

isolation of only 2:1 adducts of similar cobalt complexes.³⁰ It appears that the conditions under which we prepared these adducts (aprotic, polar solvents at low temperatures in the presence of imidazoles) may account for the difference in results. Physical studies presently in progress may elucidate more fully the thermodynamics and kinetics of the reaction of these ligands with oxygen and the electronic properties of the dioxygen adducts.

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Registry No. Co(saltmen)(BzIImid)(O₂)·THF, 60338-52-5; Co(saltmen), 60306-16-3; 2,3-diamino-2,3-dimethylbutane, 20485-44-3; salicylaldehyde, 90-02-8; H₂saltmen, 60306-02-7.

Supplementary Material Available: A continuation of Table IV, showing H-atom angles, and Table VI, a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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Structural Investigation of Two Carbonyl Complexes of Cobalt(I) and Nickel(0) with the Ligand Tris(2-diphenylphosphinoethyl)amine

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The molecular structures of two carbonyl complexes of the ligand tris(2-diphenylphosphinoethyl)amine, np₃, [Co(CO)(np₃)]BPh₄·(CH₃)₂CO and [Ni(CO)(np₃)] have been determined from three-dimensional x-ray data. The cobalt complex crystallizes in the monoclinic space group *P*2₁/*c* with $a = 12.43$ (1), $b = 20.29$ (2), $c = 23.85$ (2) Å, $\beta = 103.0$ (1)°, and $Z = 4$. The nickel complex crystallizes in the monoclinic space group *P*2₁ with $a = 20.44$ (1), $b = 8.87$ (1), $c = 10.34$ (1) Å, $\beta = 90.4$ (1)°, and $Z = 2$. Counter methods were used and full-matrix least-squares refinements gave final conventional *R* factors of 0.073 and 0.049 for the cobalt and nickel complex, respectively. The cobalt complex has a trigonal bipyramidal geometry whereas the nickel complex has a tetrahedral geometry, the central nitrogen of the ligand being not coordinated. Structural, magnetic, and spectral data of the two complexes are compared with those of the isoelectronic and isostructural metal nitrosyl complexes and discussed on the basis of a qualitative molecular orbital approach.

Introduction

In the course of previous studies performed in this laboratory a variety of 3d metal nitrosyl and carbonyl complexes with the ligand tris(2-diphenylphosphinoethyl)amine, np₃, have been

prepared and characterized.^{1,2} In particular the x-ray structures of the [M(NO)(np₃)]BPh₄ (M = Fe, Co, Ni) complexes have been determined and their spectral and magnetic properties interpreted on the basis of a simplified

molecular orbital approach.¹ A result of special interest is that the np_3 acts as a tri- or tetradentate ligand in different complexes, according to the number of metal d electrons, and there are never more than 18 electrons in the valence shell. In fact the np_3 ligand uses its four donor atoms in the iron nitrosyl complex while it coordinates only through the three phosphorus atoms in the cobalt and nickel analogues.

Of the carbonyl complexes reported previously² we have now determined the x-ray structures of $[\text{Co}(\text{CO})(np_3)]\text{BPh}_4 \cdot (\text{CH}_3)_2\text{CO}$ and $[\text{Ni}(\text{CO})(np_3)]$ which are isoelectronic with the above mentioned iron and nickel nitrosyl compounds. It seemed of interest to compare structural, spectral, and magnetic properties of the carbonyl complexes with those of the nitrosyl analogues in order to investigate the effects of the substitution of the nitrosyl with the carbonyl group.

Experimental Section

Collection and Reduction of X-Ray Intensity Data. Both compounds crystallize as rectangular prisms. The specimens were mounted so that the longest dimension was approximately parallel to the ϕ axis of a Philips computer controlled PW 1100 diffractometer. The crystal of the cobalt complex had dimensions $0.02 \times 0.03 \times 0.10$ mm, that of the nickel complex had dimensions $0.06 \times 0.10 \times 0.22$ mm. Cell constants and the Bravais lattice were determined as described previously.² The cobalt complex crystallizes in the monoclinic space group $P2_1/c$ (extinctions $h0l, l$ odd; $0k0, k$ odd) with $a = 12.43$ (1), $b = 20.29$ (2), $c = 23.85$ (2) Å, $\beta = 103.0$ (1)°. The nickel complex is monoclinic space group $P2_1/m$ or $P2_1$ (extinctions $0k0, k$ odd). The structure was successfully solved in the acentric $P2_1$. Unit cell dimensions are: $a = 20.44$ (1), $b = 8.87$ (1), $c = 10.34$ (1) Å, $\beta = 90.4$ (1)°. The calculated density of the cobalt complex, assuming four molecules in the cell, is 1.267 g cm^{-3} and the observed density (by flotation in aqueous K_2HgI_4 solution) is 1.25 g cm^{-3} . The observed density value of 1.30 g cm^{-3} measured for the nickel analogue agrees with the value of 1.312 g cm^{-3} calculated for two molecules per cell. Data collection was carried out using Mo $K\alpha$ radiation (λ 0.7107 Å) monochromatized with a flat graphite crystal at a take-off angle of 4.5°. Reflections within $2\theta \leq 40^\circ$ were collected using the ω - 2θ scan technique. The scan range for the cobalt compound was calculated using the formula of Alexander and Smith,³ scan range = $A + B \tan \theta$, with $A = 0.66$ and $B = 0.682$; while for the nickel compound a fixed scan range of 1.4° in 2θ was used. The scan speed was 0.12 and $0.14^\circ/\text{s}$, respectively. Stationary background measurements were taken before and after each scan for a time equal to half the scan time. Three standard reflections were measured every 2 h and did not show any systematic drift during data collections.

After correction for background the intensities were assigned standard deviations calculated as described elsewhere⁴ using the values of 0.04 and 0.05 for the instability factor K in the cobalt and nickel complex. The number of observed reflections having $I \geq 3 \sigma(I)$ were 1076 and 1480 for the cobalt and nickel complexes. Intensities were corrected for Lorentz-polarization effects. The linear absorption coefficients, μ , are 4.37 and 6.79 cm^{-1} for the two compounds and no absorption correction was applied.

Solution and Refinement of the Structures. All calculations were carried out using the XRY72 crystallographic system⁵ and the ORTEP program,⁶ adapted to the University of Florence CII 10070 computer. The atomic scattering factors calculated by Cromer and Waber⁷ were used for all nonhydrogen atoms; those calculated by Stewart, Davidson, and Simpson⁸ were used for hydrogen.

$[\text{Co}(\text{CO})(np_3)]\text{BPh}_4 \cdot (\text{CH}_3)_2\text{CO}$. The three-dimensional Patterson synthesis showed the position of the cobalt and of the three phosphorus atoms. Successive Fourier syntheses revealed all the nonhydrogen atoms. The refinement of the structure was then undertaken, the function minimized being $\sum w(|F_o| - |F_c|)^2$. The weights w were taken as $w = 1/\sigma^2(F_o)$. The agreement factors R and R_w are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$. Owing to the small number of observed reflections, in order to reduce the number of parameters to be refined, all the phenyl groups and the acetone molecule were treated as rigid bodies (C-C distances of 1.392 Å and C-C-C angles of 120° for the phenyl groups; C-C distances of 1.54 Å, C-O distance of 1.23 Å and angles of 120° around the central carbon atom for the acetone molecule). Individual isotropic thermal parameters were assigned to all atoms. In the last stage of the refinement the hydrogen atoms of the phenyl (C-H = 0.95 Å)

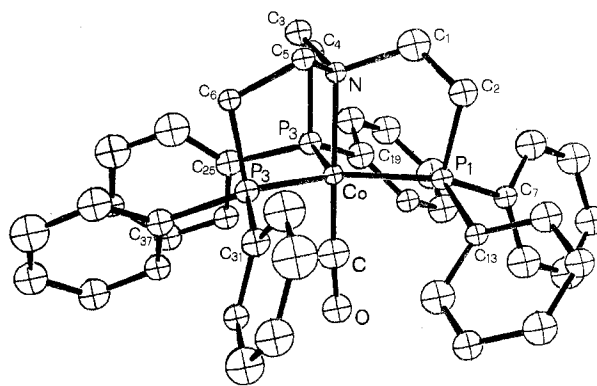


Figure 1. Perspective view of the $[\text{Co}(\text{CO})(np_3)]^+$ cation.

and methylene (C-H = 1.0 Å) groups were introduced in calculated positions with temperature factors 15% larger than those of the carbon atoms to which they are attached and were not refined. The refinement converged at $R = 0.073$ and $R_w = 0.078$. Final positional and thermal parameters are given in Table I.

$[\text{Ni}(\text{CO})(np_3)]$. The three-dimensional Patterson synthesis, successfully interpreted in the acentric space group $P2_1$, showed the positions of the nickel and of one phosphorus atom. The y coordinate of the nickel atom was fixed at $1/4$ and one of the two possible phosphorus positions related by a mirror plane at $y = 1/4$ was arbitrarily chosen. Successive Fourier syntheses revealed the position of all nonhydrogen atoms. The parameters were then refined by full-matrix least squares. Weights w were taken as $w = 1/\sigma^2(F_o)$. Several cycles of refinements using isotropic thermal parameters, followed by others during which anisotropic thermal parameters for atoms in the coordination polyhedron were assigned, reduced the conventional R factor to 0.061. Because of the polarity of the space group $P2_1$, two possible enantiomeric structures must be considered: the structure so far considered and its mirror image as reflected across a plane at $y = 1/4$. Refinement of the model initially assumed yielded $R = 0.0608$ and $R_w = 0.0736$ and refinement of the enantiomorph yielded $R = 0.0618$ and $R_w = 0.0747$ indicating that the first choice is the correct one. However, bond lengths and angles in the two structures do not differ by more than a few standard deviations, probably because the polar dispersion errors are of the order of magnitude of the atomic parameters. The hydrogen atoms were then introduced in calculated positions (C-H = 1.0 Å) with the same procedure adopted for the cobalt complex. The refinement converged at $R = 0.049$ and $R_w = 0.057$. The anomalous dispersion corrections⁹ were made using $\Delta f' = 0.4$ and $\Delta f'' = 1.2$ for nickel and $\Delta f' = 0.1$ and $\Delta f'' = 0.1$ for phosphorus. Final positional and isotropic thermal parameters are given in Table II; anisotropic thermal parameters are listed in Table III.

Description of the Structures

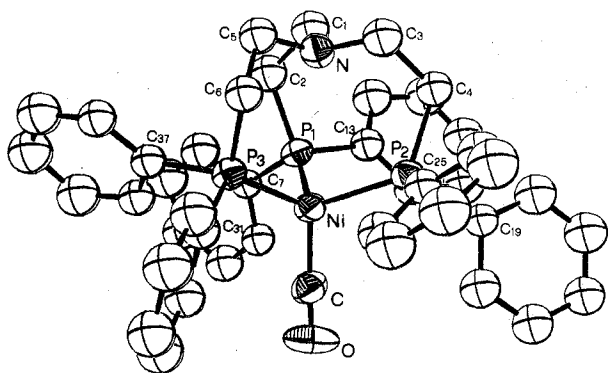
$[\text{Co}(\text{CO})(np_3)]\text{BPh}_4 \cdot (\text{CH}_3)_2\text{CO}$. The structure of this compound consists of discrete $[\text{Co}(\text{CO})(np_3)]^+$ cations, BPh_4^- anions, and acetone molecules. Figure 1 shows a perspective view of the cation. Values of selected bond distances and angles are reported in Tables IV and V. The geometry of the coordination polyhedron is nearly a regular trigonal bipyramid. Deviations from the idealized geometry are small: the axial angle N-Co-O is 178.6 (1.5)° and the N-Co-P angles are smaller than 90° so that the metal atom lies 0.10 Å out of the equatorial plane toward the carbonyl group.

The CoCO group is essentially linear with an angle of 174.4 (2.7)°. The Co-C bond distance of 1.63 (4) Å appears to be short compared with the values reported for five-coordinated cobalt carbonyl compounds.¹⁰⁻¹² The mean Co-P bond distance of 2.18 (1) Å¹³ is longer but comparable (see below) with the value of 2.112 (3) Å found in the five-coordinated hydrido cobalt(I) complex $[\text{CoH}(np_3)]$.² The Co-N distance of 2.06 (2) Å is the same as that of 2.067 (5) Å in the hydrido complex within experimental error.

Bond distances and angles in the rest of the molecule are normal; there are no unusual contact distances between the

Table I. $[\text{Co}(\text{CO})(\text{np}_3)]\text{BPh}_4 \cdot (\text{CH}_3)_2\text{CO}$ Positional and Isotropic Thermal Parameters with Estimated Standard Deviations in Parentheses

Atom	x/a	y/b	z/c	$U (\times 10^3), \text{Å}^2$	Atom	x/a	y/b	z/c	$U (\times 10^3), \text{Å}^2$
Co	0.0339 (3)	0.1873 (2)	0.0336 (2)	2.6 (1)	C(33)	-0.407 (2)	0.126 (2)	-0.017 (1)	10 (1)
P(1)	0.0047 (6)	0.1604 (4)	0.1171 (3)	3.0 (3)	C(34)	-0.416 (2)	0.064 (1)	-0.043 (1)	7 (1)
P(2)	0.1934 (7)	0.2241 (4)	0.0240 (3)	3.8 (3)	C(35)	-0.332 (2)	0.042 (1)	-0.069 (1)	8 (1)
P(3)	-0.1078 (6)	0.1909 (5)	-0.0399 (3)	3.6 (3)	C(36)	-0.240 (2)	0.081 (1)	-0.068 (1)	4 (1)
O	0.095 (2)	0.057 (1)	0.015 (1)	6 (1)	C(37)	-0.093 (2)	0.180 (1)	-0.114 (1)	5 (1)
N	-0.006 (2)	0.282 (1)	0.052 (1)	2.7 (8)	C(38)	-0.012 (2)	0.137 (1)	-0.125 (1)	4 (1)
C	0.064 (3)	0.112 (2)	0.021 (2)	6 (1)	C(39)	-0.004 (2)	0.125 (1)	-0.181 (1)	6 (1)
C(1)	0.021 (3)	0.291 (2)	0.119 (1)	7 (1)	C(40)	-0.078 (2)	0.156 (2)	-0.227 (1)	7 (1)
C(2)	-0.034 (2)	0.235 (2)	0.145 (1)	5 (1)	C(41)	-0.159 (2)	0.198 (1)	-0.216 (1)	9 (1)
C(3)	0.063 (3)	0.331 (1)	0.031 (1)	5 (1)	C(42)	-0.166 (2)	0.210 (1)	-0.159 (1)	7 (1)
C(4)	0.180 (3)	0.313 (2)	0.040 (1)	5 (1)	B	0.701 (2)	0.023 (2)	0.363 (1)	3 (1)
C(5)	-0.123 (2)	0.298 (1)	0.026 (1)	3 (1)	C(43)	0.727 (2)	-0.003 (1)	0.431 (1)	4 (1)
C(6)	-0.151 (2)	0.276 (1)	-0.038 (1)	3 (1)	C(44)	0.641 (3)	-0.033 (1)	0.450 (1)	6 (1)
C(7)	0.122 (1)	0.128 (1)	0.171 (1)	4 (1)	C(45)	0.655 (4)	-0.054 (2)	0.507 (1)	4 (1)
C(8)	0.194 (2)	0.173 (1)	0.205 (1)	6 (1)	C(46)	0.757 (5)	-0.046 (2)	0.545 (1)	4 (1)
C(9)	0.287 (2)	0.150 (1)	0.244 (1)	7 (1)	C(47)	0.844 (4)	-0.016 (1)	0.526 (2)	5 (1)
C(10)	0.308 (1)	0.082 (1)	0.250 (1)	7 (1)	C(48)	0.829 (3)	0.005 (1)	0.470 (1)	3 (1)
C(11)	0.236 (2)	0.038 (1)	0.215 (1)	7 (1)	C(49)	0.637 (2)	0.097 (1)	0.359 (1)	3 (1)
C(12)	0.144 (2)	0.061 (1)	0.176 (1)	7 (1)	C(50)	0.584 (2)	0.114 (1)	0.403 (1)	5 (1)
C(13)	-0.100 (1)	0.103 (1)	0.128 (1)	3 (1)	C(51)	0.528 (2)	0.174 (1)	0.400 (1)	6 (1)
C(14)	-0.133 (3)	0.107 (1)	0.180 (2)	6 (1)	C(52)	0.525 (2)	0.216 (1)	0.354 (1)	4 (1)
C(15)	-0.213 (3)	0.063 (2)	0.191 (3)	5 (1)	C(53)	0.578 (2)	0.199 (1)	0.310 (1)	3 (1)
C(16)	-0.259 (3)	0.016 (2)	0.150 (4)	6 (1)	C(54)	0.634 (2)	0.139 (1)	0.313 (1)	5 (1)
C(17)	-0.226 (4)	0.013 (1)	0.098 (2)	5 (1)	C(55)	0.631 (2)	-0.032 (1)	0.319 (1)	2 (1)
C(18)	-0.147 (3)	0.057 (1)	0.087 (1)	7 (1)	C(56)	0.567 (2)	-0.010 (1)	0.267 (2)	4 (1)
C(19)	0.324 (2)	0.201 (1)	0.068 (1)	6 (1)	C(57)	0.511 (3)	-0.054 (2)	0.227 (2)	5 (1)
C(20)	0.334 (2)	0.144 (1)	0.101 (1)	4 (1)	C(58)	0.518 (4)	-0.122 (3)	0.238 (1)	8 (1)
C(21)	0.437 (2)	0.126 (1)	0.135 (1)	7 (1)	C(59)	0.582 (3)	-0.144 (3)	0.290 (1)	10 (1)
C(22)	0.529 (2)	0.165 (1)	0.136 (1)	8 (1)	C(60)	0.638 (2)	-0.100 (2)	0.331 (1)	9 (1)
C(23)	0.518 (2)	0.223 (1)	0.103 (1)	7 (1)	C(61)	0.824 (1)	0.033 (1)	0.348 (1)	3 (1)
C(24)	0.416 (3)	0.241 (1)	0.069 (1)	6 (1)	C(62)	0.876 (1)	0.094 (2)	0.351 (1)	4 (1)
C(25)	0.222 (2)	0.224 (1)	-0.049 (1)	5 (1)	C(63)	0.977 (2)	0.100 (2)	0.336 (1)	6 (1)
C(26)	0.281 (2)	0.170 (2)	-0.062 (1)	5 (1)	C(64)	1.027 (3)	0.045 (2)	0.318 (1)	5 (1)
C(27)	0.299 (3)	0.162 (3)	-0.117 (1)	6 (1)	C(65)	0.976 (3)	-0.016 (2)	0.315 (1)	7 (1)
C(28)	0.257 (4)	0.209 (3)	-0.160 (2)	4 (1)	C(66)	0.874 (2)	-0.022 (2)	0.330 (1)	8 (1)
C(29)	0.197 (3)	0.263 (2)	-0.147 (2)	8 (1)	O(Ac)	0.753 (2)	0.333 (1)	0.136 (1)	9 (1)
C(30)	0.180 (2)	0.270 (1)	-0.091 (1)	9 (1)	C(1)(Ac)	0.691 (4)	0.379 (2)	0.119 (1)	7 (1)
C(31)	-0.232 (2)	0.143 (1)	-0.042 (1)	5 (1)	C(2)(Ac)	0.674 (6)	0.434 (4)	0.160 (3)	10 (1)
C(32)	-0.315 (3)	0.165 (1)	-0.016 (1)	9 (1)	C(3)(Ac)	0.629 (5)	0.381 (5)	0.055 (3)	4 (1)

Figure 2. Perspective view of the $[\text{Ni}(\text{CO})(\text{np}_3)]$ complex.

ions and the acetone molecule.

$[\text{Ni}(\text{CO})(\text{np}_3)]$. The structure of this compound consists of discrete monomeric units. Figure 2 shows a perspective view of the molecule. Selected bond distances and angles are reported in Tables IV and V. The nickel atom is considered to be four coordinated by the three phosphorus atoms of the tripod ligand and by the carbonyl group, as the central nitrogen atom of the ligand is 3.25 (1) Å away from the metal atom. The geometry of coordination is distorted tetrahedral: the angles at the metal atom range from 105.8 (1) to 115.1(5)°, the P-Ni-CO angles (112.7 (2.3)° average) being larger than the P-Ni-P ones (106.1 (3)° average).

The NiCO group is essentially linear, the Ni-C-O angle being 172.5 (1.4)°. The Ni-CO bond distance of 1.74 (2) is shorter than those reported for $\text{Ni}(\text{CO})_4$ (1.84 Å)¹⁴ and for

$[(\text{CO})_3\text{Ni}(\text{PPh}_2)_2\text{Ni}(\text{CO})_3]$ (1.803 (8) Å).¹⁵ The Ni-P bond distances (2.215 (9) Å average) are comparable with the values reported for other tetrahedral d¹⁰ nickel complexes.¹⁵⁻¹⁷ The Ni-N distance of 3.25 (1) Å is equal within experimental error to the value of 3.23 (1) Å reported for the $[\text{Ni}(\text{NO})(\text{np}_3)]^+$ complex which has the same tetrahedral geometry, with the nitrogen atom of the ligand not coordinated to the metal.¹ It is interesting to note that the C-N-C angles (114.7 (5)° average) are significantly larger than those found for the cobalt analogue (108.2 (3.6)° average) but match the values for the above $[\text{Ni}(\text{NO})(\text{np}_3)]^+$ complex (114.0(7)° average).

Bond distances and angles in the rest of the molecule are normal. None of the intermolecular contact distances is unusual.

Discussion

The present structures provide further evidence for the flexibility of the np₃ ligand; in spite of its geometry and of the presence of four potentially coordinating atoms, the ligand does not impose strict requirements on coordination. It has been found previously^{1,18-21} that this ligand is capable of forming complexes with different coordination numbers and different coordination geometries. In the present complexes np₃ acts either as a tridentate or as a tetradentate ligand, just as it does in the isoelectronic nitrosyl complexes.¹

The electronic configuration of the metal atoms seems to determine the coordination geometry in the two complexes. In order to reach the 18-outer-electron configuration, the d⁸ cobalt and d¹⁰ nickel require five- and four-electron pairs, respectively, from donor atoms. As a consequence all the four-donor atoms of np₃ ligand are coordinated to the metal

Table II. [Ni(CO)(np₃)] Positional and Isotropic Thermal Parameters with Estimated Standard Deviations in Parentheses

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (×10 ²), Å ²
Ni	0.2395 (1)	0.2500	0.5372 (1)	
P(1)	0.2154 (2)	0.0482 (4)	0.6519 (4)	
P(2)	0.3464 (1)	0.2419 (5)	0.5040 (3)	
P(3)	0.1925 (2)	0.2155 (4)	0.3449 (3)	
O	0.2005 (6)	0.5138 (13)	0.6855 (12)	
N	0.2868 (4)	-0.0608 (11)	0.4000 (10)	
C	0.2157 (7)	0.4128 (18)	0.6181 (15)	
C(1)	0.2698 (7)	-0.1744 (16)	0.4925 (13)	6.5 (4)
C(2)	0.2079 (7)	-0.1309 (17)	0.5665 (14)	6.6 (4)
C(3)	0.3566 (7)	-0.0412 (16)	0.3822 (13)	6.4 (4)
C(4)	0.3867 (6)	0.0540 (16)	0.4903 (12)	5.2 (4)
C(5)	0.2478 (6)	-0.0644 (16)	0.2805 (13)	5.7 (4)
C(6)	0.2361 (6)	0.0947 (16)	0.2307 (13)	5.4 (4)
C(7)	0.1402 (6)	0.0518 (15)	0.7481 (12)	4.4 (4)
C(8)	0.1314 (7)	0.1677 (16)	0.8332 (13)	5.4 (4)
C(9)	0.0765 (7)	0.1790 (18)	0.9097 (14)	7.3 (5)
C(10)	0.0305 (7)	0.0668 (20)	0.9015 (15)	7.7 (5)
C(11)	0.0357 (8)	-0.0496 (21)	0.8198 (17)	8.7 (5)
C(12)	0.0926 (7)	-0.0631 (18)	0.7422 (15)	7.3 (5)
C(13)	0.2736 (6)	0.0054 (16)	0.7850 (13)	5.3 (4)
C(14)	0.3079 (7)	0.1211 (16)	0.8373 (13)	5.6 (4)
C(15)	0.3539 (8)	0.0931 (19)	0.9452 (16)	8.7 (5)
C(16)	0.3588 (8)	-0.0507 (21)	0.9837 (16)	8.3 (5)
C(17)	0.3274 (8)	-0.1647 (18)	0.9348 (16)	8.5 (5)
C(18)	0.2801 (8)	-0.1436 (18)	0.8335 (15)	7.4 (5)
C(19)	0.3985 (6)	0.3353 (15)	0.6238 (13)	4.7 (4)
C(20)	0.4506 (7)	0.2721 (20)	0.6906 (13)	7.4 (4)
C(21)	0.4863 (8)	0.3547 (19)	0.7807 (16)	7.7 (5)
C(22)	0.4722 (7)	0.4997 (18)	0.8042 (14)	6.7 (5)
C(23)	0.4215 (8)	0.5657 (20)	0.7395 (15)	7.1 (5)
C(24)	0.3839 (7)	0.4865 (17)	0.6513 (14)	6.6 (5)
C(25)	0.3764 (6)	0.3424 (15)	0.3586 (12)	4.8 (4)
C(26)	0.3370 (7)	0.4511 (19)	0.3056 (15)	6.7 (5)
C(27)	0.3591 (8)	0.5301 (20)	0.1975 (16)	8.1 (5)
C(28)	0.4172 (8)	0.5042 (20)	0.1452 (16)	8.6 (5)
C(29)	0.4592 (8)	0.4003 (21)	0.2027 (17)	8.9 (5)
C(30)	0.4392 (7)	0.3205 (18)	0.3112 (15)	7.4 (5)
C(31)	0.1770 (6)	0.3834 (16)	0.2447 (13)	5.1 (4)
C(32)	0.1436 (7)	0.5034 (17)	0.3002 (14)	6.0 (4)
C(33)	0.1277 (8)	0.6360 (19)	0.2329 (16)	7.6 (5)
C(34)	0.1462 (8)	0.6449 (19)	0.1078 (16)	7.4 (5)
C(35)	0.1793 (8)	0.5358 (22)	0.0482 (16)	8.2 (5)
C(36)	0.1949 (7)	0.4004 (19)	0.1179 (15)	7.1 (5)
C(37)	0.1099 (6)	0.1378 (15)	0.3482 (13)	4.9 (4)
C(38)	0.0818 (7)	0.0580 (18)	0.2479 (13)	5.7 (4)
C(39)	0.0176 (7)	0.0025 (19)	0.2587 (15)	7.7 (5)
C(40)	-0.0191 (8)	0.0349 (21)	0.3618 (16)	8.2 (5)
C(41)	0.0063 (8)	0.1187 (19)	0.4649 (15)	8.1 (5)
C(42)	0.0722 (7)	0.1677 (17)	0.4549 (13)	5.6 (4)

Table III. [Ni(CO)(np₃)] Anisotropic Thermal^a Parameters (×10²) with Their Standard Deviations

Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Ni	4.6 (1)	3.8 (1)	4.1 (1)	0.0 (1)	-0.4 (1)	0.2 (1)
P(1)	5.3 (3)	3.6 (2)	3.9 (2)	-0.2 (2)	-0.2 (2)	-0.1 (2)
P(2)	4.9 (2)	4.1 (2)	4.6 (2)	0.1 (2)	-0.1 (2)	0.2 (2)
P(3)	5.1 (2)	4.3 (3)	4.0 (2)	-0.1 (2)	-0.2 (2)	0.0 (2)
O	12.5 (1.0)	5.5 (7)	9.5 (9)	1.8 (7)	2.3 (8)	-1.3 (7)
N	4.7 (6)	4.6 (7)	6.5 (7)	0.1 (6)	0.0 (6)	1.4 (6)
C	5.4 (9)	5.3 (1.1)	5.3 (1.0)	-1.1 (8)	-0.1 (8)	-0.5 (9)

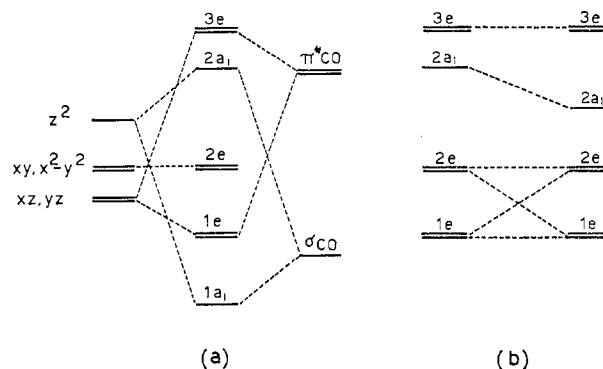
^a The form of the anisotropic thermal factor is $\exp[-2\pi^2(U_{11}h^2 + a^*a^* + U_{22}k^2b^*b^* + U_{33}l^2c^*c^* + 2U_{12}hka^*b^* \cos \gamma^* + 2U_{13}hla^*c^* \cos \beta^* + 2U_{23}klb^*c^* \cos \alpha^*)]$.

in the cobalt complex while only the three phosphorus atoms are bound to the metal in the nickel compound.

The large separation of the nitrogen and the nickel atom can be attributed to the repulsion between the electron lone pair of the nitrogen atom and the 18 electron complete shell of the metal. As a consequence the C-N-C angles are larger than usual and the phosphorus atoms seem to be drawn up

Table IV. Bond Lengths (Å) and Angles (deg) within the Coordination Polyhedra

	Co	Ni
M-P(1)	2.17 (1)	2.205 (4)
M-P(2)	2.18 (1)	2.217 (3)
M-P(3)	2.19 (1)	2.223 (3)
M-C	1.63 (4)	1.74 (2)
M-N	2.06 (2)	3.25 (1)
P(1)-M-P(2)	121.7 (3)	106.3 (1)
P(1)-M-P(3)	118.2 (4)	105.8 (1)
P(2)-M-P(3)	119.5 (4)	106.1 (1)
P(1)-M-C	91.8 (1.3)	110.6 (5)
P(2)-M-C	92.7 (1.3)	112.3 (5)
P(3)-M-C	93.3 (1.1)	115.1 (5)
P(1)-M-N	86.9 (7)	67.3 (2)
P(2)-M-N	88.4 (7)	66.9 (2)
P(3)-M-N	86.9 (6)	67.7 (2)
C-M-N	178.6 (1.5)	177.1 (5)
C-O	1.20 (5)	1.18 (2)
M-C-O	174.4 (2.7)	172.5 (1.4)

**Figure 3.** Schematic molecular orbital diagrams: (a) interaction between metal d orbitals and carbon monoxide orbitals in C_{3v} symmetry; (b) effect of tetrahedral distortion on the orbital energies.¹

by the nitrogen atom, causing the P-Ni-CO angles to be larger than the P-Ni-P angles.

These two carbonyl complexes, [Co(CO)(np₃)]⁺ and [Ni(CO)(np₃)], can be directly compared with the isolectronic and isostructural nitrosyl complexes [Fe(NO)(np₃)]⁺ and [Ni(NO)(np₃)]⁺ which were studied previously.¹ Magnetic and spectral data of the carbonyl complexes can be interpreted using the simple molecular orbital approach proposed for the nitrosyl complexes.¹ Figure 3 shows schematically the molecular orbital energy diagram resulting from the interaction of the metal d orbitals, split in the ligand field of C_{3v} symmetry, with the σ(CO) and the degenerate π*(CO) orbitals on the carbonyl ligand. The 1a₁ orbital, included in (a), has been omitted in (b), not being important to the following considerations. When all the metal d electrons are assigned to the level in (b) the [Co(CO)(np₃)]⁺ and [Ni(CO)(np₃)] complexes have the (1e)⁴(2e)⁴ and (1e)⁴(2e)⁴(2a₁)² configurations, respectively. These configurations agree with the observed diamagnetism of the compounds.

The [Co(CO)(np₃)]⁺ complex shows a band in the electronic spectrum at ca. 2.15 μm⁻¹ which corresponds to the band at ca. 2.00 μm⁻¹ found in the [Fe(NO)(np₃)]⁺ compound.^{1,2} As for the nitrosyl complex this band may be assigned to the ¹E[2e³2a₁] ← ¹A₁[2e⁴] transition. The energy separation between the 2e and 2a₁ levels does not change much on going from the nitrosyl to the carbonyl complex.

The band observed for the [Ni(NO)(np₃)]⁺ complex at ca. 2.00 μm⁻¹ appears in the carbonyl complex at ca. 2.85 μm⁻¹ as a shoulder of a charge transfer band.^{1,2} The former absorption may be assigned to the ¹E[2a₁3e] ← ¹A₁[2a₁2]

Table V. Selected Bond Lengths (Å) and Angles (deg)

	Co	Ni
P(1)-C(2)	1.76 (3)	1.82 (1)
P(1)-C(7)	1.83 (2)	1.84 (1)
P(1)-C(13)	1.81 (2)	1.85 (1)
P(2)-C(4)	1.86 (3)	1.86 (1)
P(2)-C(19)	1.78 (2)	1.83 (1)
P(2)-C(25)	1.86 (2)	1.86 (1)
P(3)-C(6)	1.81 (3)	1.83 (1)
P(3)-C(31)	1.81 (3)	1.84 (1)
P(3)-C(37)	1.82 (2)	1.82 (1)
N-C(1)	1.57 (4)	1.44 (2)
N-C(3)	1.48 (4)	1.45 (2)
N-C(5)	1.48 (3)	1.47 (2)
C(1)-C(2)	1.54 (5)	1.53 (2)
C(3)-C(4)	1.47 (4)	1.53 (2)
C(5)-C(6)	1.55 (4)	1.52 (2)
B-C(43)	1.68 (3)	
B-C(49)	1.68 (3)	
B-C(55)	1.65 (3)	
B-C(61)	1.66 (3)	
M-P(1)-C(2)	104.4 (1.1)	117.7 (5)
M-P(1)-C(7)	117.3 (8)	117.9 (5)
M-P(1)-C(13)	124.9 (1.0)	114.9 (5)
C(2)-P(1)-C(7)	106.4 (1.3)	102.1 (6)
C(2)-P(1)-C(13)	102.9 (1.3)	103.4 (6)
C(7)-P(1)-C(13)	98.9 (1.1)	97.9 (6)
M-P(2)-C(4)	100.9 (1.1)	118.5 (4)
M-P(2)-C(19)	125.2 (9)	116.8 (4)
M-P(2)-C(25)	117.9 (8)	116.1 (4)
C(4)-P(2)-C(19)	104.2 (1.2)	101.6 (6)
C(4)-P(2)-C(25)	103.6 (1.4)	102.7 (6)
C(19)-P(2)-C(25)	102.2 (1.1)	97.9 (6)
M-P(3)-C(6)	101.8 (9)	116.7 (4)
M-P(3)-C(31)	121.9 (8)	117.6 (5)
M-P(3)-C(37)	122.0 (9)	115.4 (4)
C(6)-P(3)-C(31)	104.9 (1.3)	101.1 (6)
C(6)-P(3)-C(37)	103.5 (1.3)	104.2 (6)
C(31)-P(3)-C(37)	100.3 (1.1)	99.2 (6)
M-N-C(1)	108.3 (1.6)	103.3 (7)
M-N-C(3)	111.7 (1.9)	104.5 (7)
M-N-C(5)	112.1 (1.6)	103.0 (7)
C(1)-N-C(3)	104.6 (2.1)	114.4 (1.0)
C(1)-N-C(5)	111.9 (2.3)	114.4 (1.0)
C(3)-N-C(5)	108.0 (2.1)	115.2 (1.0)
N-C(1)-C(2)	108.5 (2.4)	111.2 (1.1)
N-C(3)-C(4)	114.9 (2.5)	111.4 (1.1)
N-C(5)-C(6)	109.3 (2.3)	110.4 (1.1)
C(1)-C(2)-P(1)	107.1 (2.4)	113.2 (1.0)
C(3)-C(4)-P(2)	110.0 (2.2)	112.0 (9)
C(5)-C(6)-P(3)	107.0 (1.8)	113.6 (9)
C(43)-B-C(49)	109.1 (1.8)	
C(43)-B-C(55)	110.8 (1.7)	
C(43)-B-C(61)	105.3 (1.6)	
C(49)-B-C(55)	113.0 (1.6)	
C(49)-B-C(61)	109.3 (1.8)	
C(55)-B-C(61)	109.0 (1.8)	

transition. The ipsochromic shift observed in the spectrum of the carbonyl complex implies a larger energy separation between the $2a_1$ and $3e$ levels which is attributable to the higher energy of the $\pi^*(\text{CO})$ with respect to the $\pi^*(\text{NO})$.²² As a consequence the interaction between the d_{xz} and d_{yz} metal orbitals and the $\pi^*(\text{CO})$ orbitals is weaker than the interaction

with the $\pi^*(\text{NO})$ orbitals in the nitrosyl complexes. Indirect evidence for this seems to be given by the M-P bond distances which are shorter in the carbonyl (Co-P = 2.18 (1) average and Ni-P = 2.215 (9) Å average) than in the nitrosyl complexes (Fe-P = 2.24 (2) average and Ni-P = 2.29 (1) Å average). As it has been pointed out^{23,24} the extent of metal to phosphorus back bonding is influenced by the presence of the competing π acceptor nitrosyl or carbonyl group. Since the π bonding ability of the nitrosyl is larger than that of the carbonyl group, the metal to phosphorus back-donation is smaller in the nitrosyl than in the carbonyl complexes. This is in line with the value of the Co-P bond distance found in the above-mentioned² hydrido complex [CoH(np₃)] where the Co-H bond has only σ character.

The CO stretching frequencies observed in the infrared spectra are 1880 and 1930 cm^{-1} for the nickel and cobalt complex, respectively.² The lower stretching frequency of the nickel complex would be indicative of a larger π back-bonding M-CO in this complex than in the cobalt one. However, firm conclusions cannot be drawn because of the different coordination number and oxidation state of the two complexes.

Registry No. [Co(CO)(np₃)]BPh₄·(CH₃)₂CO, 60294-91-9; [Ni(CO)(np₃)], 54423-76-6.

Supplementary Material Available: Listings of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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