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Synthesis, Properties, and Structural Characterization of Complexes of Cobalt and Nickel in Low Oxidation States with the Tripod Ligand Tris(2-diphenylphosphinoethyl)amine

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Five-coordinate complexes of cobalt(I) and nickel(I) are formed by the action of tris(2-diphenylphosphinoethyl)amine, np3, on cobalt(II) and nickel(II) salts in the presence of sodium borohydride. The complexes have the general formula [MX(np3)] (X = halide, pseudohalide, hydride) and have a trigonal-bipyramidal stereochemistry. Further reduction of the nickel complex yields the four-coordinate zerovalent nickel complex [Ni(np3)], shown by X-ray studies to have a unique trigonal-pyramidal structure. The nitrogen atom lies at the apex of the pyramid and the metal atom lies in the plane of the three phosphorus atoms. The isoelectronic cobalt(I)–hydrido complex [CoH(np3)] is isomorphous with the nickel(0) complex but is trigonal bipyramidal by virtue of the hydride ligand which occupies the axial position opposite the nitrogen atom, a position which is vacant in the nickel complex. Both the crystals are monoclinic space group $C2/c$ with the following cell constants for the nickel and cobalt complexes, respectively: $a = 24.370$ Å, $b = 11.242$ Å, $c = 27.693$ Å, $\beta = 107.7°$; $a = 24.278$ Å, $b = 11.192$ Å, $c = 28.027$ Å, $\beta = 108.0°$. Counter methods were used and least-squares refinements gave final R factors of 0.059 and 0.054, respectively. Some significant bond lengths and angles are Ni–N = 2.178 (7) Å, Ni–P(av) = 2.119 (2) Å, N–Ni–P(av) = 90.0 (2)°, Co–N = 2.067 (5) Å, Co–P(av) = 2.112 (3) Å, Ni–Co–P(av) = 89.2 (2)°, Co–H = 1.45 (5) Å, N–Co–H = 179 (2)°.

Introduction

The potentially tetradentate ligand tris(2-diphenylphosphinoethyl)amine, np3, has a tripod shape and a donor atom combination which confer on it particular coordinative properties and occasionally unexpected chemical behavior. It forms five-coordinate complexes when treated with halides or pseudohalides of the $3d^6$, $3d^7$, and $3d^8$ metal ions.[1] These complexes have the general formula $[MX(np_3)]^+$, and some, such as $[CoI(np_3)]^+$, which is trigonal bipyramidal[2] or square pyramidal[3] according to the uncoordinated anion present, have interesting structural characteristics. When only weakly donating anions are present, the ligand shows itself in a different light; it reacts with the hexaaquonickel(II) ion as both reducing and hydrogenating agent and gives nonstoichiometric hydrides of the type $[NiH_x(np_3)]Y$ ($0 < x < 1$, Y = BF_4, ClO_4, NO_3).[4] A five-coordinate complex $[Ni(np_3)NO_3]$ is also obtained. With $[Co(H_2O)_6](BF_4)_2$ np3 forms the four-coordinate trigonal-pyramidal complex $[Co(np_3)]BF_4$.[4]

We have now studied the behavior of np3 toward cobalt(II) and nickel(II) in the presence of the reducing agent sodium borohydride. If the initial metal salt used contains a coordinating anion such as halide and pseudohalide, the anion is found as a fifth ligand in the resulting complex $[MX(np_3)]$ (X = Cl, Br, I, CN, NCS). The metal ions are reduced to the monovalent state. If the initial metal salt contains a weakly donating anion, the hydride complex is formed preferentially. Thus $[Co(H_2O)_6](BF_4)_2$ gives $[CoH(np_3)]$. In suitable circumstances the nickel(0) complex $[Ni(np_3)]$ is formed. By reaction with carbon monoxide some carbonyl complexes of both the metals were obtained.

All the compounds were characterized and their physical properties studied by usual methods.

Complete X-ray structural determinations have been carried out on the isomorphous $[CoH(np_3)]$ and $[Ni(np_3)]$. The latter is the first compound in which a metal atom is to be found in a trigonal-pyramidal environment. A partial account of this work has already been published.[5]

Experimental Section

Reagents and Characterization. All solvents were reagent grade and were throughly degassed before use. Complexes were prepared routinely in degassed solvents under a nitrogen atmosphere. Crystals were typically washed with ethanol, water, absolute ethanol, and petroleum ether and were dried under a stream of nitrogen. Magnetic susceptibilities were measured using the Gouy or Faraday methods, the apparatus and experimental techniques being those previously described.[6] Diamagnetic corrections were calculated using Pascal's constants.[7] The electronic and infrared spectra and the molar conductivities were all obtained using the methods described elsewhere.[8]

Synthesis of Metal Complexes. $[NiX(np_3)]$. X = Cl, Br, I. A solution of $NaBH_4$ (1 mmol/15 ml of absolute ethanol) was added slowly to a mixture obtained from the ligand (1 mmol/20 ml of CH_2Cl_2) and NiX_2 (1 mmol/15 ml of absolute ethanol). The crystals were obtained by evaporating at room temperature.

X = NCS. The reaction was carried out at 0°, the ligand being dissolved initially in 30 ml of acetone.

X = CN. This compound was prepared by double decomposition of NaCN and $[NiI(np_3)]$ (mole ratio 1:1) in absolute ethanol at ca. 40° for 2 hr.

$[Ni(np_3)]$. $NaBH_4$ (2.4 mmol/10 ml of absolute ethanol) was added to a mixture of the ligand (1 mmol/25 ml of acetone) and $Ni(NO_3)\cdot 6H_2O$ (1 mmol/10 ml of absolute ethanol) at ca. 50°. The solution was concentrated at about half-volume by purging with nitrogen at ca. 50°.

$[Ni(CO)(np_3)]$. This compound was prepared by treating $[Ni(np_3)]$ (1 mmol/65 ml of THF) with carbon monoxide. Absolute ethanol (20 ml) was added and the solution was slowly concentrated to give yellow crystals.

$[Ni(CO)(np_3)]Y$ (Y = BF_4, $B(C_6H_5)_4$). To a solution of ligand (1 ml in 30 ml of acetone) $Ni(BF_4)_2\cdot 6H_2O$ (1 mmol in 20 ml of absolute ethanol) was added, and the resulting mixture was concentrated. The crystals obtained (corresponding to an average formula of $[NiH_x(np_3)]BF_4$ ($x = 0.04$–0.26))[4] were dissolved in 70–80 ml of CH_2Cl_2 and a stream of CO was bubbled through, a 50% excess of $NaB(C_6H_5)_4$ being present for the latter compound.

$[CoX(np_3)]$. X = Cl, Br, I. These were prepared as the nickel compounds, with the ligand and the $NaBH_4$ both dissolved in DMF.

X = CN, NCS. The preparation of these compounds mirrors that of the nickel analogs.

$[Co(CO)(np_3)]BF_4$. This was prepared by bubbling carbon monoxide in a suspension of $[Co(np_3)]BF_4$ (1 mmol in 30 ml of absolute ethanol). To the obtained brown-red solution ligroin was then added and the solution was slowly concentrated under a CO stream to give red crystals.

$[Co(CO)(np_3)]B(C_6H_5)_4$. To the brown-red solution obtained above $NaB(C_6H_5)_4$ (1.5 mmol in 20 ml of acetone) was added and the solution was slowly concentrated.

$[CoH(np_3)]$. To a mixture of the ligand (1 mmol/30 ml of acetone) and $Co(BF_4)_2\cdot 6H_2O$ (1 mmol/10 ml of absolute ethanol) was added $NaBH_4$ (2–4 mmol/10 ml of absolute ethanol) at ca. 50°. A brown-orange precipitate was formed initially and this was transformed by heating and concentration into brick red crystals.

$[CoH(CO)(np_3)]$. This was prepared from $[CoH(np_3)]$ by

Table I. Crystal Data Collection Details

	$[Ni(np_3)]$	$[CoH(np_3)]$
Mol formula	$C_{42}H_{42}NiNP_3$	$C_{42}H_{43}CoNP_3$
Mol wt	712.4	713.7
a, Å	24.370 (7)	24.278 (5)
b, Å	11.242 (4)	11.192 (3)
c, Å	27.693 (7)	28.027 (5)
β, deg	107.7 (2)	108.0 (1)
d_{obsd}(by flot), g cm^{-3}	1.30	1.30
d_{calcd}, g cm^{-3}	1.308	1.309
U, Å^3	7229.1	7243.0
Z	8	8
Space group	*C*2/*c*	*C*2/*c*
Absorpt coeff (Mo Kα), cm^{-1}	6.99	6.57
Color	Red-brown	Red-brown
Habit	Square bipyramid	Square bipyramid
Dimensions, mm	0.22 × 0.32 × 0.40	0.30 × 0.36 × 0.48
Diffractometer	Hilger Y 290	Philips PW 1100
Radiation	Mo Kα	Mo Kα
Filter	Zr	
Monochromator		Flat graphite crystal
Takeoff angle, deg	3	4.5
Method	ω–2θ scan	ω–2θ scan
Scan speed	Scans of 100 sec, with steps of 0.01° and a count of 1 sec for each step across the peak	0.05°/sec in a range of 0.6° (a total of 12 sec) across the peak
Background time	25 sec on each side of the peak	6 sec on each side of the peak
Standards	2 every 50 reflections	3 every 2 hr
Max dev of standards	3%	2%
2θ limit	$0° < 2\theta \leqslant 40°$	$0° < 2\theta \leqslant 40°$
No. of data with $I \geqslant 3\sigma(I)$	1864	2297

treatment with carbon monoxide in THF and subsequent addition of absolute ethanol; the solution was slowly concentrated yielding yellow crystals.

Collection and Reduction of X-Ray Intensity Data. Both compounds crystallize as red-brown square bipyramids cut at the apices. Weissenberg and precession photographs taken on the nickel compound indicated that the crystal system is monoclinic *C* centered. On the basis of systematic extinctions we could not decide between centric *C*2/*c* and acentric *Cc* space groups; the former was confirmed by successful refinement of the structure.

Data for the nickel compound were collected on a Hilger automated diffractometer. The unit cell parameters were obtained by carefully measuring the setting angles of 20 reflections, in the range $8° < \theta < 12°$.

The cobalt compound was studied on a PW 1100 Philips fully automatic diffractometer. From examination of the orientation matrix **UB**[9] and its derived $\tilde{\mathbf{UB}}\cdot\mathbf{UB}$, from which the direct cell lattice constants were directly obtained, it was clear that the lattice was *C* centered also in this case and that the axial dimensions were fully comparable. Examination of systematic extinction made apparent that the two complexes are nearly isostructural. A review of crystal data is given in detail in Table I.

The data were in both cases processed in the manner previously described.[10] After correction for background, the standard deviations $\sigma(I)$ of the corrected intensities, *I*, were estimated using for both complexes a value of *p* of 0.02. The intensities were corrected for Lorentz–polarization effects. An absorption correction[11] was applied for the nickel compound. The transmission factors varied in the range 0.87–0.91. Owing to the low value of the linear absorption coefficient and to the fact that the crystal of the cobalt complex was mounted with the longest dimension parallel to the spindle axis, which was not true for the nickel crystal, the absorption correction was not applied in this second case.

Solution and Refinement of the Structures. The nickel and the three phosphorus atoms were located from an inspection of a three-dimensional Patterson function, and all the other nonhydrogen atoms were found from successive Fourier syntheses.

At this point the *R* factor defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ was 0.18. In subsequent least-squares refinement all atoms were given isotropic temperature factors. After three of these cycles with weights equal to unity, the conventional *R* factor was 0.11. Another cycle, performed with the weighting function $w = 1/\sigma^2(F_o)$, lowered R_1 to 0.099 and the weighted *R* defined as $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ to 0.088. Anisotropic temperature factors were then used for the atoms of the coordination polyhedron, i.e., Ni, P, and N atomic species. The *R* factors after two of these cycles were 0.076 and 0.070, respectively. A difference Fourier map showed the positions of almost all of the hydrogen atoms, which were introduced at calculated positions but not refined. Before each new cycle, new positions for hydrogen atoms were recalculated. All hydrogen atoms were allotted $B = 5.0$ Å^2. Final R_1 and R_2 after two more cycles are 0.059 and 0.053, respectively. No electron density is present in a final *F* map in a position corresponding to the fifth position of a trigonal bipyramid; the same map showed no peaks higher than 0.5 e/Å^3.

Since the two complexes are isostructural, the final nickel parameters were used as starting parameters for the cobalt complex. Two cycles of refinement with isotropic temperature factors followed by two cycles using anisotropic thermal parameters for Co, P, and N atoms and isotropic ones for the other atoms reduced *R* to 0.072.

At this point a difference Fourier map was calculated in order to locate the hydride hydrogen atom. The map clearly showed a peak with an electron density corresponding to 1 e/Å^3, 1.4 Å below the metal atom. The position of the hydrogen atom bound to the metal was confirmed by a successive difference Fourier synthesis calculated using only the reflections having $(\sin\theta)/\lambda \leq 0.30$ where the hydrogen atom is the most prominent feature of the map.

The other hydrogen atoms, calculated in idealized positions, were introduced in subsequent calculations with temperature factors equal to those of their own carbon atoms but were not refined.

At this point an attempt to refine the ligand hydrogen atom was undertaken. A unit population parameter and a starting thermal parameter $B = 3.0$ Å^2 were used. Three cycles of refinement, where all the parameters as described before together with x_H, y_H, z_H, and B_H were allowed to vary, gave a final R_1 of 0.054. The value of R_2 is 0.054. The refinement of the hydride hydrogen atom was successful since the largest shift error in the last cycle was 0.14, the final thermal parameter was $B = 2.7$ Å^2, and the Co–H distance was 1.45 Å.

Atomic scattering factors were taken from ref 12 for Ni, Co, P, N, and C and from ref 13 for H. Programs used were as follows. Data reduction, Fourier syntheses, and structure factors were from the series of programs written for the IBM 1130 computer by the A.R.C. unit of Structural Chemistry, University College, London. Least squares were from the X-ray 70 set of programs written or adapted by J. M. Stewart and coworkers for the CDC 6600, UNIVAC 1108, and IBM 360 computers.

Tables II–IV show the final positional and thermal parameters for both structures.

Results and Discussion of the Chemistry

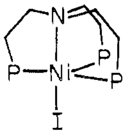
[NiX(np$_3$)] Complexes (X = Cl, Br, I, CN, NCS). These complexes are green (X = Cl) to yellow (X = I), are relatively stable in dry air, and, with the exception of the thiocyanate derivative, are fairly soluble in common polar organic solvents although the solutions are not stable. The magnetic moments (Table V) at room temperature fall in the range 1.72–1.99 BM, suggesting that the nickel has an oxidation number of +1. Their reflectance spectra (Table VI) are all similar, with two main absorptions at 10,000–12,000 and 25,000–27,000 cm^{-1}. The first band, which is split into two components, is typical of d^9 ions in a trigonal-bipyramidal ligand field. The electronic spectrum of the iodo derivative [NiI(np$_3$)] is shown in Figure 1. The spectrum of the copper(II) complex [CuBr(Me$_6$tren)]Br, which is known to have C_3 symmetry,[14] is also shown in Figure 1 for comparison purposes.

The bathochromic shift on going from the cyanide to the iodide shows that the halogen or pseudohalogen is bound to the metal and corroborates the conclusion that the complexes are five-coordinated. An X-ray structural analysis of the iodo derivative, in progress in this laboratory, has confirmed that

Table II. [Ni(np$_3$)] Positional Parameters and Isotropic Thermal Parameters, with Estimated Standard Deviations in Parentheses

Atom	x/a	y/b	z/c	10^3B, Å^2
Ni	0.10582 (5)	0.01604 (13)	0.13826 (5)	
P(1)	0.1451 (1)	0.1770 (3)	0.1709 (1)	
P(2)	0.1505 (1)	−0.1025 (3)	0.1039 (1)	
P(3)	0.0222 (1)	−0.0394 (3)	0.1368 (1)	
N	0.1430 (3)	−0.0749 (7)	0.2103 (3)	
C(1)	0.1895 (4)	0.0025 (10)	0.2430 (4)	60 (3)
C(2)	0.1769 (4)	0.1299 (10)	0.2386 (4)	61 (3)
C(3)	0.1660 (4)	−0.1901 (9)	0.2019 (4)	57 (3)
C(4)	0.1963 (4)	−0.1847 (9)	0.1609 (4)	50 (3)
C(5)	0.0959 (4)	−0.0872 (10)	0.2342 (4)	52 (3)
C(6)	0.0398 (4)	−0.1296 (9)	0.1961 (4)	51 (3)
C(7)	0.1087 (5)	0.3129 (10)	0.1797 (4)	64 (4)
C(8)	0.1318 (5)	0.3935 (12)	0.2199 (5)	83 (4)
C(9)	0.0994 (6)	0.4913 (13)	0.2254 (5)	94 (4)
C(10)	0.0464 (6)	0.5144 (13)	0.1929 (5)	95 (4)
C(11)	0.0243 (5)	0.4386 (12)	0.1530 (5)	89 (4)
C(12)	0.0547 (5)	0.3371 (11)	0.1462 (4)	69 (4)
C(13)	0.2079 (4)	0.2422 (10)	0.1549 (4)	49 (3)
C(14)	0.2038 (5)	0.3514 (11)	0.1328 (4)	74 (4)
C(15)	0.2507 (6)	0.3949 (12)	0.1166 (5)	84 (4)
C(16)	0.2969 (5)	0.3268 (12)	0.1245 (5)	78 (4)
C(17)	0.3032 (5)	0.2198 (13)	0.1470 (5)	86 (5)
C(18)	0.2557 (5)	0.1744 (11)	0.1630 (5)	75 (4)
C(19)	0.2020 (4)	−0.0621 (9)	0.0712 (4)	43 (3)
C(20)	0.1987 (4)	0.0459 (10)	0.0490 (4)	54 (3)
C(21)	0.2349 (5)	0.0795 (11)	0.0196 (4)	77 (4)
C(22)	0.2762 (5)	0.0039 (12)	0.0168 (4)	73 (4)
C(23)	0.2821 (5)	−0.1049 (12)	0.0383 (5)	81 (4)
C(24)	0.2447 (5)	−0.1385 (11)	0.0661 (5)	73 (4)
C(25)	0.1167 (4)	−0.2252 (9)	0.0616 (4)	40 (3)
C(26)	0.1002 (5)	−0.2077 (10)	0.0091 (4)	53 (3)
C(27)	0.0741 (5)	−0.2965 (11)	−0.0240 (4)	65 (4)
C(28)	0.0616 (5)	−0.4031 (11)	−0.0058 (5)	64 (4)
C(29)	0.0752 (5)	−0.4199 (11)	0.0444 (5)	74 (4)
C(30)	0.1031 (5)	−0.3330 (11)	0.0796 (4)	68 (4)
C(31)	−0.0212 (4)	−0.1422 (9)	0.0896 (4)	40 (3)
C(32)	−0.0222 (4)	−0.1263 (9)	0.0398 (4)	50 (3)
C(33)	−0.0572 (5)	−0.1965 (11)	0.0007 (4)	66 (4)
C(34)	−0.0904 (5)	−0.2825 (11)	0.0128 (5)	69 (4)
C(35)	−0.0906 (5)	−0.3030 (11)	0.0615 (5)	77 (4)
C(36)	−0.0552 (5)	−0.2315 (10)	0.1008 (4)	54 (4)
C(37)	−0.0355 (4)	0.0565 (9)	0.1435 (4)	42 (3)
C(38)	−0.0232 (4)	0.1399 (10)	0.1824 (4)	52 (3)
C(39)	−0.0646 (5)	0.2226 (10)	0.1883 (4)	64 (4)
C(40)	−0.1188 (5)	0.2167 (10)	0.1544 (5)	67 (4)
C(41)	−0.1324 (5)	0.1366 (11)	0.1160 (4)	61 (4)
C(42)	−0.0914 (5)	0.0555 (10)	0.1102 (4)	57 (3)

the chromophore has a trigonal-bipyramidal geometry with a C_3 site symmetry.



The thiocyanate derivative, though insoluble in the common organic solvents, shows a C–N stretching vibration at 2080 cm^{-1} indicating that the thiocyanate group is N bonded and terminal.^{15}

Table III. [CoH(np$_3$)] Positional Parameters and Isotropic Thermal Parameters, with Estimated Standard Deviations in Parentheses

Atom	x/a	y/b	z/c	10^3B, Å^2
Co	0.10626 (4)	0.01243 (9)	0.14008 (3)	
P(1)	0.1457 (1)	0.1724 (2)	0.1733 (1)	
P(2)	0.1514 (1)	−0.1061 (2)	0.1067 (1)	
P(3)	0.0232 (1)	−0.0453 (2)	0.1402 (1)	
N	0.1426 (2)	−0.0733 (5)	0.2078 (2)	
C(1)	0.1911 (3)	−0.0044 (8)	0.2420 (3)	71 (3)
C(2)	0.1807 (3)	0.1282 (7)	0.2400 (3)	56 (2)
C(3)	0.1654 (3)	−0.1943 (8)	0.2007 (3)	70 (3)
C(4)	0.1967 (3)	−0.1913 (7)	0.1613 (3)	51 (2)
C(5)	0.0986 (3)	−0.0936 (7)	0.2336 (3)	63 (3)
C(6)	0.0411 (3)	−0.1334 (6)	0.1993 (3)	51 (2)
C(7)	0.1072 (3)	0.3091 (7)	0.1809 (3)	50 (2)
C(8)	0.1299 (4)	0.3868 (8)	0.2217 (3)	77 (3)
C(9)	0.0968 (4)	0.4866 (9)	0.2258 (3)	91 (3)
C(10)	0.0457 (4)	0.5089 (9)	0.1929 (4)	95 (3)
C(11)	0.0230 (4)	0.4361 (9)	0.1521 (4)	89 (3)
C(12)	0.0548 (3)	0.3342 (8)	0.1470 (3)	64 (3)
C(13)	0.2065 (3)	0.2420 (7)	0.1561 (3)	50 (2)
C(14)	0.2007 (3)	0.3516 (8)	0.1331 (3)	69 (3)
C(15)	0.2466 (4)	0.3973 (8)	0.1167 (3)	85 (3)
C(16)	0.2942 (4)	0.3323 (9)	0.1243 (3)	79 (3)
C(17)	0.3018 (4)	0.2243 (8)	0.1470 (3)	77 (3)
C(18)	0.2563 (3)	0.1778 (7)	0.1635 (3)	65 (3)
C(19)	0.2024 (3)	−0.0593 (6)	0.0742 (2)	43 (2)
C(20)	0.1952 (3)	0.0498 (7)	0.0513 (3)	55 (2)
C(21)	0.2304 (4)	0.0846 (8)	0.0219 (3)	77 (3)
C(22)	0.2722 (3)	0.0084 (8)	0.0179 (3)	74 (3)
C(23)	0.2806 (4)	−0.0994 (8)	0.0398 (3)	79 (3)
C(24)	0.2452 (3)	−0.1358 (7)	0.0685 (3)	66 (3)
C(25)	0.1165 (3)	−0.2256 (6)	0.0624 (3)	42 (2)
C(26)	0.1010 (3)	−0.2056 (7)	0.0117 (3)	51 (2)
C(27)	0.0730 (3)	−0.2920 (8)	−0.0230 (3)	62 (2)
C(28)	0.0610 (3)	−0.3998 (8)	−0.0060 (3)	68 (3)
C(29)	0.0743 (4)	−0.4220 (8)	0.0435 (3)	76 (3)
C(30)	0.1022 (3)	−0.3363 (7)	0.0788 (3)	62 (2)
C(31)	−0.0208 (3)	−0.1497 (6)	0.0937 (2)	42 (2)
C(32)	−0.0220 (3)	−0.1374 (6)	0.0445 (3)	44 (2)
C(33)	−0.0570 (3)	−0.2098 (7)	0.0070 (3)	59 (2)
C(34)	−0.0917 (3)	−0.2939 (7)	0.0195 (3)	65 (3)
C(35)	−0.0908 (3)	−0.3084 (7)	0.0679 (3)	67 (2)
C(36)	−0.0552 (3)	−0.2366 (7)	0.1059 (3)	52 (2)
C(37)	−0.0354 (3)	0.0539 (6)	0.1451 (3)	41 (2)
C(38)	−0.0234 (3)	0.1359 (7)	0.1833 (3)	54 (2)
C(39)	−0.0646 (4)	0.2189 (7)	0.1886 (3)	64 (2)
C(40)	−0.1183 (3)	0.2167 (7)	0.1536 (3)	64 (2)
C(41)	−0.1321 (3)	0.1377 (7)	0.1152 (3)	66 (3)
C(42)	−0.0903 (3)	0.0546 (7)	0.1100 (3)	54 (2)
H(1)	0.082 (2)	0.072 (4)	0.092 (2)	34 (16)

Table IV. Anisotropic Thermal Parameters with Their Standard Deviations (All × 10^4)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	280 (7)	411 (9)	334 (8)	10 (6)	99 (5)	38 (6)
P(1)	370 (14)	557 (17)	427 (14)	−64 (12)	133 (11)	−23 (12)
P(2)	311 (13)	449 (15)	372 (14)	19 (11)	94 (10)	45 (11)
P(3)	310 (13)	435 (16)	411 (14)	11 (11)	137 (11)	58 (11)
N	350 (37)	535 (45)	393 (38)	−33 (34)	110 (31)	4 (34)
Ni	313 (9)	505 (12)	339 (10)	4 (9)	86 (7)	26 (9)
P(1)	397 (21)	603 (26)	372 (21)	−105 (19)	100 (17)	−27 (19)
P(2)	343 (20)	493 (23)	391 (21)	47 (17)	137 (16)	59 (18)
P(3)	312 (19)	457 (24)	354 (19)	38 (17)	96 (15)	60 (17)
N	328 (51)	650 (69)	330 (55)	2 (49)	47 (43)	103 (51)

[Ni(np$_3$)]. We have shown that [Ni(H$_2$O)$_6$](NO$_3$)$_2$ reacts in 1-butanol with np$_3$ in the presence of up to 1 mol of sodium borohydride per nickel atom to give the nonstoichiometric hydrides [NiH$_x$(np$_3$)](NO$_3$) ($0 < x < 1$). However, when the molar ratio of borohydride to metal is larger than 2, red crystals with the formula [Ni(np$_3$)] are obtained from boiling butanol. The compound is diamagnetic and does not show any absorption up to 19,000 cm^{-1}. With hot hydrochloric acid in dichloroethane it liberates 1 mol of hydrogen gas per gram-atom of nickel, and the resulting solution contains only nickel(II). This shows that the metal atom has oxidation number 0. An X-ray structural analysis has shown that the complex is four-coordinate with a trigonal-pyramidal geometry. To our knowledge this is the first example of a metal complex with this geometry.

The compound [Ni(np$_3$)] undergoes oxidative addition with HBF$_4$ or HClO$_4$ to give yellow, moderately air-stable crystals of the hydrido complexes [NiH$_x$(np$_3$)]Y (Y = BF$_4$, ClO$_4$). The value of x is nearly equal to 1, so these compounds

Table V. Physical Constants and Analytical Data for the Complexes

Compd	Λ_M,[f] cm^2 ohm^{-1} mol^{-1}	% calcd				% found				μ_{eff}(293 K), BM
		C	H	N	M	C	H	N	M	
[CoCl(np$_3$)][a]		67.43	5.66	1.87	7.88	67.46	5.84	1.75	7.75	3.24
[CoBr(np$_3$)][b]		63.64	5.34	1.77	7.44	63.90	5.39	1.65	7.40	3.27
[CoI(np$_3$)]		60.08	5.04	1.67	7.02	60.67	5.27	1.50	6.62	3.30
[Co(CN)(np$_3$)]		69.91	5.73	3.79	7.98	69.24	5.85	3.64	7.70	0.0
[Co(NCS)(np$_3$)]		67.00	5.49	3.64	7.65	67.31	5.67	3.64	7.46	3.31
[CoH(np$_3$)]		70.68	6.07	1.96	8.26	70.0	6.23	1.80	8.08	0.0
[CoH(CO)(np$_3$)]		69.63	5.84	1.89	7.95	69.12	5.97	1.89	7.81	0.0
[Co(CO)(np$_3$)] BF$_4$		62.34	5.12	1.69	7.12	62.48	5.30	1.58	7.02	0.0
[Co(CO)(np$_3$)] B(C$_6$H$_5$)$_4$	24	75.92	5.90	1.32	5.56	75.42	6.10	1.26	5.20	0.0
[NiCl(np$_3$)][c]		67.45	5.66	1.87	7.85	67.16	5.75	1.76	7.58	1.94
[NiBr(np$_3$)][d]		63.66	5.34	1.77	7.41	62.60	5.28	1.62	7.14	1.92
[NiI(np$_3$)][e]		60.10	5.04	1.67	6.99	59.63	4.92	1.57	6.45	1.99
[Ni(CN)(np$_3$)]		69.94	5.73	3.79	7.95	68.94	5.74	3.63	7.44	1.72
[Ni(NCS)(np$_3$)]		67.03	5.49	3.64	7.62	66.87	5.71	3.68	7.72	1.94
[Ni(CO)(np$_3$)]		69.75	5.72	1.89	7.93	69.44	5.92	1.83	7.67	0.0
[Ni(CO)(np$_3$)] BF$_4$	25	62.34	5.12	1.69	7.10	63.00	5.22	1.69	6.80	1.79
[Ni(CO)(np$_3$)] B(C$_6$H$_5$)$_4$		75.94	5.94	1.32	5.54	75.36	5.95	1.22	5.18	1.87
[Ni(np$_3$)]		70.80	5.94	1.97	8.24	70.90	5.99	1.97	8.00	0.0

[a] Cl: calcd, 4.73; found, 4.69. [b] P: calcd, 11.72; found, 11.56. [c] Cl: calcd, 4.74; found, 4.61. P: calcd, 12.34; found, 12.16. [d] Br: calcd, 10.08; found, 9.78. P: calcd, 11.73; found, 11.44. [e] P: calcd, 11.07; found, 10.70. [f] 1,2-Dichloroethane solution.

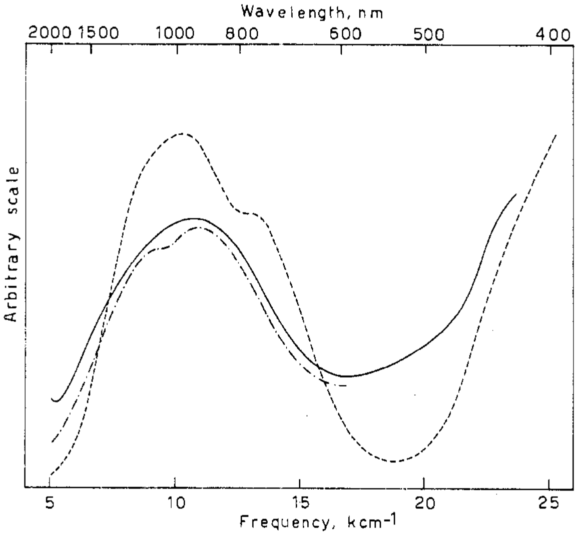


Figure 1. Reflectance spectra of [NiI(np$_3$)] at room temperature (——) and 113 K (-·-·-) and of [CuBr(Me$_6$tren)]Br (- - -).

Table VI. Maxima and Extinction Coefficients for the Electronic Spectra of the Complexes

Compd	Absorption max,[a] cm^{-1} (ϵ_M for soln)
[CoCl(np$_3$)]	a: 5550, 9610 sh, 10,530, 14,920, 17,090 sh, 18,520, 27,030
[CoBr(np$_3$)]	a: 5260, 9570, 10,420, 14,290, 17,590, 26,670
[CoI(np$_3$)]	a: 5000, 9220, 10,200 sh, 14,080, 17,530 sh, 22,220 sh
[Co(NCS)(np$_3$)]	a: 5000, 9300, 10,150 sh, 13,330, 17,240 sh, 22,220 sh
[Co(CN)(np$_3$)]	a: 19,800 sh, 24,390 b: 21,070 sh, 27,780 (5800)
[CoH(np$_3$)]	a: 24,390
[CoH(CO)(np$_3$)]	a: 25,000 sh
[Co(CO)(np$_3$)] BF$_4$	a: 21,300 b: 21,070 (3700)
[Co(CO)(np$_3$)] B(C$_6$H$_5$)$_4$	a: 21,500 b: 21,070 (3600)
[NiCl(np$_3$)]	a: 10,000 sh, 12,400, 27,030 b: 13,160 (288)
[NiBr(np$_3$)]	a: 10,000 sh, 12,500, 26,670 b: 10,000 sh, 12,500 (320)
[NiI(np$_3$)]	a: 8695 sh, 10,810, 27,030 b: 9480 (280)
[Ni(NCS)(np$_3$)]	a: 10,000 sh, 12,420, 20,000 sh, 26,670
[Ni(CN)(np$_3$)]	a: 10,000 sh, 12,500, 25,320 b: 12,820 (78)
[Ni(CO)(np$_3$)] BF$_4$	a: 8330 sh, 12,120, 23,810 sh b: 8170 (66), 13,245 (267)
[Ni(CO)(np$_3$)] B(C$_6$H$_5$)$_4$	a: 8330 sh, 12,270, 25,000 sh
[Ni(np$_3$)]	a: 20,000 sh, 23,260
[Ni(CO)(np$_3$)]	a: 28,570 sh

[a] a = solid; b = 1,2-dichloroethane solution.

represent the upper composition limit for the nonstoichiometric hydrides already described.[4]

[Ni(CO)(np$_3$)]Y (Y = BF$_4$, B(C$_6$H$_5$)$_4$) and [Ni(CO)(np$_3$)]. The green complexes [Ni(CO)(np$_3$)]Y are moderately stable in air and have magnetic moments (Table V) indicating the presence of one unpaired electron per nickel ion. The tetrafluoroborate is a 1:1 electrolyte in dichloroethane. The reflectance spectra of both compounds are similar to these of the halo derivatives, with a band at 12,200 cm^{-1} and a shoulder at 8300 cm^{-1} so that the same trigonal-bipyramidal structure may be assigned to these compounds as was given to the halo complexes [NiX(np$_3$)].

[Ni(CO)(np$_3$)] is obtained from [Ni(np$_3$)] by the action of carbon monoxide. It is yellow, diamagnetic, and nonconducting in dichloroethane. It is stable in solution. The electronic spectrum shows no absorption below 25,000 cm^{-1} and reaction with hydrochloric acid liberates 1 mol of hydrogen for nickel, as expected for a nickel(0) compound.

The B(C$_6$H$_5$)$_4$ salt of [Ni(CO)(np$_3$)]$^+$ shows a C–O stretching band at 1988 cm^{-1} while the BF$_4$ salt shows bands at 2020 and 2032 cm^{-1}. The C–O stretching frequency for the nickel(0) complex is found at 1880 cm^{-1}. The lower frequency is in accordance with the greater π-bonding capability of nickel(0) compared to that of nickel(I).

Possibly in these carbonyl complexes a potentially donor atom, such as the apical nitrogen, is not linked to the nickel atom; this would lead to an EAN not greater than 36. That the apical nitrogen atom of the np$_3$ ligand may be not bound to the metal in a complex is shown by an X-ray structure analysis in progress in this laboratory. Other evidence can be found looking at the study made on different complexes of the potentially seven-coordinated trenpy ligand, for which the apical nitrogen to metal distance varies as expected from bonding arguments.[16]

[CoX(np$_3$)]. (a) X = Cl, Br, I, NCS. These compounds

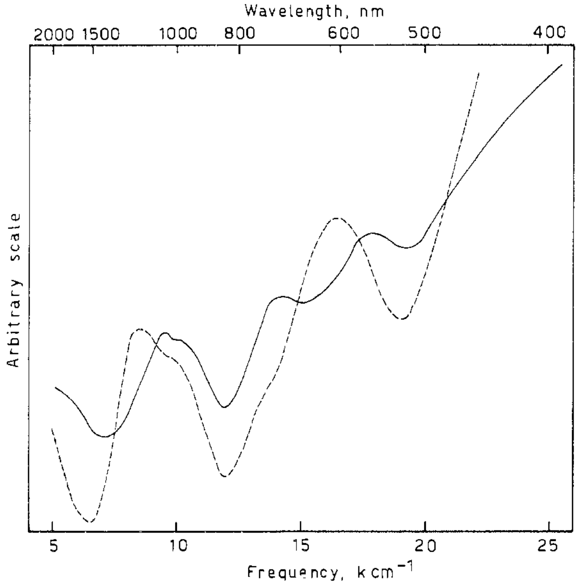


Figure 2. Reflectance spectra of [CoBr(np$_3$)] (——) and of [Ni(SalMeDPT)] (- - -) at room temperature.

vary from yellow (X = Cl) to green (X = I), are stable in the solid state, but are unstable in solution, even under nitrogen. The magnetic moments indicate the presence of two unpaired electrons of high-spin cobalt(I). The C–N stretching band of the thiocyanate is doubled, presumably by intermolecular interactions. The mean value of 2052 cm^{-1} indicates the thiocyanate is N bonded.[15] The reflectance spectra which show five sharp bands at ca. 5000, 9200–9600, 10,100–10,500, 13,300–14,900, and 17,100–17,600 cm^{-1} recall those of high-spin trigonal-bipyramidal nickel(II) complexes. The F → F transitions are at lower energies as expected in view of the spectrochemical properties of the d^8 ions cobalt(I) and nickel(II), so that a five-coordinate stereochemistry can be expressed for these compounds. Figure 2 shows the electronic spectrum of the [CoX(np$_3$)] complex together with the spectrum of the distorted trigonal-bipyramidal complex [Ni(SalMeDPT)].[17]

(b) X = CN, H. These compounds are red-brown and diamagnetic. The cobalt(I) is therefore low spin. Both are stable in air as solids and the cyanide is also stable in dichloroethane, in which it is a nonelectrolyte. The hydride was characterized by quantitative determination of the hydrogen gas liberated on treatment with hydrochloric acid. Both complexes show a band at 24,300 cm^{-1} in the reflectance spectra and the cyanide has a shoulder at 20,000 cm^{-1}. The absorption spectrum of the cyanide in dichloroethane shows a band at 27,800 cm^{-1} with a shoulder at 21,100 cm^{-1}. These spectra also can be compared with those of analogous five-coordinate nickel(II) complexes.[4]

The X-ray analysis has shown that the hydrido complex has a trigonal-bipyramidal structure.

The hydride shows an infrared band at 1870 cm^{-1} and a triplet at 607, 612, and 620 cm^{-1}. These bands are not present in the deuterated complex. In [CoD(np$_3$)] a band appears at 1350 cm^{-1} corresponding to a ν(H)/ν(D) ratio of 1.38. The high-frequency band can obviously be assigned to a Co–H stretching vibration. The "triplet" at ca. 600 cm^{-1} corresponds to the "doublet" at ca. 595 cm^{-1} found in the nonstoichiometric hydrido compounds [NiH$_x$(np$_3$)]BF$_4$. Although bands assignable to M–H vibrations have not been found in this spectral region (M–H deformation modes have been assigned in the range 700–950 cm^{-1} [18]), they are certainly connected with the presence of a hydride ligand. A more detailed assignment seems premature, and we hope to shed further light on this problem by studying the spectra of other hydrido complexes.

[CoH(np$_3$)] is transformed in boiling dichloroethane in the presence of sodium tetraphenylborate into the magenta complex [CoCl(np$_3$)]B(C$_6$H$_5$)$_4$ previously described by us;[1a] presumably the chloride ligand is extracted from the solvent.

It is interesting to compare the properties of the compounds [CoH(np$_3$)] and [Ni(np$_3$)]. The comparison is based on the structures described below. The compounds are isoelectronic and isomorphous. Indeed the cobalt complex is formally derived from the nickel complex by extracting a proton from the nucleus and removing it to the metal–hydrogen bond distance. The two complexes give diamagnetic solid solutions in all proportions, which can be considered to contain two M(np$_3$) moieties; those containing nickel have an empty "cage" below the metal atom while in those containing cobalt this "cage" is occupied by a hydride ligand. Clearly the nickel and cobalt atoms are randomly distributed. The fact that all solid solutions are diamagnetic and have spectra which are simple sums of the components' spectra proves that the hydride is bound only to the cobalt(I).

The compound [Co(np$_3$)]BF$_4$ takes up carbon monoxide in dichloroethane to give [Co(CO)(np$_3$)]BF$_4$ or [Co(CO)(np$_3$)]B(C$_6$H$_5$)$_4$. These products are diamagnetic 1:1 electrolytes in dichloroethane. Their electronic spectra show a band at ca. 21,400 cm^{-1} which is often found in five-coordinate cobalt(I) complexes. The B(C$_6$H$_5$)$_4$ salt has an infrared band at 1930 cm^{-1} and the BF$_4$ salt has a band at 1912 cm^{-1} due to the C–O stretching vibration.

The yellow diamagnetic hydride derivative [CoH(CO)(np$_3$)] has no electronic transition below 25,000 cm^{-1}. It is sparingly stable even in dichloroethane where it is a nonelectrolyte. The infrared spectrum shows a carbonyl band at 1875 cm^{-1} and an easily assignable M–H stretching band at 1943 cm^{-1}. The latter has disappeared in the spectrum of the deuterated compound. There is no band in the 600-cm^{-1} region. This suggests that such a band is peculiar of the five-coordinated hydrido complexes with tetradentate tripod ligands L having the formula MLH. The effective atomic number, if all possible donor atoms are coordinate, would be 38, which is rather rare especially for cobalt compounds, but also in this case it is probable that not all of the potentially donor atoms are linked to the metal.

Some of the cobalt derivatives [CoX(np$_3$)] are high spin, while some are low spin. This magnetic behavior can be usefully contrasted with the behavior of the corresponding nickel(II) complexes [NiX(np$_3$)]$^+$ which are all low spin. Since both groups of compounds have the same ligand donor set, the same d^8 electronic configuration, and presumably the same trigonal-bipyramidal geometry, the different magnetic behavior can only be attributable to the difference in formal oxidation state of the metal. As is well-known, both the nephelauxetic effect and the ligand donor strength increase with increasing charge on the metal ion, two factors which both strongly favor the low-spin state.[19]

As regards the nature of the donor atoms in the complexes [CoX(np$_3$)], we can see that when X is equal to the more electronegative ligands such Cl, Br, I, and NCS, the complexes are high spin; when X is equal to the more nucleophilic ligands H, CN, and CO (the last two are also capable of accepting electrons in π bonds), the complexes are low spin. This correlates well with previous findings[2] that relate the spin state of five-coordinate 3d metal complexes with electronegativity (χ) and nucleophilicity (n°) of the donor atoms, as shown in Table VII

Results and Discussion of the Structures of [Ni(np$_3$)] and [CoH(np$_3$)]

The crystals are formed from discrete monomeric units. In Tables VIII and IX a comparison of bond distances and angles

Table VII. Donor Sets and Spin States of Five-Coordinate d^8 Metal Complexes with the np$_3$ Ligand

Donor set	Σn°	$\Sigma\chi$	Spin state Co(I)	Spin state Ni(II)
Cl(np$_3$)	32.51	12.08	H	L
(NCS)(np$_3$)	33.12	12.32	H	L
Br(np$_3$)	33.65	11.99	H	L
I(np$_3$)	34.89	11.46	H	L
(CN)(np$_3$)	36.47	11.75	L	L
(CO)(np$_3$)		11.75	L	
H(np$_3$)		11.45	L	L

Table VIII. Bond Lengths (Å) and Angles (deg), with Their Standard Deviations, within the Coordination Polyhedra

	Nickel	Cobalt
M-P(1)	2.117 (4)	2.106 (3)
M-P(2)	2.121 (3)	2.114 (3)
M-P(3)	2.118 (3)	2.117 (3)
M-N	2.178 (7)	2.067 (5)
M-H(1)		1.45 (5)
N-M-P(1)	90.1 (2)	89.0 (2)
N-M-P(2)	89.4 (2)	89.0 (2)
N-M-P(3)	90.6 (2)	89.6 (2)
P(1)-M-P(2)	120.1 (1)	120.1 (1)
P(1)-M-P(3)	124.5 (1)	124.2 (1)
P(2)-M-P(3)	115.4 (1)	115.7 (1)
N-M-H(1)		179 (2)
P(1)-M-H(1)		91 (2)
P(2)-M-H(1)		90 (2)
P(3)-M-H(1)		91 (2)

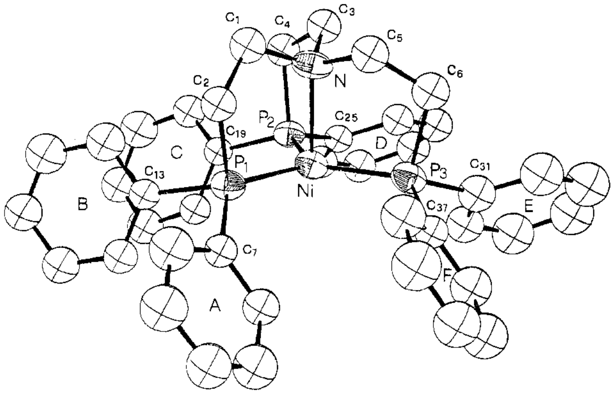


Figure 3. Perspective view of the [Ni(np$_3$)] complex. ORTEP diagram showing 30% probability ellipsoids.

Table IX. Bond Lengths (Å) and Angles (deg), with Their Standard Deviations, in the Remaining of the Molecule

	Nickel	Cobalt
P(1)-C(2)	1.874 (11)	1.866 (8)
P(1)-C(7)	1.812 (12)	1.840 (8)
P(1)-C(13)	1.867 (11)	1.861 (9)
P(2)-C(4)	1.875 (11)	1.849 (8)
P(2)-C(19)	1.814 (10)	1.826 (8)
P(2)-C(25)	1.835 (10)	1.844 (7)
P(3)-C(6)	1.866 (11)	1.861 (8)
P(3)-C(31)	1.822 (10)	1.830 (7)
P(3)-C(37)	1.824 (10)	1.844 (8)
N-C(1)	1.50 (1)	1.48 (1)
N-C(3)	1.46 (1)	1.50 (1)
N-C(5)	1.49 (1)	1.48 (1)
C(1)-C(2)	1.46 (2)	1.50 (1)
C(3)-C(4)	1.53 (1)	1.52 (1)
C(5)-C(6)	1.53 (1)	1.50 (1)
M-P(1)-C(2)	100.4 (4)	102.8 (3)
M-P(1)-C(7)	126.7 (4)	125.5 (2)
M-P(1)-C(13)	122.1 (4)	122.0 (3)
C(2)-P(1)-C(7)	100.0 (5)	101.2 (4)
C(2)-P(1)-C(13)	103.2 (5)	102.7 (3)
C(7)-P(1)-C(13)	100.0 (5)	98.9 (4)
M-P(2)-C(4)	100.7 (3)	102.4 (3)
M-P(2)-C(19)	126.5 (4)	124.4 (2)
M-P(2)-C(25)	124.5 (3)	124.1 (3)
C(4)-P(2)-C(19)	102.7 (5)	103.9 (3)
C(4)-P(2)-C(25)	101.8 (5)	102.4 (3)
C(19)-P(2)-C(25)	96.5 (5)	96.4 (4)
M-P(3)-C(6)	100.3 (3)	101.7 (2)
M-P(3)-C(31)	123.0 (3)	122.7 (3)
M-P(3)-C(37)	126.2 (3)	125.0 (2)
C(6)-P(3)-C(31)	102.4 (5)	102.7 (3)
C(6)-P(3)-C(37)	102.1 (5)	103.0 (4)
C(31)-P(3)-C(37)	98.7 (4)	98.3 (3)
M-N-C(1)	108.0 (6)	112.3 (5)
M-N-C(3)	110.1 (6)	111.6 (4)
M-N-C(5)	106.6 (5)	110.6 (4)
C(1)-N-C(3)	110.9 (7)	107.6 (5)
C(1)-N-C(5)	109.2 (7)	108.3 (6)
C(3)-N-C(5)	111.8 (8)	106.2 (6)
N-C(1)-C(2)	114.7 (8)	113.5 (5)
N-C(3)-C(4)	112.2 (8)	111.4 (7)
N-C(5)-C(6)	111.8 (8)	113.7 (7)
C(1)-C(2)-P(1)	111.9 (8)	108.5 (5)
C(3)-C(4)-P(2)	110.3 (7)	108.1 (5)
C(5)-C(6)-P(3)	110.8 (7)	109.2 (5)

of the two structures is made. Distances and angles within the phenyl rings are not reported, as such results are fully comparable with those found in structures where the np$_3$ ligand is engaged.[3,4] The nickel complex (Figure 3) is four-coordinate with a trigonal-pyramidal geometry while the coordination polyhedron of the cobalt complex (Figure 4) is a trigonal bipyramid.

In both cases the ligand is tetradentate with the nitrogen atom at the apical position of the pyramid. In the cobalt complex the hydride occupies the second apex of the bipyramid. The nickel atom lies in the plane of the three phosphorus atoms whereas the cobalt atom is 0.03 Å below this plane, away from the nitrogen atom. Thus the mean N–Ni–P angle is 90.0 (3)° and N–Co–P is 89.2 (2)°.

The metal–phosphorus distances are not significantly different in the two complexes. The mean Ni–P distance is 2.119 (2) Å and the mean Co–P distance is 2.112 (3) Å. These values can be compared with the M–P distances in [Ni(PF$_3$)$_4$] of 2.116 (10) Å[20] and in CoH[P(Ph)(OEt)$_2$]$_4$ of 2.115 (5) Å.[21] These relatively short distances could be indicative of a π component in the metal–phosphorus bond. The N–Co–H angle is quite near 180° and the Co–H distance of 1.45 (5) Å can be compared with the values of 1.38, 1.54[21] and 1.64, 1.67 Å[22] reported for other hydrido complexes of cobalt(I).

The fact that the Co–N distance, 2.067 (5) Å, is shorter than the corresponding Ni–N distance, 2.178 (7) Å, can be attributed to the higher oxidation state of the cobalt and is in line with the electroneutrality principle. The M–P distances appear to be less sensitive to the ion's oxidation state perhaps because of the fact that the crystal field stabilization energy is more sensitive to small changes in the axial bonds than the equatorial bonds and probably also on account of the partial π character of the M–P bonds.

The equatorial P–M–P angles are significantly different from 120°. In [Ni(np$_3$)] they are 124.5 (1), 120.1 (1), and 115.4 (1)° and in [CoH(np$_3$)] they are 124.2 (1), 120.1 (1), and 115.7 (1)°. Packing factors are probably operative; the short contact distances between the two phenyl rings A and F (C_{12}–C_{38} = 3.27 and 3.28 Å for nickel and cobalt, respectively) are related to the angles P(1)–M–P(3) being larger than 120°.

As regards bonding, there are five pairs of electrons in the valence shell of the nickel atom, directed toward the corners of a trigonal bipyramid. Four of these pairs are of the σ-bonding type (in molecular orbital language) and the fifth, which occupies the axial position, is nonbonding. This seems to be the first time that the nonbonding pair in a set of five pairs is to be found in the axial position. In the well-known

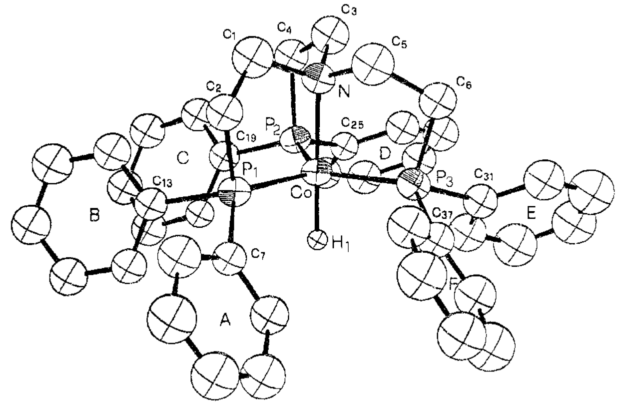


Figure 4. Perspective view of the [CoH(np$_3$)] complex. An artificial factor $B = 1.5$ Å^2 for the hydride atom was used.

tetrahalides of the group VI elements, *e.g.*, SF$_4$, the lone pair is in an equatorial position.[23]

The role of hydride ligands in determining the geometry of metal complexes has been extensively discussed.[24] In this case, however, the geometry of the complex is imposed by the steric requirements of the tripod ligand and is practically unaffected by the presence of the hydride ligand. The influence of the hydrogen atom is so slight that the dimensions of the "cage" formed by the phenylic hydrogens below the metal atom are practically the same in the two complexes. If anything, they are smaller in the hydride cobalt case than in the empty nickel case.

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Registry No. [CoCl(np$_3$)], 29946-09-6; [CoBr(np$_3$)], 54353-69-4; [CoI(np$_3$)], 54353-70-7; [Co(NCS)(np$_3$)], 54382-81-9; [Co(CN)(np$_3$)], 54353-71-8; [CoH(np$_3$)], 53687-39-1; [CoH(CO)(np$_3$)], 54423-75-5; [Co(CO)(np$_3$)]BF$_4$, 54353-73-0; [Co(CO)(np$_3$)]B(C$_6$H$_5$)$_4$, 54353-74-1; [NiCl(np$_3$)], 54423-06-2; [NiBr(np$_3$)], 54382-82-0; [NiI(np$_3$)], 54353-75-2; [Ni(NCS)(np$_3$)], 54382-83-1; [Ni(CN)(np$_3$)], 54353-76-3; [Ni(CO)(np$_3$)]BF$_4$, 54516-86-8; [Ni(CO)(np$_3$)]B(C$_6$H$_5$)$_4$, 54516-85-7; [Ni(np$_3$)], 52633-73-5; [Ni(CO)(np$_3$)], 54423-76-6.

Supplementary Material Available. Listings 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 $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC40709T.

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Amine–Sulfur Dioxide Complexes. Structure of *N*,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine–Bis(sulfur dioxide)

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The crystal structure of the 1:2 complex between *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine and SO$_2$ has been determined by X-ray diffraction. The crystal is monoclinic, space group $P2_1/c$, with four formula units of the complex in a cell of dimensions $a = 6.339$ (2) Å, $b = 19.163$ (4) Å, $c = 12.7148$ (7) Å, and $\beta = 120.11$ (3)°. The intensity data (2765) were collected on an automatic diffractometer. The structure was determined from a Patterson synthesis and refined by full-matrix least-squares methods. The final R was 0.037 for all data. The N–S charge-transfer distances are 2.337 (2) and 2.340 (2) Å. The average S–O bond distance is 1.434 (1) Å and the OSO bond angles are 113.5 (1) and 115.0 (1)°. The phenyl group is planar but the nitrogen geometry is partially tetrahedral, indicating n donation by those atoms. The angles (α) between the N–S charge-transfer bonds and the perpendicular to the SO$_2$ planes are 15.2 (1)° for both SO$_2$ groups.

Introduction

Although reports of structural, spectral and thermodynamic investigations of the molecular complexes formed between amines and halogens are numerous,[1] little attention has been given to the corresponding complexes involving sulfur dioxide. In spite of this lack of information some structural generalizations based on crystallographic data for the SO$_2$ adducts of trimethylamine[2] and certain organometallic complexes[3–6] in which the SO$_2$ ligand functions as an electron acceptor are possible. (1) The complexes appear to be stabilized by the

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