BF_4)$ Compounds

		% found[a]						
Sample	Prepn	C	H	N	Ni	μ_{eff}, BM	x	ν_{594}/ν_{513}[b]
1	$Ni(np_3) + HBF_4$	63.27	5.74	1.70		0.88	0.83	
2	$Ni(BF_4)_2 + np_3 + NaBH_4$	63.20	5.29	1.78	7.11	1.00	0.78	
3	$Ni(np_3) + HBF_4$	63.04	5.34	1.70		1.02	0.77	
4	$Ni(np_3) + HBF_4$	62.81	5.55	1.77		1.10	0.73	
5	$Ni(BF_4)_2 + np_3 + NaBH_4$	63.39	5.43	1.66		1.16	0.70	
6	$Ni(BF_4)_2 + np_3 + NaBH_4$	63.16	5.41	1.70	7.17	1.17	0.69	0.72
7	$Ni(BF_4)_2 + np_3 + NaBH_4$	62.46	5.50	1.62	7.11	1.19	0.68	
8	$Ni(BF_4)_2 + np_3 + NaBH_4$	62.87	5.47	1.73		1.20	0.68	
9	$Ni(BF_4)_2 + np_3 + NaBH_4$	63.16	5.70	1.67		1.21	0.67	0.69
10	$Ni(BF_4)_2 + np_3 + NaBH_4$	62.66	5.54	1.65		1.24	0.66	0.67
11	$Ni(BF_4)_2 + np_3 + NaBH_4$	63.21	5.66	1.62		1.25	0.65	0.62
12	$Ni(BF_4)_2 + np_3 + NaBH_4$	63.12	5.51	1.67	7.29	1.26	0.65	
13	$Ni(BF_4)_2 + np_3 + NaBD_4$	62.52	5.47	1.68		1.38	0.58	
14	$Ni(BF_4)_2 + np_3 + NaBH_4$	62.58	5.20	1.92		1.45	0.53	
15	$Ni(BF_4)_2 + np_3 + NaBH_4$	63.24	5.43	1.74		1.46	0.53	
16	$Ni(BF_4)_2 + np_3 + NaBH_4$	62.60	5.67	1.73		1.54	0.47	
17	$Ni(BF_4)_2 + np_3 + NaBH_4$	63.16	5.41	1.70		1.54	0.47	
18	$Ni(BF_4)_2 + np_3 + NaBH_4$	63.32	5.51	1.60	6.95	1.55	0.47	
19	$Ni(BF_4)_2 + np_3 + NaBH_4$	63.42	5.47	1.61		1.56	0.46	0.61
20	$Ni(BF_4)_2 + np_3 + NaBH_4$	62.45	5.05	1.80		1.66	0.39	
21	$Ni(BF_4)_2 + np_3 + NaBH_4$	63.15	5.46	1.73		1.73	0.33	
22	$Ni(BF_4)_2 + np_3$	63.43	5.31	1.82		1.82	0.26	0.24
23	$Ni(BF_4)_2 + np_3$	63.41	5.27	1.80		1.91	0.19	0.18
24	$Ni(BF_4)_2 + np_3$	63.47	5.32	1.58		2.01	0.10	
25	$Ni(BF_4)_2 + np_3$	63.27	5.49	1.63		2.02	0.09	0.21
26	$Ni(BF_4)_2 + np_3$	63.50	5.38	1.56		2.02	0.09	
27	$Ni(BF_4)_2 + np_3$	63.50	5.41	1.59		2.07	0.05	
28	$Ni(BF_4)_2 + np_3$	63.35	5.72	1.83		2.08	0.04	
29	$Ni(BF_4)_2 + np_3$	63.14	5.27	1.63	7.07	2.08	0.04	
30	$Ni(BF_4)_2 + np_3$	63.40	5.20	1.64		2.08	0.04	0.09

[a] Calcd for $C_{42}H_{43}NP_3NiBF_4$: C, 63.04; H, 5.42; N, 1.75; Ni, 7.34. Calcd for $C_{42}H_{42}NP_3NiBF_4$: C, 63.12; H, 5.30; N, 1.75; Ni, 7.35.
[b] Ratio between heights of the bands at 594 cm^{-1} and at 513 cm^{-1}.

complexes of the series. A nitrosyl complex of nickel with the ethyl analog of p_3 has also been characterized by X-ray methods.[3]

In order to find out more about the ways in which nickel(I) complexes can be formed, we have decided to examine the reactions of other polydentate tertiary phosphine ligands. A tripod ligand which again has three peripheral phosphorus atoms but which is potentially tetradentate is tris(2-diphenylphosphinoethyl)amine, $N(CH_2CH_2PPh_2)_3$ (np_3). Apart from the obvious structural similarity of the ligand with p_3, it is known that np_3 forms complexes of the type $[M(np_3)X]Y$[4] (M = Co, Ni; X = halogen, pseudohalogen; Y = I, BF_4, BPh_4, PF_6); the cation $[Co(np_3)I]^+$ is particularly interesting as it exhibits either trigonal-bipyramidal or square-pyramidal geometry depending on the nature of the counterion.[5]

The reactions of np_3 with Ni^{2+} ions in the presence of the anions BF_4^-, ClO_4^-, and NO_3^- (all of which are weak donors) will be discussed in this paper. The structures of a typical product in the nickel fluoroborate series, $[NiH_x(np_3)]BF_4$, and of the isomorphous cobalt complex $[Co(np_3)]BF_4$ have been determined.

Experimental Section

The ligand np_3 was prepared by the method previously described.[6]

The hydrido complexes were prepared and manipulated under dry nitrogen, unless stated otherwise.

Synthesis of Metal Complexes. $[NiH_x(np_3)]BF_4$. Series I (x = 0.04–0.26). The ligand (1 mmol) dissolved in methylene chloride (or acetone) (10 ml) was added to a solution of $Ni(BF_4)_2 \cdot 6H_2O$ (1 mmol) in ethanol (15 ml). The yellow-green crystals that precipitated when the solution was evaporated slowly were washed with absolute alcohol, water, alcohol again, and finally petroleum ether, before being dried in a current of dry nitrogen.

Table II. Volumetric Titration of H_2 Evolved by the Reaction $[NiH_xL]BF_4$ + HCl (Excess) at 70° in THF

			Ratio H_2:Ni	
Sample	Amt, μmol	H_2 evolved, μmol	Calcd	Found
6	17.9	13.3	0.84	0.74
9	15.0	11.5	0.83	0.76
9	17.1	14.2	0.83	0.83
10	6.28	5.26	0.83	0.84
10	11.4	10.5	0.83	0.92
11	6.01	4.81	0.82	0.80
11	6.06	4.70	0.82	0.78
18	12.3	8.52	0.73	0.69
19	14.2	13.3	0.73	0.94
19	17.5	16.9	0.73	0.96
25	16.5	10.2	0.54	0.62
25	9.20	5.40	0.54	0.59
29	14.8	7.60	0.52	0.51
29	21.8	11.6	0.52	0.53
30	25.7	14.1	0.52	0.55
30	6.65	3.11	0.52	0.47

Series II (x = 0.33–0.78). The ligand (1 mmol) in methylene chloride (10 ml) was added to a solution of $Ni(BF_4)_2 \cdot 6H_2O$ (1 mmol) in ethanol (15 ml). Sodium tetrahydroborate (1 mmol) in ethanol (10 ml) was then added dropwise with stirring over some minutes. The color of the solution changed from an intense green to orange. The solution was concentrated in a stream of cold nitrogen and golden yellow crystals quickly appeared. They were washed and dried as above.

Series III (x = 0.73–0.83). An ethanolic solution of HBF_4 (1.2 mmol) was added to a suspension of $Ni(np_3)$ (1 mmol) in THF (40 ml). Yellow crystals were obtained immediately. The suspension was maintained at 50° with stirring for 30 min. The product was washed twice by decantation with ethanol and then recrystallized from methylene chloride–ethanol.

$[NiH_x(np_3)]ClO_4$. Series I (x = 0.04–0.17). The compounds were obtained when equimolar amounts of $Ni(ClO_4)_2 \cdot 6H_2O$ and

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

(4) L. Sacconi, *Pure Appl. Chem.*, **27**, 161 (1970).

(5) L. Sacconi, M. Di Vaira, and A. Bianchi, *J. Amer. Chem. Soc.*, **92**, 4465 (1970); C. Mealli, P. L. Orioli, and L. Sacconi, *J. Chem. Soc. A*, 2691 (1971).

(6) L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, **90**, 5443 (1968).

Table III. Analytical Magnetic and Infrared Data for the $[NiH_x(np_3)]ClO_4$ Complexes

Sample	Prepn	% found[a] C	H	N	Ni	μ_{eff}, BM	x	ν_{594}/ν_{513}[b]
1	$Ni(np_3) + HClO_4$	61.60	5.44	1.70		0.64	0.9	0.74
2	$Ni(ClO_4)_2 + np_3 + NaBH_4$	62.21	5.65	1.62	7.37	0.94	0.80	0.69
3	$Ni(np_3) + HClO_4$	62.19	5.41	1.68	7.03	1.04	0.76	
4	$Ni(ClO_4)_2 + np_3 + NaBH_4$	61.35	5.48	1.68	6.86	1.56	0.45	
5	$Ni(ClO_4)_2 + np_3 + NaBH_4$	62.32	5.32	1.73	6.83	1.61	0.42	0.52
6	$Ni(ClO_4)_2 + np_3 + NaBH_4$	61.20	5.28	1.67	7.00	1.66	0.39	0.45
7	$Ni(ClO_4)_2 + np_3 + NaBH_4$	61.91	5.31	1.72	7.12	1.72	0.32	0.56
8	$Ni(ClO_4)_2 + np_3$	62.18	5.48	1.66	7.19	1.93	0.17	0.37
9	$Ni(ClO_4)_2 + np_3$	61.92	5.48	1.76	6.94	2.03	0.08	0.13
10	$Ni(ClO_4)_2 + np_3$	60.09	5.31	1.68	6.83	2.08	0.04	0.12

[a] Calcd for $C_{42}H_{43}NP_3NiClO_4$: C, 62.04; H, 5.33; N, 1.72; Ni, 7.22. Calcd for $C_{42}H_{42}NP_3NiClO_4$: C, 62.13; H, 5.22; N, 1.72; Ni, 7.23.
[b] Ratio between heights of the bands at 594 cm^{-1} and at 513 cm^{-1}.

Table IV. Analytical Magnetic and Infrared Data for the $[NiH_x(np_3)]NO_3$ Derivatives and for the $Ni(np_3)NO_3$ Complex

Sample	Prepn	% found[a] C	H	N	Ni	μ_{eff}, BM	x	ν_{593}/ν_{512}[b]	ν_{NO_3}, cm^{-1}
1	$Ni(NO_3)_2 + np_3 + NaBD_4$	65.36	5.70	3.42	7.17	1.45	0.53		1343
2	$Ni(NO_3)_2 + np_3 + NaBH_4$	64.33	5.62	3.51		1.62	0.42		
3	$Ni(NO_3)_2 + np_3 + NaBH_4$	65.25	5.58	3.63	7.40	1.65	0.40		
4	$Ni(NO_3)_2 + np_3 + NaBH_4$	65.01	5.56	3.58	6.88	1.71	0.35	0.45	1340
5	$Ni(NO_3)_2 + np_3 + NaBH_4$	65.00	5.62	3.70	7.35	1.77	0.30	0.50	1340
6	$Ni(NO_3)_2 + np_3 + NaBH_4$	65.09	5.56	3.60	7.44	1.92	0.18	0.26	1340
7	$Ni(NO_3)_2 + np_3$	65.23	5.61	3.62		2.12			1380 1296

[a] Calcd for $C_{42}H_{43}N_2P_3NiO_3$: C, 65.05; H, 5.59; N, 1.81; Ni, 7.57. Calcd for $C_{42}H_{42}N_2P_3NiO_3$: C, 65.14; H, 5.47; N, 1.81; Ni, 7.58.
[b] Ratio between heights of the bands at 593 cm^{-1} and at 512 cm^{-1}.

np_3 were allowed to react by the method used to prepare the corresponding tetrafluoroborate derivatives.

Series II ($x = 0.34$–0.80). The compounds were obtained when equimolar amounts of $Ni(ClO_4)_2 \cdot 6H_2O$, np_3, and $NaBH_4$ were allowed to react by the method used to prepare the corresponding tetrafluoroborate derivatives.

Series III ($x = 0.76$–0.92). The compounds were prepared by action of $HClO_4$ on $Ni(np_3)$ in ethanol-THF solution.

$[NiH_x(np_3)]NO_3$ ($x = 0.18$–0.53). The compounds were obtained when equimolar amounts of $Ni(NO_3)_2 \cdot 6H_2O$, np_3, and $NaBH_4$ were allowed to react by the method used to prepare the tetrafluoroborate derivatives of series II.

$Ni(np_3)NO_3$. The complex was obtained when equimolar amounts of $Ni(NO_3)_2 \cdot 6H_2O$ and np_3 were allowed to react by the method used to prepare the series I tetrafluoroborate derivatives.

$[Co(np_3)]BF_4$. An ethanolic solution of $Co(BF_4)_2 \cdot 6H_2O$ (1 mmol, 10 ml) was added to a solution of the ligand (1 mmol, 15 ml) in acetone. Sodium tetrahydroborate (1 mmol) in ethanol (10 ml) was then added dropwise with stirring over some minutes. The color of the solution changed from orange-brown to green. The green crystals that precipitated after about 15 min were washed with absolute alcohol, water, alcohol again, and finally light petrol, before being dried in a current of dry nitrogen.

Deuterated Derivatives. The compounds were prepared by the method used to prepare the series II derivatives using the appropriate nickel(II) salts and $NaBD_4$ as reagents and CH_2Cl_2, C_2H_5OD, and D_2O as solvents.

Hydrogen Content Analysis. The compounds were treated under argon with an excess of HCl in THF or 1,2-dichloroethane or with an excess of iodine in THF, in an apparatus connected to a gas-liquid chromatograph (Carlo Erba Fractovap, Model B) as previously described.[7]

Materials and Physical Measurements. All solvents were purified and dried by standard methods. The physical measurements were executed by previously described methods.[8]

Compound 12 (Table I) was studied between 255 and 84 K and its paramagnetism was found to obey the Curie–Weiss law with Θ = 40°.

See Tables I–IV for analytical, magnetic, ir, and H_2 titration data.

Collection and Reduction of X-Ray Intensity Data. A survey of *hkl* and *h*0*l* Weissenberg photographs of both complexes revealed the systematic absences *hkl* for $h + k = 2n + 1$, *h*0*l* for $l = 2n + 1$, and 0*k*0 for $k = 2n + 1$. Although both acentric *Cc* and centric *C*2/*c* space groups were possible at this point, the acentric *Cc* was chosen from a consideration of the formula of the compounds, which allow neither a symmetry center nor a binary axis. Details of crystal data and data collection are given in Table V.

Table V. *Crystal Data and Data Collection Details*

	$[NiH_{0.5}(np_3)]BF_4$	$[Co(np_3)]BF_4$
Molecular formula	$C_{42}H_{42.5}NP_3NiBF_4$	$C_{42}H_{42}NP_3CoBF_4$
Mol wt	800.2	799.4
a, Å	16.739 (2)	17.032 (2)
b, Å	12.666 (1)	12.637 (2)
c, Å	18.064 (2)	17.979 (2)
β, deg	90.41 (2)	90.04 (2)
d_{obsd}(by flot), g cm^{-3}	1.40	1.40
d_{calcd}, g cm^{-3}	1.39	1.38
U, $Å^3$	3829.7	3869.7
Z	4	4
Space group	*Cc*	*Cc*
Absorpt coeff (Mo Kα), cm^{-1}	6.87	5.22
Color	Yellowish-orange	Green
Habit	Irregular rombic plate	Parallelepiped
Dimensions, mm	0.4 × 0.3 × 0.1	0.33 × 0.15 × 0.1
Diffractometer	Hilger Y 290	Philips PW 1100
λ(Mo Kα), Å	0.7107	0.7107
Filter	Zr	
Monochromator		Flat graphite crystal
Takeoff angle, deg	3	4.5
Method	ω–2θ scan	ω–2θ scan
Scan speed	Scans of 80 sec, with steps of 0.01° and a count of 1 sec for each step across the peak	0.07°/sec in a range of 1° (a total of 14 sec) across the peak
Background time	20 sec on each side of the peak	7 sec on each side of the peak
Standards	2 every 100 reflections	3 every 220 reflections
Max dev of standards	10%	8%
2θ limit	$0° < 2\theta \leqslant 40°$	$0° < 2\theta \leqslant 40°$
No. of data	1768	1802
No. of data with $I \geqslant 2.5\sigma(I)$	1440	
No. of data with $I \geqslant 2\sigma(I)$		1193

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(7) A. Sacco and M. Rossi, *Inorg. Chim. Acta*, **2**, 127 (1968).
(8) L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, **6**, 262 (1967).

The intensities as well as the standard deviations of the intensity were calculated as previously reported.[9]

The observed intensities were corrected for Lorentz and polarization effects. Absorption corrections were neglected, owing to the small value of the calculated linear absorption coefficient (μ(Mo Kα) = 6.87 cm^{-1} for the Ni complex and μ(Mo Kα) = 5.22 cm^{-1} for the Co complex). The effect of anomalous dispersion for metal atom was considered in the calculation of F_c.[10] Scattering factors for nonhydrogen atoms were taken from ref 11 and for hydrogens from ref 12.

Solution and Refinement of the Structures. $[NiH_{0.5}(np_3)]BF_4$. A three-dimensional Patterson function yielded the positional parameters of the nickel atom and of one phosphorus atom. The x and z coordinates of the nickel atom were set at $^1/_2$ to fix the origin of the unit cell and their values were not refined. Successive Fourier maps showed all nonhydrogen atoms. These calculations were performed on an IBM 1130 computer.[13] Refinement was then undertaken by means of full-matrix least-squares techniques.[14] A series of isotropic followed by mixed cycles, isotropic on the carbon atoms and anisotropic on the heavier atoms, dropped R to 8.1%. At this point a ΔF Fourier map showed the positions of 34 hydrogen atoms. These hydrogen atoms were introduced in the last cycle with B = 5.5 Å^2 and not refined. The function minimized in the least-squares calculation was $\Sigma w(|F_o| - |F_c|)^2$ and the weighting scheme was $w = 1$ for reflections with $F_o \leqslant 17$ and $\sqrt{w} = 17/F_o$ for reflections with $F_o > 17$. Owing to the polar nature of the space group Cc two possible orientations of the structure must be considered: the structure x, y, z and the inverted $\bar{x}, y, \bar{z}$. The absolute configuration of the structure was determined taking into account the following arguments. (i) Two mixed cycles on the two structures gave R values 6.98 (x, y, z) and 7.10% ($\bar{x}, y, \bar{z}$), respectively. On the basis of Hamilton's test[15] the structure $\bar{x}, y, \bar{z}$ must be rejected at the 99.5% significance level. (ii) The analysis of the standard deviations confirmed that the x, y, z structure was the correct one. In order to locate the hydride atom bound to the metal atom, a new difference Fourier map was calculated using a technique largely applied:[16] to enhance the peaks of the hydrogen atoms, whose scattering power is confined to the low-angle reflections, some high-angle data were omitted ($(\sin\theta)/\lambda_{max} = 0.293$ Å^{-1}). Investigation of this difference map revealed a prominent peak of positive electronic density (0.8 e/Å^3) at a bond distance from the nickel atom. Supposing that this might be the peak due to the hydride ligand, attempts were made to refine a hydrogen atom in this position. The refinement, carried out using the low-angle data, gave hydrogen atom parameters which showed some oscillation, but this oscillation was far less than the estimated standard deviation on the same parameters. This refinement, therefore, did not diverge; rather it converged to reasonable values (Ni-H = 1.57 (20) Å, B_H = 8.9 Å^2). To allow the other atoms to "adjust" to the presence of the hydride atom, a final cycle on all the parameters was carried out using all the data.

Final values of the parameters with their estimated standard deviations are reported in Tables VI-VIII. The final R and R_w values are 7.0 and 9.0%, respectively, R_w being defined as $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

$[Co(np_3)]BF_4$. Because of the isomorphism of the nickel and cobalt complexes, we have resolved the structure of the $[Co(np_3)]BF_4$ complex, with the help of the known atom positions of the $[NiH_{0.5}(np_3)]BF_4$ compound. The refinement of the structure was performed by means of full-matrix least squares on a CDC 6600 computer.[14] A series of isotropic and mixed cycles, isotropic on the carbon atoms and anisotropic on the heavier atoms, led to R = 8.2%. A ΔF Fourier synthesis showed the positions of 33 hydrogen atoms, which were introduced with B = 5.5 Å^2 and not refined. The weight-

Table VI. $[NiH_{0.5}(np_3)]BF_4$ Positional Parameters (×10^4) and Isotropic Temperature Factors with Estimated Standard Deviations in Parentheses

Atom	x/a	y/b	z/c	B, Å^2
Ni	5000	4574 (2)	−5000	*a*
P(1)	6311 (3)	4505 (4)	−5022 (3)	*a*
P(2)	4271 (3)	3442 (4)	−5649 (3)	*a*
P(3)	4405 (3)	5851 (4)	−4382 (3)	*a*
F(1)	4990 (12)	1222 (15)	−3176 (12)	*a*
F(2)	4289 (10)	2150 (21)	−2417 (13)	*a*
F(3)	5547 (12)	2296 (24)	−2407 (14)	*a*
F(4)	4945 (24)	2789 (24)	−3256 (22)	*a*
N	5045 (8)	5542 (11)	−5917 (9)	*a*
C(1)	6470 (11)	5623 (15)	−5612 (10)	4.4 (4)
C(2)	5857 (11)	5608 (15)	−6228 (10)	4.7 (4)
C(3)	4506 (14)	3932 (19)	−6587 (13)	6.3 (5)
C(4)	4497 (11)	5179 (15)	−6513 (10)	4.6 (4)
C(5)	4103 (12)	6679 (16)	−5174 (11)	4.8 (4)
C(6)	4779 (12)	6631 (15)	−5676 (10)	4.6 (4)
C(7)	6960 (11)	4650 (15)	−4251 (10)	4.2 (4)
C(8)	7575 (16)	5367 (22)	−4217 (15)	8.0 (6)
C(9)	8051 (17)	5408 (24)	−3549 (16)	8.6 (7)
C(10)	7897 (20)	4830 (27)	−3002 (19)	9.8 (8)
C(11)	7289 (16)	4088 (22)	−3003 (14)	7.6 (6)
C(12)	6809 (12)	4042 (16)	−3624 (10)	4.9 (4)
C(13)	6745 (10)	3381 (14)	−5525 (9)	3.6 (3)
C(14)	6392 (12)	2390 (16)	−5342 (11)	5.4 (4)
C(15)	6706 (14)	1483 (19)	−5659 (13)	6.5 (5)
C(16)	7257 (13)	1590 (17)	−6189 (11)	5.6 (5)
C(17)	7584 (13)	2517 (18)	−6421 (12)	6.2 (5)
C(18)	7327 (13)	3461 (18)	−6003 (12)	5.8 (5)
C(19)	4446 (10)	2004 (14)	−5702 (10)	3.6 (3)
C(20)	4394 (13)	1503 (19)	−6327 (13)	6.3 (5)
C(21)	4491 (14)	389 (20)	−6355 (13)	6.9 (5)
C(22)	4588 (15)	−135 (21)	−5702 (14)	7.3 (6)
C(23)	4598 (14)	361 (20)	−5050 (14)	7.0 (5)
C(24)	4520 (13)	1513 (18)	−5069 (12)	5.7 (5)
C(25)	3186 (9)	3492 (12)	−5572 (9)	3.2 (3)
C(26)	2915 (13)	3485 (17)	−4911 (12)	5.6 (5)
C(27)	2060 (14)	3475 (18)	−4691 (12)	6.3 (5)
C(28)	1630 (15)	3557 (21)	−5299 (14)	7.1 (6)
C(29)	1826 (14)	3546 (20)	−5997 (14)	7.0 (6)
C(30)	2684 (16)	3530 (23)	−6193 (15)	8.0 (6)
C(31)	4987 (10)	6706 (14)	−3830 (9)	3.8 (3)
C(32)	4775 (14)	7790 (20)	−3702 (13)	6.9 (5)
C(33)	5206 (15)	8447 (20)	−3229 (13)	7.1 (6)
C(34)	5857 (14)	7975 (20)	−2820 (13)	7.1 (5)
C(35)	6027 (13)	6950 (20)	−2912 (12)	6.5 (5)
C(36)	5596 (11)	6352 (15)	−3407 (10)	4.7 (4)
C(37)	3516 (10)	5680 (13)	−3860 (9)	3.8 (3)
C(38)	3479 (11)	4844 (16)	−3377 (10)	4.9 (4)
C(39)	2808 (15)	4669 (20)	−2970 (13)	7.0 (5)
C(40)	2147 (13)	5290 (19)	−3028 (12)	6.3 (5)
C(41)	2165 (14)	6152 (19)	−3500 (12)	6.4 (5)
C(42)	2860 (12)	6341 (17)	−3898 (11)	5.6 (5)
B	4926 (14)	2048 (18)	−2778 (12)	4.9 (5)
H[b]	498 (12)	400 (16)	−423 (12)	8.9 (3.0)

[a] These atoms were refined anisotropically. [b] The hydrogen positional parameters are multiplied by 10^3.

Table VII. $[NiH_{0.5}(np_3)]BF_4$ Anisotropic Thermal[a] Parameters (×10^3) with Estimated Standard Deviations in Parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	41 (1)	30 (2)	67 (2)	3 (1)	−4 (1)	2 (1)
P(1)	45 (3)	38 (3)	71 (3)	−1 (2)	−2 (2)	0 (3)
P(2)	48 (3)	30 (3)	68 (3)	1 (2)	−1 (2)	−3 (2)
P(3)	47 (3)	30 (3)	66 (3)	8 (2)	−6 (2)	5 (2)
F(1)	157 (16)	131 (15)	207 (20)	32 (12)	−26 (15)	−95 (15)
F(2)	99 (12)	235 (25)	242 (22)	−13 (14)	54 (14)	−117 (20)
F(3)	128 (15)	297 (31)	232 (23)	30 (17)	−72 (16)	−172 (24)
F(4)	323 (41)	182 (26)	334 (40)	36 (26)	66 (36)	105 (27)
N	43 (9)	42 (10)	91 (11)	−5 (7)	7 (8)	−25 (9)

[a] The temperature factor is defined as $\exp(-2\pi^2 \Sigma_{i=1} \Sigma_{j=1} U_{ij} h_i h_j \cdot a_i^* a_j^*)$.

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Table VIII. [$NiH_{0.5}(np_3)$]BF_4 Positional Parameters (×10^3) of Hydrogen Atoms (Numbered According to the Atom to Which They Are Attached)

Atom	*x/a*	*y/b*	*z/c*
H(1,1)	600	600	−540
H(1,2)	684	552	−590
H(2,1)	592	620	−666
H(2,2)	598	484	−654
H(3,1)	500	390	−670
H(3,2)	420	390	−700
H(4,1)	400	530	−626
H(4,2)	480	530	−690
H(5,1)	420	740	−480
H(5,2)	364	621	−536
H(6,1)	520	690	−540
H(6,2)	484	680	−620
H(8)	762	584	−460
H(9)	782	600	−364
H(10)	760	454	−260
H(11)	708	360	−256
H(14)	590	232	−486
H(16)	700	100	−640
H(17)	810	240	−684
H(18)	770	418	−590
H(20)	450	188	−680
H(21)	470	40	−680
H(24)	450	176	−442
H(28)	98	364	−504
H(30)	308	328	−668
H(32)	416	790	−360
H(35)	636	680	−230
H(36)	592	566	−365
H(38)	408	460	−352
H(39)	304	390	−260
H(40)	180	510	−248
H(41)	190	640	−400
H(42)	290	640	−450

Table IX. [$Co(np_3)$]BF_4 Positional Parameters (×10^4) and Isotropic Temperature Factors, with Estimated Standard Deviations in Parentheses

Atom	*x/a*	*y/b*	*z/c*	*B*, Å^2
Co	−5000	4440 (2)	5000	*a*
P(1)	−6322 (4)	4530 (6)	5029 (4)	*a*
P(2)	−4226 (4)	3379 (5)	5706 (4)	*a*
P(3)	−4414 (4)	5788 (5)	4410 (4)	*a*
F(1)	−5016 (14)	1220 (19)	3229 (16)	*a*
F(2)	−4279 (13)	2268 (24)	2538 (16)	*a*
F(3)	−5548 (13)	2363 (26)	2460 (16)	*a*
F(4)	−5003 (26)	2826 (32)	3461 (26)	*a*
N	−5048 (12)	5472 (17)	5991 (11)	*a*
C(1)	−6480 (15)	5631 (21)	5653 (15)	4.7 (6)
C(2)	−5922 (14)	5539 (20)	6271 (14)	4.5 (5)
C(3)	−4499 (16)	3901 (22)	6620 (15)	4.9 (6)
C(4)	−4530 (17)	5122 (24)	6625 (16)	5.5 (7)
C(5)	−4074 (14)	6548 (19)	5210 (13)	3.9 (5)
C(6)	−4768 (17)	6582 (23)	5800 (17)	5.5 (6)
C(7)	−7005 (15)	4736 (21)	4257 (14)	4.6 (6)
C(8)	−7540 (21)	5561 (29)	4284 (21)	8.2 (8)
C(9)	−8026 (22)	5619 (30)	3567 (22)	8.9 (9)
C(10)	−7964 (23)	4990 (34)	2954 (22)	9.0 (9)
C(11)	−7398 (21)	4209 (27)	2976 (19)	7.4 (8)
C(12)	−6874 (18)	4052 (25)	3632 (17)	6.4 (7)
C(13)	−6748 (15)	3390 (21)	5504 (15)	5.1 (6)
C(14)	−6347 (14)	2460 (19)	5329 (14)	4.2 (5)
C(15)	−6606 (19)	1526 (26)	5718 (18)	7.1 (8)
C(16)	−7243 (16)	1517 (23)	6214 (16)	5.7 (7)
C(17)	−7598 (16)	2460 (22)	6387 (16)	5.4 (6)
C(18)	−7343 (13)	3429 (18)	5994 (12)	3.4 (5)
C(19)	−4345 (14)	1961 (19)	5729 (15)	4.2 (5)
C(20)	−4321 (18)	1397 (26)	6428 (18)	6.6 (7)
C(21)	−4498 (20)	289 (28)	6437 (19)	7.4 (8)
C(22)	−4546 (17)	−220 (24)	5776 (18)	6.0 (7)
C(23)	−4537 (20)	310 (30)	5085 (21)	8.1 (9)
C(24)	−4460 (17)	1408 (24)	5141 (17)	5.9 (7)
C(25)	−3198 (12)	3460 (16)	5686 (12)	3.0 (4)
C(26)	−2833 (21)	3539 (26)	4953 (21)	7.6 (8)
C(27)	−2001 (22)	3540 (30)	4898 (20)	7.9 (9)
C(28)	−1538 (16)	3621 (22)	5440 (16)	5.3 (6)
C(29)	−1800 (20)	3545 (26)	6135 (19)	7.4 (8)
C(30)	−2721 (18)	3461 (25)	6299 (18)	6.5 (7)
C(31)	−4984 (13)	6676 (18)	3868 (12)	3.5 (5)
C(32)	−4804 (16)	7682 (23)	3793 (16)	5.6 (6)
C(33)	−5221 (22)	8431 (29)	3296 (22)	8.9 (9)
C(34)	−5842 (20)	7990 (28)	2891 (20)	7.8 (8)
C(35)	−5987 (16)	6946 (24)	2938 (16)	6.1 (7)
C(36)	−5578 (13)	6301 (18)	3436 (13)	3.9 (5)
C(37)	−3505 (14)	5625 (20)	3865 (13)	4.1 (5)
C(38)	−3484 (14)	4776 (19)	3408 (14)	4.3 (5)
C(39)	−2803 (16)	4568 (22)	3027 (15)	5.7 (6)
C(40)	−2178 (17)	5290 (23)	3067 (16)	6.0 (6)
C(41)	−2184 (21)	6134 (30)	3549 (20)	8.2 (9)
C(42)	−2902 (17)	6290 (23)	3930 (17)	6.3 (7)
B	−4929 (23)	2143 (29)	2906 (22)	6.2 (8)

[a] These atoms were refined anisotropically.

ing scheme was $w = 1$ for reflections with $F_o \leqslant 7$ and $\sqrt{w} = 7/F_o$ for reflections with $F_o > 7$. The absolute configuration of the structure (two orientations are possible: x, y, z and $\bar{x}, y, \bar{z}$) was determined as for the nickel complex. On the basis of Hamilton's test the structure $\bar{x}, y, \bar{z}$ ($R = 7.3\%$) was the correct one and the x, y, z structure ($R = 7.5\%$) was rejected at the 99.5% significance level.

Final values of the parameters with their estimated standard deviations are given in Tables IX-XI. The final R and R_w values are 7.3 and 10.8%, respectively. Listings of the observed and calculated structure factors of both compounds are available (see paragraph at end of paper regarding supplementary material).

Results and Discussion

Tetrafluoroborate Derivatives. When $Ni(BF_4)_2$ is treated with np_3 in ethanol and methylene chloride under an inert atmosphere, crystalline compounds (I) are obtained varying in color from olive green to yellow. Elemental analyses of the compounds thus obtained in nine separate preparations are in reasonable agreement with the formula $Ni(np_3)BF_4$ (Table I) but the magnetic moment of each product is different, lying in the range 1.82-2.08 BM. The solid compounds are fairly stable in air but decompose rapidly in 1,2-dichloroethane unless air is excluded, in which case they behave as 1:1 electrolytes.

The room-temperature reflectance spectra, taken under nitrogen, show a band at *ca.* 8000 cm^{-1} with a shoulder at 6250 cm^{-1} and three shoulders at *ca.* 14,300, 20,000, and 25,000 cm^{-1} (Figure 1, curve 2). All bands are more clearly resolved at liquid nitrogen temperature (curve 1). The absorption spectrum in air-free dichloroethane shows three resolved bands at *ca.* 7800, 14,180, and 20,830 cm^{-1} (Figure 2, curve 1).

If $Ni(BF_4)_2$ and np_3 react in the presence of $NaBH_4$, well-formed orange-yellow crystals are obtained (series II). These compounds also analyze reasonably well as $Ni(np_3)BF_4$; the magnetic moment varies over each of 18 preparations from 1.0 to 1.73 BM. The compounds behave like those of series I. The reflectance spectra show about the same maxima, but the intensities of the 6250-, 8000-, and 14,300-cm^{-1} bands seem to decrease with the increasing magnetic moment in various samples (Figure 1, curve 3). The high-frequency band at 25,000 cm^{-1} is almost always clearly resolved (Figure 1, curve 3; Figure 2, curve 2).

A third series of compounds (III) can be obtained by oxidation of the nickel(0) complex $Ni(np_3)$. This red diamagnetic complex can be prepared by the reaction of np_3 with nickel(II) nitrate in the presence of excess borohydride. An X-ray analysis has shown the presence of trigonal-pyramidal molecules in the crystal.[17] Reaction of $Ni(np_3)$ with HBF_4 gives compounds similar to series II, but with the

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(17) C. Mealli and L. Sacconi, *J. Chem. Soc., Chem. Commun.*, 886 (1973).

Table X. $[Co(np_3)]BF_4$ Anisotropic Thermal Parameters ($\times 10^3$) with Estimated Standard Deviations in Parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	44 (2)	38 (2)	63 (3)	−5 (2)	−4 (1)	−6 (2)
P(1)	49 (4)	49 (5)	56 (5)	2 (4)	−4 (3)	1 (4)
P(2)	49 (4)	42 (4)	42 (4)	−6 (3)	3 (3)	−4 (3)
P(3)	60 (5)	39 (4)	54 (5)	3 (3)	−13 (3)	7 (3)
F(1)	124 (18)	132 (20)	226 (29)	−14 (16)	37 (19)	−113 (21)
F(2)	94 (15)	217 (28)	206 (26)	−18 (17)	41 (16)	−105 (23)
F(3)	106 (17)	252 (34)	200 (26)	−7 (18)	−45 (18)	−142 (24)
F(4)	257 (41)	209 (36)	288 (45)	−23 (30)	18 (34)	77 (34)
N	62 (14)	52 (13)	63 (15)	−4 (11)	17 (11)	−18 (12)

Table XI. $[Co(np_3)]BF_4$ Positional Parameters ($\times 10^3$) of Hydrogen Atoms (Numbered According to the Atom to Which They Are Attached)

Atom	x/a	y/b	z/c
H(1,1)	−640	640	554
H(1,2)	−694	540	600
H(2,1)	−600	462	640
H(3,1)	−510	380	690
H(3,2)	−420	360	708
H(4,1)	−418	544	640
H(4,2)	−480	540	716
H(5,1)	−400	720	500
H(5,2)	−360	630	566
H(6,1)	−530	660	550
H(8)	−774	642	440
H(9)	−812	624	350
H(11)	−708	372	252
H(12)	−628	366	348
H(14)	−584	210	493
H(15)	−630	70	554
H(16)	−734	66	600
H(17)	−806	290	640
H(20)	−450	170	690
H(23)	−440	0	440
H(24)	−448	172	456
H(26)	−315	320	462
H(27)	−200	318	450
H(29)	−206	328	654
H(30)	−318	362	680
H(32)	−432	832	360
H(33)	−518	920	360
H(34)	−630	840	280
H(35)	−646	660	250
H(36)	−570	552	346
H(38)	−390	410	340
H(40)	−172	500	280
H(42)	−284	680	448

lowest magnetic moments of the three series, varying from 0.88 to 1.10 BM. The reflectance spectrum of the compound with $\mu_{eff} = 0.88$ BM shows practically only a single band at *ca.* 25,000 cm^{-1} (Figure 1, curve 4) that persists in solution (ϵ 3510) together with a weak band at *ca.* 14,300 cm^{-1} (ϵ 45) (Figure 2, curve 3).

The infrared spectra of the compounds of the three series show a band at 595 cm^{-1} whose intensity correlates inversely with the compound's magnetic moment (Figure 3). The band shifts on deuteration to 491 cm^{-1}, showing that the band arises from a vibration of a hydrogen atom. In spite of the fact that no stretching band could be found in the region 1700-2250 cm^{-1}, we conclude that compounds of the three series contain hydrogen atoms bound to the nickel atom in variable proportions. In other words the compounds are nonstoichiometric hydrides of the general formula $[NiH_x(np_3)]BF_4$ ($0 < x < 1$) containing nickel in the two oxidation states +1 and +2. Confirmation of this hypothesis is obtained by semiquantitative calculations of x by at least three different methods: magnetic, analytical, and infrared.

Magnetic Moment Analysis. The nickel(I) complex $[Ni(np_3)]BF_4$ probably has a magnetic moment of 2.1 BM; this value can be predicted from known trends in magnetic moment with ligand type and stereochemistry (see later). The nickel(II) compound is diamagnetic. The proportion of nickel(I) is therefore given by the molar susceptibility, *i.e.*, by the expression $1 - x = \mu_{eff}{}^2/4.41$ (Table I). This proportion varies from *ca.* 0.17 ($\mu_{eff} = 0.88$ BM) to nearly 1 ($\mu_{eff} = 2.08$ BM), while x varies from a maximum of 0.83 to a minimum of 0.04. The constant presence of an infrared band at 595 cm^{-1} shows that x never attains a value of zero.

As x approaches unity, it becomes more imprecise because the smaller magnetic moment is more difficult to measure. In particular the diamagnetic correction of -501×10^{-6} cgsu (equivalent to a magnetic moment of 1.1 BM) is the determining factor. Also, as the first-order paramagnetism decreases, the second-order effects, such as temperature-independent paramagnetism (TIP) whose magnitude is unknown, become more important, so that the calculated x is subject to further uncertainty. These considerations suggest that

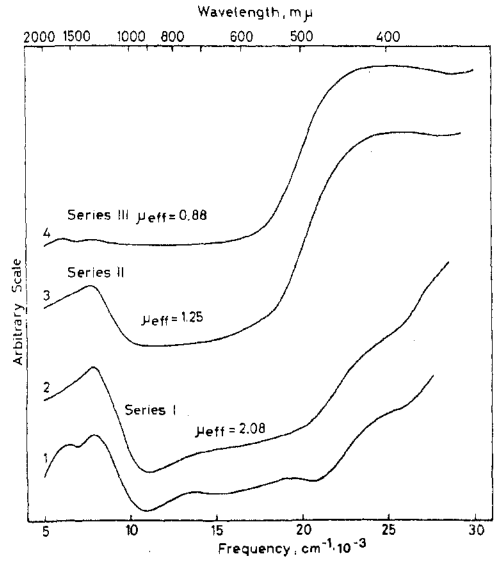

Figure 1. Reflectance spectra of solid $[NiH_x(np_3)]BF_4$ compounds: $x = 0.04$ (curve 1, at −160°; curve 2, at room-temperature); $x = 0.65$ (curve 3); $x = 0.83$ (curve 4).

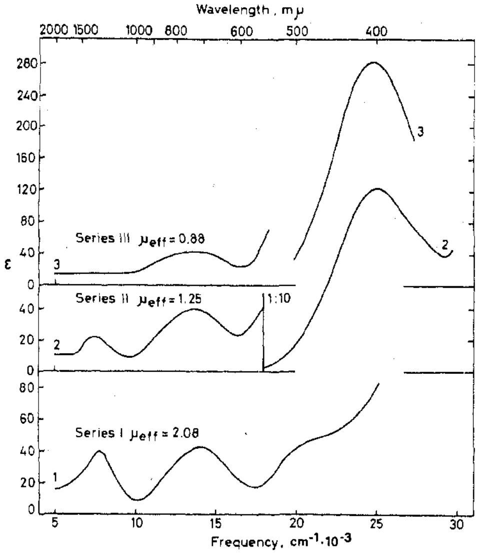

Figure 2. Absorption spectra of $[NiH_x(np_3)]BF_4$ compounds in 1,2-dichloroethane: $x = 0.04$ (curve 1); $x = 0.65$ (curve 2); $x = 0.83$ (curve 3).

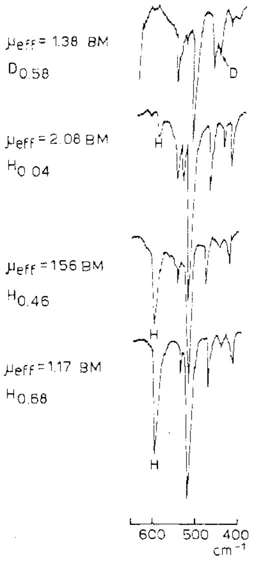

Figure 3. Infrared spectra of solid $[NiD_{0.58}(np_3)]BF_4$ and $[NiH_x(np_3)]BF_4$ compounds ($x = 0.04, 0.46, 0.68$).

the true value of x may be higher than the value calculated from the simple formula. It is very likely that values of μ_{eff} up to 0.6 BM are due entirely to the TIP contribution. For example, the formula $[NiH_{0.8}(np_3)]BF_4$ is to be considered close to the limiting formula $[NiH(np_3)]BF_4$; this is supported by the spectral evidence, as practically only one band at 25,000 cm^{-1} is observed.

Hydrogen Content Analysis. The action of concentrated hydrochloric acid above 60° on a dichloroethane solution of the complexes liberated hydrogen gas quantitatively. Suppose that the two limiting complexes react according to

$$[Ni^{I}(np_3)]^+ + H^+ \rightarrow {}^1/_2 H_2 + Ni^{2+} + np_3 \qquad (1)$$

$$[Ni^{II}H(np_3)]^+ + H^+ \rightarrow H_2 + Ni^{2+} + np_3 \qquad (2)$$

The hydride content x may be calculated accordingly: moles of H_2/moles of Ni $= {}^1/_2(1 - x) + x = {}^1/_2(1 + x)$. Absorption spectrometry shows that Ni^{2+} ions are indeed produced.

The experimental results, given in Table II, show that the chromatographic determination of the hydrogen evolved gives values of x in reasonable agreement with the values obtained from magnetic measurements. Clearly this analytical technique is not very accurate and reproducible (presumably side reactions occur) but the general trend is in agreement with that deduced from the magnetic measurements.

Hydrogen displacement by iodine always gave lower values of x. This is not surprising since hydrogen iodide is formed under these conditions; hence not all hydride is liberated as hydrogen gas. Moreover, simple addition of iodine to the complex, without hydrogen displacement, may take place.

Infrared Spectrophotometric Analysis. A crude estimate of the hydride content is given by the height of the 595-cm^{-1} peak, relative to the ligand band at 513 cm^{-1} as an internal standard (Figure 3). Table I shows a direct correlation between this estimator and the magnetic one.

In conclusion, the analytical, magnetic, and spectroscopic (ultraviolet, visible, infrared) evidences are all in agreement with the nonstoichiometric hypothesis for the three series of compounds. X-Ray powder patterns show that all the compounds are isomorphous, and in a few cases single-crystal measurements have given identical cell dimensions.

Perchlorate Derivatives. When nickel(II) perchlorate is used in place of the fluoroborate, under analogous conditions, yellow crystals are obtained which are nonstoichiometric hydrides with the general formula $[NiH_x(np_3)]ClO_4$. The compounds with the highest values of x are obtained by the action of perchloric acid on $Ni(np_3)$. The values of μ_{eff} vary from 0.64 to 2.08 BM, corresponding to the extreme formulas $[NiH_{0.93}(np_3)]ClO_4$ and $[NiH_{0.04}(np_3)]ClO_4$ (Table III). The electronic spectra, both in reflectance and absorption, are in all respects similar to those of the fluoroborate derivatives (Figure 4). All of the compounds show infrared bands at *ca.* 595 cm^{-1} whose relative intensities increase with x (Table III). Also two bands at 621 and 1090 cm^{-1} diagnostic of the ionic perchlorate ion are present.

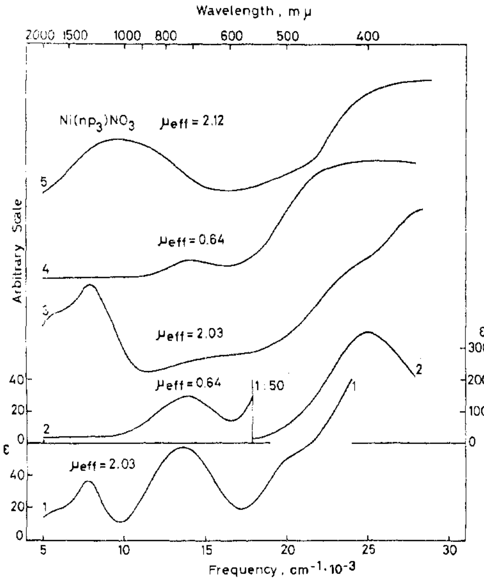

Figure 4. Absorption spectra of $[NiH_x(np_3)]ClO_4$ compounds in 1,2-dichloroethane: $x = 0.08$ (curve 1); $x = 0.92$ (curve 2). Reflectance spectra of solid $[NiH_x(np_3)]ClO_4$ compounds: $x = 0.08$ (curve 3); $x = 0.92$ (curve 4). Reflectance spectrum of solid $Ni(np_3)NO_3$ (curve 5).

Nitrate Derivatives. Nickel(II) nitrate reacts with np_3 and $NaBH_4$ to give nonstoichiometric hydrides of the general formula $[NiH_x(np_3)]NO_3$, which are in all respects similar to the fluoroborates of series II. The observed magnetic moment varies over six preparations from 1.45 to 1.92 BM with a corresponding variation in x of 0.53 to 0.18 (Table IV). The compounds all show spectral and conductivity properties similar to those of the fluoroborate, including the infrared band at 595 cm^{-1} whose intensity increases with x (Figure 5). The infrared spectra also contain a band at 1340 cm^{-1}, characteristic of the ionic nitrate group.

In the absence of $NaBH_4$ nickel nitrate gives a yellow product that analyzes as before but that has a magnetic moment of 2.12 BM (Table IV). The crystal field spectrum is however quite different, showing two broad bands centered at *ca.* 9090 and 11,100 cm^{-1} (Figure 4, curve 5). The infrared spectrum is also distinctive: the 595-cm^{-1} band is missing and in place of the 1340-cm^{-1} band there are two bands at 1295 and 1380 cm^{-1} (Figure 5), consistent with a monodentate nitrate group. This nitrate complex is therefore not a hydride but a five-coordinate complex of nickel(I) with the nitrate acting as the fifth ligand. This spectrum clearly corresponds to the spectra of other five-coordinate halo derivates of nickel(I) having the formula $Ni(np_3)X$.[18] The magnetic moment of 2.12 BM is consistent with the value of 2.1 assumed for $[Ni(np_3)]BF_4$.

Cobalt Derivative. $[Co(np_3)]BF_4$. If $Co(BF_4)_2$ and np_3

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[18] Unpublished results of this laboratory.

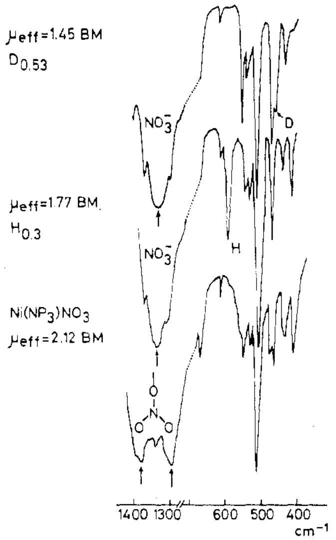

Figure 5. Infrared spectra of solid $[NiD_{0.53}(np_3)]NO_3$, $[NiH_{0.3}(np_3)]NO_3$, and $Ni(np_3)NO_3$ compounds.

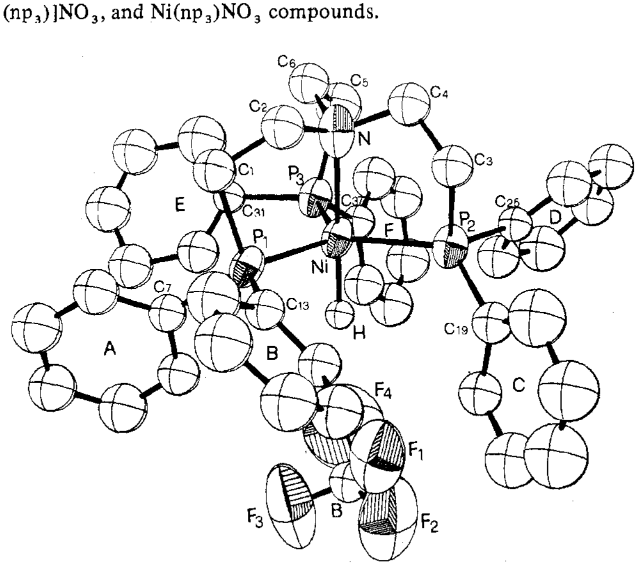

Figure 6. Perspective view of the $[NiH(np_3)]^+$ cation (ORTEP diagram, showing 30% probability ellipsoids). An artificial thermal factor of 2.5 Å^2 for hydrogen atom was used.

are treated with $NaBH_4$, emerald green crystals are formed which analyze well as $[Co(np_3)]BF_4$. They are fairly stable in dry air but decompose in organic solvents even under nitrogen. The magnetic moment of 3.11 BM is indicative of a high-spin compound of cobalt(I). The reflectance spectrum shows three bands at 5400, 8000, and 15,300 cm^{-1}.

X-Ray Structures of $[NiH_{0.5}(np_3)]BF_4$ and $[Co(np_3)]BF_4$. A single-crystal determination has been performed on the fluoro salt 14, with μ_{eff} = 1.45 BM, corresponding roughly to the formula $[NiH_{0.5}(np_3)]BF_4$. The asymmetric unit was found to contain a single molecule, showing that, whether or not they contain hydrogen, all molecules are crystallographically indistinguishable. Figure 6 shows a perspective view of the cation $[NiH(np_3)]^+$, and selected bond lengths and angles are given in Tables XII and XIII.

Table XII. Bond Lengths (Å) and Angles (deg), with Estimated Standard Deviations, in the Coordination Polyhedra

	Ni	Co
	Distances	
M-P(1)	2.197 (5)	2.251 (7)
M-P(2)	2.214 (5)	2.267 (7)
M-P(3)	2.207 (5)	2.246 (7)
M-N	2.062 (16)	2.206 (21)
M-H	1.57 (20)	
	Angles	
P(1)-M-P(2)	120.8 (0.2)	126.4 (0.3)
P(1)-M-P(3)	119.6 (0.2)	114.8 (0.3)
P(2)-M-P(3)	119.6 (0.2)	117.1 (0.2)
P(1)-M-N	88.1 (0.4)	84.9 (0.5)
P(2)-M-N	89.0 (0.4)	85.2 (0.6)
P(3)-M-N	89.4 (0.4)	87.2 (0.6)
N-Ni-H	171.1 (4.5)	

The nickel atom lies at the center of an almost regular trigonal bipyramid. The three phosphorus atoms form a planar equilateral triangle, each being 2.2 ± 0.01 Å from the nickel atom with P-Ni-P angles of 120 ± 0.8°. A nitrogen atom lies at one of the apices, and the other apex holds a hydrogen atom in about half of the molecules. The nickel atom lies 0.04 Å below the plane of phosphorus atoms, away from the nitrogen. Although caution must be taken considering hydrogen-metal distances from X-ray analysis, the Ni-H distance, 1.57 (20) Å, is in agreement with other hydrogen-metal distances involving first-row transition elements.[19]

One fluoride of the tetrafluoroborate anion points toward the hydride ion, but the H-F(4) distance of 2.34 Å suggests that there is at best only a weak interaction. The Ni· · ·F(4) distance is 3.88 Å. The distance between the nickel and phenyl hydrogen atoms is always greater than 3.1 Å. Contact distances between the fluorides and the other atoms in the structure are given in Table XIV. No other contacts of less than 3.5 Å have been found. The bond lengths and angles in the ligand appear to be normal, but the B-F distances are somewhat shorter than expected,[20] perhaps because no correction for the thermal motion of the fluoride was applied.

Since any one cation must either have or not have a hydridic ligand, the structure can be described as a disordered one, the disorder consisting in the random holes left by the absent hydride ligands.

The nickel(I) cation $[Ni(np_3)]^+$ has a trigonal-pyramidal structure obtained by removing the hydride ligand from the bipyramid. The other bond lengths and angles are not, however, significantly dependent on this difference. An alternative description of the disorder is that the cation sites in the crystal are randomly occupied by $[Ni(np_3)]^+$ and $[Ni(np_3)H]^+$ ions of the same general dimensions. In the present case about half of the cations are without hydrogen.

Support for these conclusions is provided by a structure determination of an analogous cobalt complex $[Co(np_3)]BF_4$. This is isomorphous with the nickel compound studied above and the structure of the cation which is trigonal pyramidal is very similar, as will be seen from Figure 7. Selected bond lengths and angles are given in Tables XII and XIII. The structural difference between the cobalt and nickel complexes can be summarized by saying that the Co-N apical bond, 2.206 (21) Å, is longer than the Ni-N bond, 2.062 (16) Å, and consequently the phosphorus atoms are pulled, *via* the methylene chains, out of the equilateral triangle configuration. The P-Co-P angles are 114.8 (3), 117.1 (2), and 126.4 (3)° instead of 120°, and the P-Co distances are 0.05 Å longer than the P-Ni distances. The cobalt atom lies 0.16 Å below the mean equatorial plane of the three phosphorus atoms.

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(19) B. A. Freus and J. A. Ibers, "Transition Metal Hydrides," Marcel Dekker, New York, N. Y., 1971, p 42.

(20) M. R. Churchill and A. H. Reis, *Inorg. Chem.*, 11, 1811 (1972); R. M. Tuggle and D. L. Weaver, *ibid.*, 11, 2237 (1972); F. S. Stephen, *J. Chem. Soc., Dalton Trans.*, 1350 (1972).

Table XIII. Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in the Remainder of the Molecule

	Ni	Co
	Distances	
P(1)-C(1)	1.79 (2)	1.80 (2)
P(1)-C(7)	1.77 (2)	1.83 (3)
P(1)-C(13)	1.84 (2)	1.82 (3)
P(2)-C(3)	1.85 (2)	1.82 (3)
P(2)-C(19)	1.85 (2)	1.80 (3)
P(2)-C(25)	1.82 (2)	1.76 (2)
P(3)-C(5)	1.84 (2)	1.82 (2)
P(3)-C(31)	1.76 (2)	1.77 (2)
P(3)-C(37)	1.78 (2)	1.84 (2)
N-C(2)	1.48 (2)	1.57 (2)
N-C(4)	1.48 (2)	1.52 (4)
N-C(6)	1.51 (2)	1.52 (4)
C(1)-C(2)	1.51 (3)	1.47 (3)
C(3)-C(4)	1.58 (3)	1.54 (4)
C(5)-C(6)	1.46 (3)	1.59 (4)
B-F(1)	1.27 (3)	1.31 (5)
B-F(2)	1.26 (3)	1.30 (4)
B-F(3)	1.27 (3)	1.36 (4)
B-F(4)	1.28 (4)	1.32 (6)
	Angles	
M-P(1)-C(1)	97.3 (0.6)	101.8 (1.1)
M-P(1)-C(7)	126.1 (0.6)	128.9 (0.9)
M-P(1)-C(13)	116.0 (0.6)	111.9 (1.1)
C(1)-P(1)-C(7)	107.0 (0.9)	104.9 (1.2)
C(1)-P(1)-C(13)	104.8 (0.8)	105.2 (1.3)
C(7)-P(1)-C(13)	103.1 (0.8)	101.9 (1.4)
M-P(2)-C(3)	98.5 (0.8)	98.4 (1.0)
M-P(2)-C(19)	125.4 (0.6)	122.6 (0.6)
M-P(2)-C(25)	118.9 (0.6)	122.1 (0.8)
C(3)-P(2)-C(19)	104.3 (1.0)	108.3 (1.1)
C(3)-P(2)-C(25)	106.1 (0.9)	104.5 (1.3)
C(19)-P(2)-C(25)	101.3 (0.7)	99.3 (1.0)
M-P(3)-C(5)	98.5 (0.7)	99.7 (0.7)
M-P(3)-C(31)	119.1 (0.6)	119.7 (0.7)
M-P(3)-C(37)	124.1 (0.6)	122.5 (0.8)
C(5)-P(3)-C(31)	103.7 (0.9)	105.7 (1.1)
C(5)-P(3)-C(37)	104.8 (0.9)	102.1 (0.9)
C(31)-P(3)-C(37)	103.7 (0.8)	104.2 (0.9)
M-N-C(2)	112.2 (1.1)	109.2 (1.3)
M-N-C(4)	111.9 (1.1)	114.6 (1.7)
M-N-C(6)	107.3 (1.1)	110.5 (1.6)
C(2)-N-C(4)	108.0 (1.4)	108.9 (1.8)
C(2)-N-C(6)	109.3 (1.4)	108.5 (2.0)
C(4)-N-C(6)	108.1 (1.3)	104.8 (2.0)
P(1)-C(1)-C(2)	109.0 (1.3)	108.1 (1.9)
N-C(2)-C(1)	110.1 (1.5)	111.9 (1.7)
P(2)-C(3)-C(4)	104.8 (1.4)	112.3 (2.3)
N-C(4)-C(3)	111.3 (1.5)	107.6 (2.5)
P(3)-C(5)-C(6)	104.5 (1.3)	107.4 (1.6)
N-C(6)-C(5)	116.6 (1.6)	111.2 (2.1)
F(1)-B-F(2)	116.8 (2.3)	115.9 (3.0)
F(1)-B-F(3)	115.4 (2.3)	110.7 (3.1)
F(1)-B-F(4)	102.7 (2.4)	104.3 (3.5)
F(2)-B-F(3)	113.1 (2.2)	109.3 (3.1)
F(2)-B-F(4)	107.4 (2.7)	112.0 (3.6)
F(3)-B-F(4)	98.6 (2.6)	103.9 (3.6)

Mean Distances and Angles in the Benzene Rings[a]

	Ni		Co	
Ring A	1.37 (2)	120.0 (1.0)	1.43 (3)	120.0 (2.6)
Ring B	1.39 (3)	119.9 (1.6)	1.40 (2)	120.0 (1.3)
Ring C	1.36 (2)	120.0 (0.9)	1.39 (2)	119.8 (1.9)
Ring D	1.38 (4)	120.0 (3.0)	1.41 (5)	119.9 (1.2)
Ring E	1.39 (2)	120.0 (1.6)	1.38 (2)	120.0 (1.4)
Ring F	1.38 (1)	120.0 (0.9)	1.37 (1)	119.9 (1.3)

[a] The estimated error of the means is calculated using the formula $[\Sigma_m(d_m - \bar{d})^2/m(m-1)]^{1/2}$, where d_m and $\bar{d}$ are the distances and the mean distances, respectively.

Table XIV. Shortest Contacts (<3.5 Å) Involving the Fluorine Atoms[a]

	Ni	Co
$F(3)\cdots C(2^{I})$	3.44	3.47
$C(9)\cdots F(1^{II})$	3.47	>3.5
$F(3)\cdots C(29^{III})$	3.48	3.38
$C(17)\cdots F(2^{IV})$	3.41	>3.5
$M\cdots F(4)$	(3.88)	3.43

[a] Superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z: (I) $x, 1-y, {}^1/_2+z$; (II) ${}^1/_2+x, {}^1/_2+y, z$; (III) ${}^1/_2+x, {}^1/_2-y, {}^1/_2+z$; (IV) ${}^1/_2+x, {}^1/_2-y, {}^3/_2+z$.

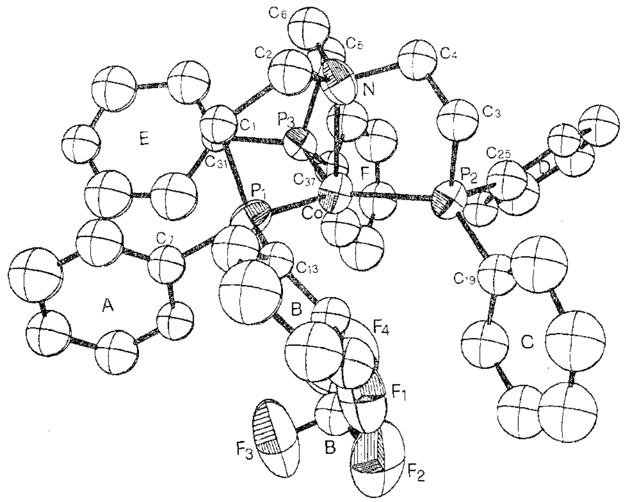

Figure 7. ORTEP perspective view of the $[Co(np_3)]^+$ cation, showing 30% probability ellipsoids.

The increase in bond lengths on going from nickel to cobalt is usual for this type of compound: greater differences are found in the trigonal-bipyramidal cations of the type $[Co^{II}(np_3)X]^+$ (X = halogen), which are very distorted toward the tetrahedral configuration.[21] In the present case the fact that the cobalt atom is in a lower oxidation state than the mean nickel one must also be considered. The difference between the nickel- and cobalt-nitrogen distances appears to be due mainly to the lowering of the cobalt atom below the equatorial plane, with the consequent decrease in the N-Co-P apical angles (85.7° (average) against 88.8° (average) in the nickel complex).

In the $[Co(np_3)]BF_4$ complex the fluoride atom is 0.4 Å closer to the metal than in the nickel complex. This can be interpreted as an additional evidence for the presence of the hydrogen ligand between the nickel and the fluoride atom. However one cannot speak of a truly bonding interaction between the cobalt and the very electronegative fluoride (there clearly is some interaction), since the usual Co(II)-F bond length is of the order of 2.0 Å. Apart from the difference in the Co· · ·F distance, the other structural parameters relating to the "hole" below the cobalt atom are similar to those of the nickel complex.

Conclusions

It is rather unusual that the nickel(II) hydride complexes are formed from nickel(II) in the absence of a specific reducing or hydrogenating agent. Hydride complexes are formed in similar circumstances by either of two possible mechanisms. The metal complex acting as an acid forms an alkoxide complex which then undergoes intramolecular hydride transfer to give the metal hydride complex and an aldehyde. In this case the phosphine ligand acts as a "base" bonding to the hydrogen cation. Alternatively the phosphine ligand may be oxidized to, for example, a phosphine halide leaving a very strongly reducing complex of the metal in a lower oxidation state.

(21) L. Sacconi, *Coord. Chem. Rev.*, **8**, 351 (1972).

In the present case the essential condition for the formation of these nickel hydride complexes is that the anions have low coordinating power since even the moderately coordinating nitrate anion leads to nonhydridic products. This can be understood by considering the nature of the complex which is presumably formed first $[Ni^{II}(np_3)]^{2+}$. Because of the steric requirements and donor properties of the ligand the nickel(II) atom is both coordinatively unsaturated and highly electrophilic. If no other donors are present, the electrophilic nature of the nickel is sufficient to enable it to abstract a hydride ion from the solvent. In effect the large positive charge carried by the nickel atom (a charge which is not effectively neutralized by the np_3 ligand) presents a sterically unhindered target for nucleophilic attack by any donor present. This explains the fact that borohydride promotes the formation of the hydridic products. It also acts as a convenient reducing agent so that the nickel(II) complex is converted into a nickel(I) complex.

Even in the presence of excess borohydride the ratio of hydrogen to nickel(II) is not equal to 1. This suggests that the postulated complex $[Ni^{II}(np_3)]^{2+}$ can also be reduced by another route leading to a nickel(I) complex that does not contain hydrogen. It seems that this complex cannot be quantitatively converted into the hydride by excess borohydride. This could result either from the weakness of the Ni^{II}-H bond or from the insolubility of $[Ni^{I}(np_3)]^+$. Further reduction can be accomplished by the borohydride to give the nickel(0) complex $[Ni^{0}(np_3)]$. This compound, in which the nickel atom has the d^{10} configuration, can be protonated by acids such as HBF_4 to give $[Ni^{0}H(np_3)]^+$ which may then undergo an intramolecular redox reaction to give $[Ni^{II}H(np_3)]^+$. In fact this is the best method for preparing the nickel(II) hydride. Bearing in mind that species such as $[Ni^{II}H(np_3)]^+$, $[Ni^{I}(np_3)]^+$, and $[Ni^{0}(np_3)]$ were isolated as solids, one can only conjecture that the equilibria obtaining in solution are as outlined above and summarized in Scheme I.

Scheme I

$$\begin{tikzcd}
{[Ni^{II}(H_2O)_n]^{2+} + np_3} \arrow[r, rightleftharpoons] & {[Ni^{II}(np_3)]^{2+}} \arrow[r, rightleftharpoons, "H^-"] \arrow[d, rightleftharpoons, "+e"] & {[Ni^{II}H(np_3)]^+} \arrow[d, rightleftharpoons, "+e"] \\
& {[Ni^{I}(np_3)]^+} \arrow[r, rightleftharpoons, "H^-"] \arrow[d, rightleftharpoons, "+e"] & {[Ni^{I}H(np_3)]} \arrow[d, rightleftharpoons] \\
& {[Ni^{0}(np_3)]} \arrow[r, rightleftharpoons, "H^+"] & {[Ni^{0}H(np_3)]^+}
\end{tikzcd}$$

A neutral nickel(I) hydride is a possible intermediate, and this would be more likely to remain in solution than the ionic salts.

The structure determinations reveal no evidence that the presence of a hydride ligand has any substantial effect on the molecular dimensions. In particular, the arrangement of atoms under and around the "hole" is very similar in both the nickel and cobalt complexes, the only significant difference being in the distance of the closest fluoride. The steric requirements of the phenyl groups are not critical, for while one may suppose that they form a "cage" below the metal into which the hydrogen will fit, the size of this cage depends largely upon the orientation of the phenyl groups. These groups are free to rotate about the P-C bonds and it would seem that they arrange themselves into configurations suitable to the accommodation of the atoms below the metal. This is shown, *e.g.*, by the structure of the complex $[Ni(np_3)I]^+$ [22] where the iodide ion is placed in the apical position at a bond distance from the nickel.

With regard to the infrared spectra, the absence of a metal-hydrogen stretching vibration between 1700 and 2250 cm^{-1} is unusual, though not unique. It is interesting that the isoelectronic uncharged cobalt(I) complex $[CoH(np_3)]$, which has been shown to have practically the same configuration as $[NiH(np_3)]^+$,[23] displays both a band at 1870 cm^{-1} and a triplet at *ca.* 595 cm^{-1}. We conclude that the high-frequency Ni-H (stretching) vibration is "accidentally" forbidden. We are preparing other suitable complexes in order to clarify the problem.

Acknowledgments. Thanks are due to Mr. F. Cecconi and Mr. F. Zanobini for technical assistance and to Mr. F. Nuzzi and Mr. G. Vignozzi for microanalyses.

Registry No. $[Ni(np_3)]NO_3$, 52951-35-6; $[NiH(np_3)]ClO_4$, 52920-72-6; $[NiH(np)_3]NO_3$, 52920-73-7; $[Co(np_3)]BF_4$, 52760-73-3; $[NiH(np_3)]BF_4$, 52760-75-5.

Supplementary Material Available. Listings of structure factor amplitudes for $[NiH_{0.5}(np_3)]BF_4$ and $[Co(np_3)]BF_4$ 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-74-2850.

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(22) P. Dapporto and L. Sacconi, *J. Chem. Soc. A*, 1804 (1970).

(23) C. A. Ghilardi and L. Sacconi, *Cryst. Struct. Commun.*, 3, 415 (1974).