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Insertion Reaction of Carbon Monoxide into M–C Bonds. Synthesis and Structural Characterization of Cobalt(II) and Nickel(II) Acyl Complexes with Tri(tertiary arsines and phosphines)

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Nickel(II) acyl complexes with the general formula [Ni(COR)(L)]BPh_4 (L = tris(2-diphenylarsinoethyl)amine (nas_3), tris(2-diphenylphosphinoethyl)amine (np_3); R = CH_3, C_2H_5, $CH_2C_6H_5$) have been obtained by insertion reactions of carbon monoxide with alkyl compounds of the type [NiR(L)]BPh_4. The structure of the [Ni($COCH_3$)(np_3)]BPh_4·2.5THF derivative has been determined by an x-ray analysis using diffractometric data. The crystals are triclinic, space group $P\bar{1}$, with a = 18.168 (4) Å, b = 17.537 (4) Å, c = 10.789 (3) Å, α = 95.62 (4)°, β = 100.88 (4)°, γ = 85.80 (4)°, and Z = 2. The structure was refined to a final conventional R factor of 0.094 over the 1208 independent reflections. The structure consists of $[Ni(COCH_3)(np_3)]^+$ cations, of tetraphenylborate anions, and of interposed tetrahydrofuran molecules. The chromophore is a distorted trigonal bipyramid with the acetyl group linked to the nickel in an axial position, the Ni–C distance being 1.97 (6) Å. Some intermediate products of the acyl compounds have also been isolated for the np_3 derivatives. The structure of the intermediate of the methyl derivative has been determined by three-dimensional x-ray data. The crystals are monoclinic, space group $P2_1/n$, with a = 35.169 (7) Å, b = 17.347 (4) Å, c = 10.905 (3) Å, β = 95.15 (4)°, and Z = 4. The structure was refined to a R factor of 0.102. The crystals consist of a solid solution of $[Ni(CO)(np_3)]^+$ and $[Ni(COCH_3)(np_3)]^+$, in a ratio of ca. 1:1, of tetraphenylborate anions and of interposed tetrahydrofuran molecules. In these two species having distorted trigonal-bipyramidal geometries, the nickel atom is bonded to the four donor atoms of the ligand np_3 and to the carbon atom of either a carbonyl or an acetyl group, respectively. The results of this analysis allow an hypothesis to be put forward for the mechanism of the insertion of carbon monoxide. Some alkyl and aryl cobalt(I) and cobalt(II) complexes with tetradentate tripod ligands are also reported. The reactivity of these complexes toward carbon monoxide has been studied.

Introduction

Various examples of insertion of carbon monoxide into metal–carbon σ bonds have been reported,[1] but only in a few instances are the mechanisms of such reactions known. In this work we studied the action of carbon monoxide on alkyl complexes of nickel with poly(tertiary arsines and phosphines) with the aim of obtaining the corresponding acyl derivatives, which are, as yet, extremely rare.[2] In fact, the only acyl complexes of nickel obtained by insertion of carbon monoxide into the M–C bond presently known are square-planar complexes of the type [Ni($COCH_3$)X($P(CH_3)_3)_2$][3] (X = Cl, Br).

Several five-coordinate alkyl complexes of the type [NiR(L)]BPh_4 (R = CH_3, C_2H_5, $CH_2C_6H_5$; L = tris(2-diphenylphosphinoethyl)amine (np_3), tris(2-diphenylarsinoethyl)amine (nas_3)) have been described and characterized in a previous study.[4] By the action of carbon monoxide on these alkyl complexes the corresponding acyl derivatives with the formula [Ni(COR)(L)]BPh_4 (R = CH_3, C_2H_5, $CH_2C_6H_5$; L = np_3, nas_3) have been obtained, which have been characterized by the usual physical–chemical techniques. A complete x-ray structural analysis has been carried out on the acetyl derivative with np_3. For this ligand, intermediate products have also been isolated; x-ray analysis has revealed that for the methyl derivative the intermediate product is a solid solution of the carbonyl and acetyl compounds. By examination of these compounds we have tried to put forward a hypothesis about the mechanism of the insertion of carbon monoxide into the Ni–C σ bond in these pentacoordinate cationic complexes.

In a way analogous to that for the previously described nickel(II) complexes, cobalt(I) complexes of general formula [CoR(L)] (L = np_3, R = CH_3, C_6H_5) and cobalt(II) of the type [CoR(np_3)]BPh_4 (R = CH_3, $CH_2C_6H_5$) have been synthesized. By the action of carbon monoxide on the cobalt(II) methyl derivative a complex of formula [Co($COCH_3$)(np_3)]BPh_4 has been obtained which is the first acyl cobalt(II) complex so far reported.[5]

Experimental Section

The solvents were dried by standard methods. All the reactions were performed under a nitrogen atmosphere. The alkyl complexes with the formula [NiR(L)]BPh_4 (R = CH_3, C_2H_5, $CH_2C_6H_5$; L = np_3, nas_3, pp_3) were prepared as previously described.[4]

Physical Measurements. Magnetic, conductometric, and spectrophotometric (both visible and infrared) measurements were carried

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Table I. Physical Constants and Analytical Data

Compd	Λ_M,[a] cm^2 Ω^{-1} mol^{-1}		Anal., %								ν(CO), cm^{-1}	μ_{eff} (293 K), μ_B
			Calcd				Found					
	A	B	C	H	N	M	C	H	N	M		
[Ni(COCH$_3$)(nas$_3$)]BPh$_4$[b]	23	45	67.7	5.4	1.2	4.9	67.4	5.5	1.2	4.9	1660	
[Ni(COC$_2$H$_5$)(nas$_3$)]BPh$_4$·THF	25		67.8	5.9	1.1	4.5	67.8	6.1	1.1	4.3	1662	
[Ni(COCH$_2$C$_6$H$_5$)(nas$_3$)]BPh$_4$	24	46	69.3	5.4	1.1	4.6	69.3	5.5	1.1	4.4	1658	
[Ni(COCH$_3$)(np$_3$)]BPh$_4$·2.5THF[c]	24	47	74.6	6.8	1.1	4.7	74.6	6.8	1.1	4.6	1665	
[Ni(COC$_2$H$_5$)(np$_3$)]BPh$_4$·THF		47	75.5	6.5	1.2	5.1	75.3	6.6	1.1	5.0	1655	
[Ni(COCH$_2$C$_6$H$_5$)(np$_3$)]BPh$_4$·THF	24		76.6	6.4	1.2	4.8	76.6	6.4	1.2	4.8	1655	
[0.5{Ni(COCH$_3$)(np$_3$)}·0.5{Ni(CO)(np$_3$)}]BPh$_4$·2THF[d]	24	45	74.9	6.6	1.2	4.8	74.9	6.7	1.2	4.6	1665, 1988	
[0.5{Ni(COC$_2$H$_5$)(np$_3$)}·0.5{Ni(CO)(np$_3$)}]BPh$_4$·THF	26	44	75.5	6.4	1.2	5.1	75.5	6.5	1.2	4.9	1655, 1988	
[0.5{Ni(COCH$_2$C$_6$H$_5$)(np$_3$)}·0.5{Ni(CO)(np$_3$)}]BPh$_4$·THF		46	76.0	6.3	1.2	5.0	76.0	6.3	1.2	4.7	1665, 1988	
[Co(CH$_3$)(np$_3$)]			71.0	6.2	1.9	8.1	71.0	6.3	1.9	8.1		
[Co(CH$_3$)(pp$_3$)]·THF[e]			69.1	6.5		7.2	68.9	6.6		7.1		
[Co(C$_6$H$_5$)(np$_3$)][f]			73.0	6.0	1.8	7.5	73.0	6.2	1.8	7.4		
[Co(C$_6$H$_5$)(pp$_3$)]			71.5	5.9		7.3	71.4	6.0		7.2		
[Co(CH$_3$)(np$_3$)]BPh$_4$	24	48	76.9	6.2	1.3	5.6	76.8	6.3	1.3	5.4		2.03
[Co(CH$_2$C$_6$H$_5$)(np$_3$)]BPh$_4$·THF	23	44	77.4	6.5	1.2	4.9	77.4	6.5	1.2	4.7		2.11
[Co(COCH$_3$)(np$_3$)]BPh$_4$·THF	24	46	75.4	6.7	1.1	4.8	75.3	6.8	1.1	4.7		2.18

[a] Molar conductance of a ca. 10^{-3} M solution in (A) 1,2-dichloroethane and (B) nitroethane at 20 °C. [b] Calcd: As, 18.6. Found: As, 18.4. [c] Calcd: P, 7.4. Found: P, 7.3. [d] Calcd: P, 7.7. Found: P, 7.6. [e] Calcd: P, 15.2. Found: P, 15.2. [f] Calcd: P, 11.7. Found: P, 11.7.

out using methods already described.[6] Proton magnetic resonance spectra were recorded with a Varian EM 390 spectrometer. The solutions in $(C^2H_3)_2CO$ were prepared under a nitrogen atmosphere and then poured in the sample tube which was sealed. Gas chromatographic determinations were made using a Carlo Erba "Fractovap C".

Preparation of [Ni(COR)(nas$_3$)]BPh$_4$ (R = CH$_3$, C$_2$H$_5$, CH$_2$C$_6$H$_5$). The appropriate alkyl complex (0.5 mmol) was dissolved in tetrahydrofuran (30 mL); carbon monoxide was bubbled through the solution until the starting compound had reacted to give a red solution. By addition of ethanol, red crystals of the acyl derivatives [Ni(COR)(nas$_3$)]BPh$_4$ are obtained. The compounds were separated by filtration and then washed with ethanol and light petroleum.

Reaction of Carbon Monoxide with [NiR(np$_3$)]BPh$_4$ (R = CH$_3$, C$_2$H$_5$, CH$_2$C$_6$H$_5$). The alkyl complex (0.5 mmol) was dissolved in tetrahydrofuran (30 mL) in a Schlenk tube and the reaction vessel was filled with carbon monoxide. After stirring for 30 min the solution was concentrated under vacuum until greenish red crystals appeared which were separated by filtration, washed with a 1:1 tetrahydrofuran–ethanol mixture, and dried. Elemental analysis (Table I) and x-ray diffraction studies carried out on the product obtained from the methyl derivative showed that this substance was a solid solution with composition [0.5{Ni(CO)(np$_3$)}·0.5{Ni(COCH$_3$)(np$_3$)}]BPh$_4$·2THF.

Preparation of [Ni(COR)(np$_3$)]BPh$_4$ (R = CH$_3$, C$_2$H$_5$, CH$_2$C$_6$H$_5$). The solid solution (0.5 mmol) was dissolved at room temperature in tetrahydrofuran (30 mL); with addition of ethanol brick red crystals precipitated. These crystals were filtered off, washed with ethanol and light petroleum, and then dried.

No reaction occurred when [NiR(pp$_3$)]BPh$_4$ (R = CH$_3$, C$_2$H$_5$, CH$_2$C$_6$H$_5$) dissolved in tetrahydrofuran was reacted with carbon monoxide.

Synthesis of [CoR(np$_3$)]BPh$_4$ (R = CH$_3$, CH$_2$C$_6$H$_5$). A solution of the appropriate Grignard reagent (1 mmol) in ether was slowly added at 0 °C to the complex [CoBr(np$_3$)]BPh$_4$ (1 mmol) dissolved in tetrahydrofuran (30 mL). The resulting solution was stirred for 10 min and then a few drops of water were added and filtered. Crystalline products were obtained by concentration under vacuum. The compounds were filtered and then washed with ethanol and light petroleum.

Synthesis of [CoR(L)] (L = np$_3$, R = CH$_3$, C$_6$H$_5$; L = pp$_3$, R = CH$_3$, C$_6$H$_5$). These complexes have been prepared as cobalt(II) derivatives by addition of a stoichiometric amount of the appropriate lithium salt to the complexes [CoBr(L)] in tetrahydrofuran (30 mL).

Cobalt(II) alkyl complexes were allowed to react with carbon monoxide in the same manner as the nickel(II) complexes.

Table II. Crystal Data and Data Collection Details

	Compound I	Compound II
Mol formula	$C_{78}H_{85}O_{3.5}BNP_3Ni$	$C_{75.5}H_{79.5}O_3BNP_3Ni$
Mol wt	1254.99	1211.41
a, Å	18.168 (4)	35.169 (7)
b, Å	17.537 (4)	17.347 (4)
c, Å	10.789 (3)	10.905 (3)
α, deg	95.62 (4)	90
β, deg	100.88 (4)	95.15 (4)
γ, deg	95.80 (4)	90
d_{obsd}(by flotn), g cm^{-3}	1.24	1.21
d_{calcd}, g cm^{-3}	1.25	1.21
V, Å^3	3342.30	6626.27
Z	2	4
Space group	$P\bar{1}$	$P2_1/n$
λ, Å	1.5418 (Cu Kα)	0.7093 (Mo Kα)
Abs coeff (Mo Kα), cm^{-1}	14.52	3.40
Monochromator	Flat graphite crystal	Flat graphite crystal
Takeoff angle, deg	2.0	2.0
Method	ω–2θ	ω–2θ
Scan speed	0.05°/s for 0.9°	0.07°/s for 0.8°
Background time	9 s on each side	6 s on each side
Standards	3 every 120 min	3 every 100 min
2θ limit	$6° \leq 2\theta \leq 80°$	$6° \leq 2\theta \leq 40°$
No. of data	4033	6786
No. of obsd data	1208 ($I \geq 3\sigma(I)$)	1746 ($I \geq 2\sigma(I)$)

Collection and Reduction of X-Ray Intensity Data. [Ni(COCH$_3$)(np$_3$)]BPh$_4$·2.5THF (I). The red crystals of this complex are parallelepiped shaped. The crystal used for the structure analysis had dimensions 0.7 × 0.13 × 0.05 mm. Because of the air sensitivity of this complex, the crystal under examination was sealed in a glass capillary. Cell parameters were determined at room temperature (about 22 °C) by carefully measuring the setting angles of 25 reflections on a Philips PW 1100 diffractometer. Details of crystal data and data collection are given in Table II. During the collection of the data the intensity of the standard reflections slowly and continuously diminished to about 70% of their initial value at the end of data collection. The intensities of the reflections have therefore been rescaled on the basis of intensities of these standard reflections. The standard deviations on the intensities were calculated as described elsewhere,[7] using a value of the instability factor *k* of 0.03. The observed reflections were corrected for Lorentz and polarization effects and for absorption using a numerical method.[8] Atomic scattering factors for Ni, P, O, N, C, and B and those for hydrogen atoms (all in the neutral state) were taken from ref 9 and 10, respectively. Corrections for anomalous dispersion effects for nickel and phosphorus atoms were applied in the refinement.[11]

Table III. Atomic Parameters for the Structure of $[Ni(COCH_3)(np_3)]BPh_4 \cdot 2.5THF^a$ (All Quantities $\times 10^4$)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	2505 (4)	2167 (4)	3439 (8)	1157 (82)	835 (66)	1334 (101)	298 (56)	162 (73)	188 (66)
P(1)	3742 (7)	1995 (6)	3711 (12)	952 (125)	684 (99)	960 (150)	231 (89)	−8 (101)	155 (97)
P(2)	1764 (7)	2068 (6)	4924 (13)	1150 (132)	730 (103)	1173 (162)	256 (93)	157 (124)	105 (102)
P(3)	2110 (7)	2879 (7)	1802 (13)	831 (121)	803 (97)	1183 (162)	156 (92)	134 (109)	74 (107)
N	2953 (15)	3365 (15)	4567 (30)	847 (277)	782 (242)	1068 (345)	293 (213)	279 (244)	440 (238)
C(100)	2145 (35)	1098 (36)	2650 (63)	1883 (657)	1290 (490)	918 (783)	284 (449)	1273 (699)	289 (687)
O(1)	2321 (23)	459 (23)	3202 (48)	926 (398)	704 (349)	930 (522)	103 (319)	385 (336)	381 (380)
C(101)	2000 (25)	1131 (23)	1302 (37)	2440 (417)	1221 (306)	1511 (444)	255 (271)	671 (442)	−10 (395)

[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots)]$. F(rel) scale factor = 82800.

Table IV. Atomic Parameters for the Structure of $[Ni(COCH_3)(np_3)]BPh_4 \cdot 2.5THF$ (All Quantities $\times 10^4$)

Atom	x	y	z	U, Å^2
C(1)	3722 (21)	3310 (21)	5198 (38)	936 (153)
C(2)	4184 (19)	2941 (19)	4319 (35)	722 (138)
C(3)	2466 (21)	3513 (23)	5539 (40)	1036 (164)
C(4)	2267 (21)	2803 (22)	6158 (37)	966 (155)
C(5)	2910 (22)	3971 (20)	3709 (38)	932 (151)
C(6)	2170 (20)	3822 (18)	2720 (34)	677 (133)
B	2992 (24)	6434 (23)	4515 (43)	663 (174)
C(67)[a]	2377 (38)	7796 (39)	377 (75)	2867 (374)
C(68)	2515 (41)	8070 (47)	−940 (75)	2891 (383)
C(69)	2717 (42)	8866 (46)	−562 (73)	3149 (420)
C(70)	3161 (33)	8994 (34)	451 (58)	2085 (289)
C(71)	2939 (38)	8518 (39)	1309 (68)	2817 (383)
C(80)	53 (47)	202 (45)	674 (64)	3084 (392)
C(90)	1436 (34)	4456 (38)	8257 (60)	2610 (324)
C(91)	1426 (38)	5434 (41)	8887 (66)	2994 (352)

[a] Atoms of THF molecules.

$[0.5\{Ni(COCH_3)(np_3)\} \cdot 0.5\{Ni(CO)(np_3)\}]BPh_4 \cdot 2THF$ (II). The greenish red crystals of this solid solution are parallelepiped shaped. The crystal used for the structure analysis had dimensions 0.80 × 0.20 × 0.10 mm. This crystal, as well, was sealed in a glass capillary, due to its air sensitivity. Cell parameters were determined as for the compound I. Details of crystal data and data collection are given in Table II. Again, during data collection, there was a continuous diminution of the intensities of the reflections to about 65% of their initial value and, as above, the intensities have been recalculated. The instability factor k, used in the calculation of the standard deviations of the intensities, was 0.03. The observed reflections were corrected for Lorentz and polarization effects and for absorption using a numerical method. Atomic scattering factors and the anomalous scattering corrections for nickel and phosphorus are those used for the atoms of compound I.

Solution and Refinement of the Structures. Compound I. A three-dimensional Patterson synthesis yielded the positional parameters of the nickel and phosphorus atoms. Successive F_o Fourier synthesis showed the positions of all nonhydrogen atoms, including some atoms from a molecule of tetrahydrofuran. These solvent molecules are randomly distributed, and it was therefore impossible, even in the final stage of the refinement, to locate the positions of some of the carbon (or oxygen) atoms of these molecules by either F_o Fourier synthesis or ΔF Fourier synthesis. One of these molecules is positioned in a region close to the center of symmetry and has been assigned an occupation factor of 0.5. For these molecules it was not possible to distinguish between carbon and oxygen atoms and therefore all atoms were treated as if they were carbon atoms.

The structure was refined by a full-matrix least-squares program.[12] The minimized function is $\sum w(|F_o| - |F_c|)^2$, in which w is the weight assigned to the F_o values according to the expression $w = 1/\sigma(F_o)^2$. The carbon atoms belonging to the phenyl groups were refined using rigid-body models for the phenyl rings. On the basis of prior suggestions,[13] a subtle distinction was made between rings attached to phosphorus atoms (D_{6h} geometry) and rings attached to boron atoms (α angle equal to 114°). The hydrogen atoms of the np$_3$ ligand and BPh_4^- ion were introduced in calculated positions (C–H distance of 0.95 Å), with a thermal factor for each hydrogen atom equal to that of the attached carbon atom, and were not refined. An isotropic cycle, in which the nickel, phosphorus, nitrogen, carbon, and oxygen atoms of the acetyl group were allowed to vibrate anisotropically, was carried out to a conventional R factor of 0.094. This relatively high R factor is probably due to the decomposition of the crystal during data collection and to disorder shown by the solvent. The high standard deviations associated to the positional and thermal parameters of the atoms of the acetyl group (and the related distances) can be explained by the crystal decomposition which consists in loss of carbon monoxide. With regard to this, a ΔF Fourier calculated at the end of the refinement has demonstrated zones of positive electron density (the high is about 1 e Å^{-3}) in the vicinity of the solvent molecules. Tables III–VI report the positional and thermal parameters of all nonhydrogen atoms.

Compound II. This structure, also, was solved by the heavy-atom technique. The carbon atom linked to the nickel and the other nonhydrogen atoms belonging to the np$_3$ ligand and to the BPh_4^- ion were located from successive three-dimensional F_o Fourier maps, which also revealed other zones of fairly high electron density, due to the presence of the molecules of tetrahydrofuran. The presence of these molecules was also evident from a ΔF Fourier synthesis calculated at an R factor of about 0.2. One of these two molecules shows disorder such that some carbon atoms have been assigned two distinct positions, with occupation factors of 0.5. It was not possible to distinguish between carbon and oxygen atoms in either of the molecules, so that all atoms have been treated as if they were carbon atoms. On this point particular attention has been given to the study of electron density in the region of the carbon bonded to the metal, both by F_o Fourier synthesis and by ΔF Fourier synthesis. Figure 1 shows the electron density found in this region with a F_o Fourier synthesis calculated at an R factor of about 0.2. The existence of four maxima, shown in Figure 1, leads to the hypothesis that these crystals are a solid solution of ions of both the carbonyl and acetyl derivatives, the only difference from a structural point of view being the presence of either the CO or COCH$_3$ ligand. Since the carbon atom bound to the metal occupies an almost identical position in the two cases, it is impossible

Table V. Final Least-Squares Parameters for $[Ni(COCH_3)(np_3)]BPh_4 \cdot 2.5THF$ "Groups"[a]

Group	x'	y'	z'	θ	ϕ	ψ
1	0.4377 (10)	0.1064 (7)	0.5811 (16)	0.973 (14)	−2.033 (34)	0.223 (28)
2	0.4556 (9)	0.1522 (10)	0.1552 (16)	0.927 (18)	1.403 (35)	2.156 (11)
3	0.0172 (10)	0.2477 (9)	0.4214 (21)	1.300 (17)	2.887 (38)	−2.784 (16)
4	0.1454 (9)	0.0662 (10)	0.6229 (19)	1.890 (18)	0.512 (34)	1.959 (18)
5	0.3133 (10)	0.3101 (12)	−0.0030 (16)	0.626 (16)	1.577 (39)	1.388 (16)
6	0.0640 (11)	0.2675 (10)	−0.0122 (19)	1.109 (17)	−0.826 (37)	−2.673 (21)
7	0.1457 (10)	0.5516 (8)	0.3663 (17)	1.856 (13)	−0.265 (37)	2.524 (14)
8	0.2748 (9)	0.8151 (9)	0.5121 (14)	2.360 (17)	−0.313 (30)	1.085 (21)
9	0.3941 (9)	0.5865 (8)	0.6752 (18)	1.763 (15)	−0.921 (32)	−2.597 (15)
10	0.3955 (9)	0.6443 (10)	0.2395 (15)	0.806 (15)	1.118 (33)	2.197 (12)

[a] x', y', z' (fractional coordinates) define the origin of the working system of the group. The Goldstein definition is used for Euler angles θ, ϕ, ψ (rad): H. Goldstein, "Classical Mechanics", Addison-Wesley, Reading, Mass., 1959.

Table VI. $[Ni(COCH_3)(np_3)]BPh_4 \cdot 2.5THF$
Thermal and Derived Positional Parameters of Group Atoms (All Quantities ×10^4)

Atom	*x*	*y*	*z*	*U*, A^2
C(7)	4103 (24)	1407 (11)	4973 (23)	725 (142)
C(8)	4831 (24)	1209 (11)	5038 (23)	1101 (166)
C(9)	5151 (24)	810 (11)	6016 (23)	889 (155)
C(10)	4742 (24)	608 (11)	6929 (23)	659 (135)
C(11)	4014 (24)	806 (11)	6864 (23)	1030 (161)
C(12)	3695 (24)	1205 (11)	5886 (23)	781 (148)
C(13)	4291 (18)	1715 (26)	2447 (23)	1064 (167)
C(14)	4829 (18)	2220 (26)	2078 (23)	863 (149)
C(15)	5138 (18)	1995 (26)	1035 (23)	1139 (170)
C(16)	4910 (18)	1265 (26)	360 (23)	1065 (169)
C(17)	4372 (18)	760 (26)	728 (23)	1073 (171)
C(18)	4062 (18)	985 (26)	1772 (23)	1034 (157)
C(19)	797 (11)	2310 (18)	4492 (51)	846 (147)
C(20)	484 (11)	2714 (18)	5398 (51)	1493 (192)
C(21)	−245 (11)	2910 (18)	5074 (51)	1766 (227)
C(22)	−662 (11)	2701 (18)	3844 (51)	1068 (166)
C(23)	−349 (11)	2297 (18)	2938 (51)	1444 (201)
C(24)	381 (11)	2101 (18)	3262 (51)	1550 (209)
C(25)	1572 (20)	1216 (15)	5701 (40)	659 (132)
C(26)	1076 (20)	582 (15)	5060 (40)	933 (153)
C(27)	939 (20)	−63 (15)	5676 (40)	1195 (175)
C(28)	1297 (20)	−75 (15)	6932 (40)	1260 (178)
C(29)	1794 (20)	558 (15)	7573 (40)	1403 (190)
C(30)	1931 (20)	1204 (15)	6957 (40)	1163 (170)
C(31)	2682 (11)	3026 (30)	634 (23)	1048 (165)
C(32)	3015 (11)	2392 (30)	224 (23)	1650 (213)
C(33)	3542 (11)	2480 (30)	−552 (23)	1054 (161)
C(34)	3735 (11)	3202 (30)	−917 (23)	1662 (216)
C(35)	3402 (11)	3835 (30)	−506 (23)	1851 (230)
C(36)	2875 (11)	3747 (30)	269 (23)	1851 (229)
C(37)	1222 (15)	2721 (22)	625 (37)	907 (155)
C(38)	661 (15)	3160 (22)	884 (37)	1432 (191)
C(39)	−19 (15)	3108 (22)	13 (37)	1183 (175)
C(40)	−137 (15)	2615 (22)	−1118 (37)	1249 (178)
C(41)	424 (15)	2176 (22)	−1377 (37)	2078 (257)
C(42)	1104 (15)	2228 (22)	−506 (37)	1758 (227)
C(43)	2195 (11)	5951 (14)	4008 (50)	901 (150)
C(44)	1745 (11)	5897 (14)	2799 (50)	976 (157)
C(45)	1033 (11)	5479 (14)	2457 (50)	1094 (165)
C(46)	745 (11)	5095 (14)	3330 (50)	894 (149)
C(47)	1157 (11)	5125 (14)	4530 (50)	995 (154)
C(48)	1867 (11)	5547 (14)	4853 (50)	809 (144)
C(49)	2838 (20)	7352 (10)	4822 (30)	655 (136)
C(50)	3357 (20)	7858 (10)	5724 (30)	1025 (162)
C(51)	3276 (20)	8627 (10)	6018 (30)	1012 (161)
C(52)	2661 (20)	8922 (10)	5408 (30)	938 (158)
C(53)	2131 (20)	8458 (10)	4516 (30)	790 (147)
C(54)	2223 (20)	7690 (10)	4236 (30)	1001 (166)
C(55)	3502 (17)	6153 (14)	5683 (30)	645 (140)
C(56)	3357 (17)	6258 (14)	6906 (30)	728 (137)
C(57)	3776 (17)	5983 (14)	7941 (30)	1444 (202)
C(58)	4365 (17)	5587 (14)	7783 (30)	1016 (160)
C(59)	4536 (17)	5463 (14)	6610 (30)	1000 (165)
C(60)	4110 (17)	5743 (14)	5587 (30)	886 (153)
C(61)	3459 (15)	6516 (26)	3282 (25)	802 (145)
C(62)	3981 (15)	7119 (26)	3127 (25)	926 (154)
C(63)	4461 (15)	7056 (26)	2276 (25)	1014 (160)
C(64)	4434 (15)	6373 (26)	1539 (25)	1161 (175)
C(65)	3936 (15)	5760 (26)	1644 (25)	1063 (166)
C(66)	3461 (15)	5836 (26)	2502 (25)	1216 (176)

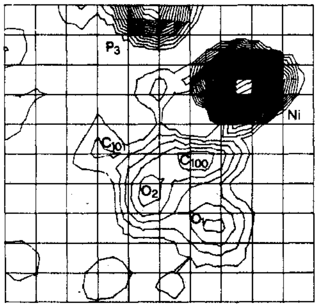


Figure 1. Electron density map in the zone occupied by the acetyl and carbonyl groups. Countour lines are drawn each 0.5 e/Å^3.

to distinguish between them. At this point, the refinement of the structure was carried out using the same technique and the same program as used for compound I. This refinement started with an isotropic cycle for all atoms, with the carbon atoms of the phenyl rings refined as a rigid group (as in compound I), and then proceeded with mixed cycles (anisotropic temperature factors for Ni, P, and N and isotropic for the other atoms). The hydrogen atoms of the ligand np_3 and the BPh_4^- ion were introduced in calculated positions (C–H distance of 0.95 Å) with isotropic temperature factors equal to those of the bonded carbon atoms and were not refined. A refinement was also carried out on the population parameters of the oxygen atoms of the carbonyl group and the oxygen and the terminal carbon atom of the acetyl group, with the condition that the sum of the population parameters must be equal to unity. Since the refinement has led to a value very close to 50% for the two forms (51% for the carbonyl derivative and 49% for the acyl derivative), population parameters of 0.5 for these three atoms have been used in the final calculation. The refinement of these three atoms has produced values which are understandable in terms of the geometry of these groups and also in terms of the temperature factors which have been converted to realistic values. The final value of the *R* factor, 0.102, is rather high and can be attributed to the disorder of the solvent and to the decomposition of the crystal during data collection. The positional and thermal parameters of all nonhydrogen atoms are reported in Tables VII–X.

Results and Discussion

Nickel Complexes. The acyl derivatives of the ligand nas_3 having the general formula $[Ni(COR)(nas_3)]BPh_4$ (R = CH_3, C_2H_5, $CH_2C_6H_5$) are obtained as the only products by direct reaction of carbon monoxide with the alkyl nickel(II) complexes $[NiR(L)]BPh_4$. Analytical data of the acetyl derivatives are reported in Table I. The compounds show ν(CO) at about 1660 cm^{-1}, characteristic of the acetyl group (Table I). The complexes are all diamagnetic in the solid state and behave as 1:1 electrolytes in 1,2-dichloroethane and nitroethane solutions. The products are stable both in the solid state and in solution under carbon monoxide but under an inert atmosphere they evolve carbon monoxide reverting to the original alkyl derivatives, demonstrated by gas chromatographic measurements on the evolved gas and NMR spectra of the remaining solution. This behavior is analogous to that of the only other known acetyl derivative of nickel $[Ni(COCH_3)X(P(CH_3)_3)_2]$,[3b] for which it has been found that the insertion of carbon monoxide is reversible. Electronic spectral data of these acyl complexes are reported in Table XI, both in the solid state and in 1,2-dichloroethane and nitroethane solutions. These spectra, which are characterized by an intense band between 2.08 and 2.10 μm^{-1} (ϵ 2450–2990), can be correlated with the spectra of the corresponding trigonal-bipyramidal nickel(II) alkyl complexes with the formula $[NiR(nas_3)]BPh_4$.[4] Since the highest symmetry field consistent with the geometry

Table VII. Atomic Parameters for the Structure of $[0.5\{Ni(COCH_3)(np_3)\} \cdot 0.5\{Ni(CO)(np_3)\}]BPh_4 \cdot 2THF^a$ (All Quantities ×10^4)

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	1350 (1)	2606 (2)	5045 (4)	538 (26)	452 (28)	1024 (42)	38 (27)	206 (27)	−25 (36)
P(1)	1702 (2)	2546 (5)	6903 (9)	483 (56)	603 (67)	1108 (94)	21 (59)	88 (62)	102 (81)
P(2)	723 (2)	2232 (5)	4793 (10)	465 (57)	490 (64)	1315 (99)	−72 (50)	221 (62)	112 (71)
P(3)	1525 (2)	3453 (5)	3576 (10)	521 (63)	478 (61)	932 (97)	54 (52)	360 (64)	−41 (71)
N	1104 (7)	3712 (12)	5844 (29)	777 (216)	446 (184)	1106 (289)	211 (154)	153 (215)	393 (207)

[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots)]$. *F*(rel) scale factor = 82800.

Table VIII. Atomic Parameters for the Structure of $[0.5\{Ni(COCH_3)(np_3)\}\cdot 0.5\{Ni(CO)(np_3)\}]BPh_4\cdot 2THF$ (All Quantities $\times 10^4$)

Atom	x	y	z	U, Å^2
C(100)	1554 (12)	1671 (28)	4484 (48)	1202 (176)
O(2)	1668 (14)	1290 (30)	3581 (60)	1256 (200)
O(1)	1423 (13)	1015 (29)	4760 (49)	1265 (193)
C(101)	1666 (34)	1999 (74)	3374 (134)	2526 (681)
C(1)	1348 (9)	3937 (18)	7028 (35)	742 (121)
C(2)	1456 (9)	3232 (19)	7849 (35)	987 (126)
C(3)	702 (9)	3551 (17)	6254 (31)	675 (105)
C(4)	497 (8)	3170 (16)	5194 (30)	586 (102)
C(5)	1112 (8)	4361 (17)	5039 (30)	574 (97)
C(6)	1483 (8)	4337 (15)	4347 (30)	518 (98)
B	4041 (10)	1836 (20)	−35 (37)	664 (129)
C(67)[a]	4062 (18)	3962 (47)	5359 (67)	2555 (337)
C(68)	4101 (15)	4278 (33)	4266 (75)	1726 (249)
C(69)	3953 (23)	3845 (51)	3365 (75)	3071 (405)
C(701)[b]	3746 (21)	3149 (42)	3852 (79)	774 (240)
C(711)[b]	4018 (29)	3045 (54)	4683 (111)	1568 (421)
C(702)[b]	3614 (26)	3778 (56)	3992 (103)	1666 (397)
C(712)[b]	3787 (29)	3187 (57)	5082 (104)	1548 (397)
C(72)	2626 (25)	915 (56)	4796 (74)	3322 (403)
C(73)	2608 (24)	138 (50)	5186 (80)	2692 (382)
C(74)	2953 (27)	−15 (39)	5848 (68)	2754 (351)
C(75)	3212 (19)	479 (52)	5240 (68)	2916 (314)
C(76)	3016 (26)	1137 (41)	5158 (67)	2625 (363)

[a] Atoms of THF molecules. [b] Population parameter of 0.5.

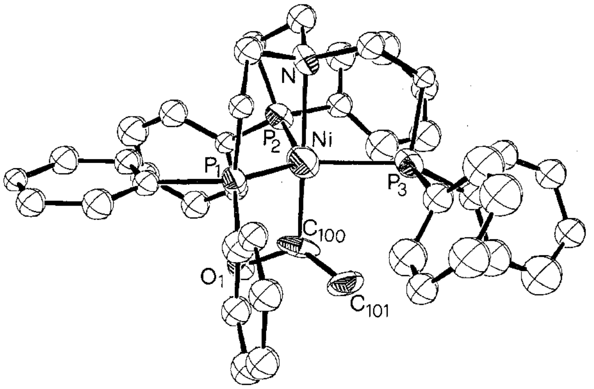


Figure 2. Perspective view of the $[Ni(COCH_3)(np_3)]^+$ cation in structure I.

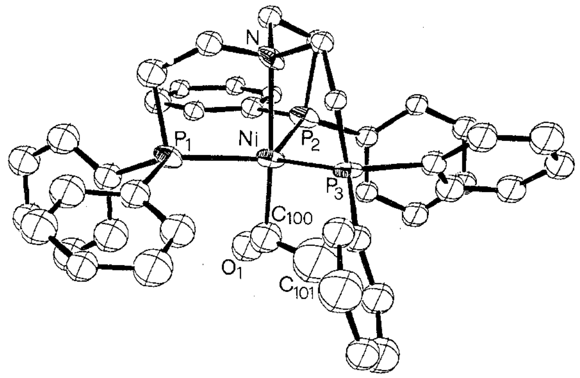


Figure 3. Perspective view of the $[Ni(COCH_3)(np_3)]^+$ cation in structure II.

of the tetradentate ligand is C_{3v}, the intense band shown by these acyl complexes may be assigned to the $(a_1')^2 \rightarrow a_1'e'$ transition; this band, which is shifted to higher frequencies with respect to the corresponding halo complexes $[NiX(nas_3)]BPh_4$ by the presence of the acetyl group bonded to the metal, probably masks the expected band of the $(a_1')^2 \rightarrow a_1'e''$ transition.[14]

The np_3 derivatives behave differently; in fact, when they are treated with carbon monoxide in mild conditions, they first yield crystals which show in the infrared, both in Nujol mull and in methylene chloride solution, bands due both to ν(CO) of acetyl (ca. 1650 cm^{-1}) and to the ν(CO) band due to the terminal carbonyl ligand bonded to the metal (1988 cm^{-1}) (Table I). When these crystals were dissolved in tetrahydrofuran and ethanol was added, compounds separate which have composition corresponding to the formula $[Ni(COR)(np_3)]BPh_4$ (R = CH_3, C_2H_5, $CH_2C_6H_5$) and which show only the ν(CO) acetyl band at ca. 1660 cm^{-1} (Table I). The reflectance spectra of the acetyl compounds, both in the solid state and in 1,2-dichloroethane and nitroethane solutions, are typical of trigonal-bipyramidal complexes of nickel(II) (Table XI).[15] They behave in an entirely similar way to the nas_3 derivatives in either an inert atmosphere or one of carbon monoxide. A complete x-ray structural analysis has been carried out on the acetyl derivative. The complex consists of $[Ni(COCH_3)(np_3)]^+$ cations, tetraphenylborate anions, and interposed molecules of tetrahydrofuran. Figure 2 shows an ORTEP diagram of the cationic species. The nickel atom is pentacoordinate, being bound to four donor atoms of np_3 and to the carbon atom of the acetyl group, forming a distorted trigonal bipyramid. The Ni–C distance, 1.97 (6) Å, is not far from the analogous distances found in the methyl derivative (2.02 Å).[4] This value is longer than that found in an acetyl derivative in a square-planar nickel complex (1.84 Å),[16] but this difference is not very significant on account of the high standard deviations found for this distance in the title compound. Comparing the other metal bond distances with those found for the methyl derivative, one sees that in the acetyl derivative both the Ni–N distance (2.31(3) Å) and Ni–P_{av} (2.29 Å) are significantly longer (2.11 and 2.23 Å, respectively). Regarding the geometry of the acetyl group, the C–O distance is 1.36 (8) Å and C–C is 1.44 (8) Å and the internal bond angles are not very different from those required for sp^2 hybridation.

To investigate further the nature of the crystals of compound II, which shows two ν(CO) bands, a complete x-ray structural analysis was carried out. The crystals are a solid solution of the ions $[Ni(CO)(np_3)]^+$ and $[Ni(COCH_3)(np_3)]^+$, in the ratio of about 1:1, as obtained with a least-squares refinement of the population parameters, together with tetraphenylborate ions and interposed molecules of tetrahydrofuran. Figures 3 and 4 show ORTEP diagrams of the two cationic species. The principal distances and angles are reported in Table XII. The

Table IX. Final Least-Squares Parameters for $[0.5\{Ni(COCH_3)(np_3)\}\cdot 0.5\{Ni(CO)(np_3)\}]BPh_4\cdot 2THF$ "Groups"

Group	x'	y'	z'	θ	ϕ	ψ
1	0.2538 (4)	0.3001 (6)	0.7157 (18)	1.704 (15)	0.453 (25)	2.903 (15)
2	0.1754 (4)	0.1110 (9)	0.8498 (18)	1.180 (21)	0.596 (28)	1.267 (18)
3	0.0339 (3)	0.1680 (7)	0.2358 (14)	1.218 (16)	1.477 (19)	−2.189 (10)
4	0.0421 (4)	0.1137 (7)	0.6684 (13)	1.978 (12)	0.844 (16)	2.603 (14)
5	0.1024 (4)	0.3635 (9)	0.1103 (15)	2.027 (12)	−1.540 (21)	1.797 (9)
6	0.2310 (4)	0.3507 (9)	0.2560 (15)	2.438 (14)	2.606 (25)	−0.423 (16)
7	0.3232 (4)	0.1240 (6)	0.0170 (15)	1.333 (12)	0.070 (19)	2.840 (10)
8	0.4560 (3)	0.1645 (7)	0.2464 (13)	1.965 (12)	−1.460 (18)	2.091 (8)
9	0.3971 (4)	0.3583 (8)	−0.0543 (11)	0.579 (13)	0.330 (27)	1.235 (22)
10	0.4461 (3)	0.1022 (6)	−0.2086 (14)	1.563 (13)	2.324 (16)	0.694 (11)

Table X. [0.5 {$Ni(COCH_3)(np_3)$}·0.5 {$Ni(CO)(np_3)$}]BPh_4·2THF Thermal and Derived Positional Parameters of Group Atoms (All Quantities ×10^4)

Atom	*x*	*y*	*z*	*U*, Å^2
C(11)	2206 (4)	2845 (11)	7087 (36)	935 (125)
C(21)	2380 (4)	3036 (11)	6030 (36)	1215 (135)
C(31)	2767 (4)	3219 (11)	6111 (36)	1467 (163)
C(41)	2980 (4)	3210 (11)	7250 (36)	920 (121)
C(51)	2806 (4)	3019 (11)	8307 (36)	1293 (157)
C(61)	2419 (4)	2836 (11)	8226 (36)	1263 (157)
C(12)	1723 (6)	1697 (13)	7928 (31)	901 (122)
C(22)	1878 (6)	1049 (13)	7411 (31)	1454 (170)
C(32)	1914 (6)	363 (13)	8076 (31)	1551 (192)
C(42)	1794 (6)	327 (13)	9258 (31)	1175 (141)
C(52)	1639 (6)	976 (13)	9775 (31)	1255 (161)
C(62)	1604 (6)	1661 (13)	9110 (31)	1212 (146)
C(13)	444 (6)	1870 (13)	3384 (15)	666 (103)
C(23)	593 (6)	1209 (13)	2883 (15)	709 (113)
C(33)	470 (6)	987 (13)	1685 (15)	941 (123)
C(43)	199 (6)	1428 (13)	989 (15)	873 (118)
C(53)	51 (6)	2089 (13)	1490 (15)	870 (120)
C(63)	174 (6)	2310 (13)	2688 (15)	672 (101)
C(14)	542 (7)	1546 (10)	5930 (18)	730 (109)
C(24)	186 (7)	1198 (10)	5693 (18)	591 (105)
C(34)	46 (7)	720 (10)	6573 (18)	601 (99)
C(44)	260 (7)	591 (10)	7689 (18)	594 (96)
C(54)	616 (7)	939 (10)	7926 (18)	979 (126)
C(64)	757 (7)	1417 (10)	7047 (18)	586 (97)
C(15)	1197 (6)	3566 (18)	2089 (16)	729 (114)
C(25)	1019 (6)	2929 (18)	1513 (16)	983 (123)
C(35)	817 (6)	3010 (18)	362 (16)	1035 (133)
C(45)	793 (6)	3727 (18)	−212 (16)	980 (140)
C(55)	972 (6)	4364 (18)	365 (16)	1221 (151)
C(65)	1174 (6)	4283 (18)	1515 (16)	959 (134)
C(16)	2000 (5)	3508 (16)	2923 (23)	791 (109)
C(26)	2265 (5)	4069 (16)	3329 (23)	964 (127)
C(36)	2627 (5)	4067 (16)	2905 (23)	1788 (180)
C(46)	2724 (5)	3505 (16)	2076 (23)	1026 (134)
C(56)	2458 (5)	2945 (16)	1670 (23)	1343 (156)
C(66)	2096 (5)	2947 (16)	2094 (23)	1073 (143)
C(17)	3621 (4)	1473 (10)	80 (28)	593 (100)
C(27)	3444 (4)	1513 (10)	1170 (28)	823 (109)
C(37)	3070 (4)	1291 (10)	1266 (28)	866 (124)
C(47)	2857 (4)	1015 (10)	256 (28)	596 (100)
C(57)	3013 (4)	961 (10)	−839 (28)	917 (121)
C(67)	3388 (4)	1187 (10)	−915 (28)	790 (116)
C(18)	4368 (5)	1724 (14)	1248 (15)	592 (97)
C(28)	4618 (5)	2276 (14)	1781 (15)	702 (94)
C(38)	4804 (5)	2206 (14)	2950 (15)	684 (98)
C(48)	4745 (5)	1569 (14)	3637 (15)	973 (121)
C(58)	4503 (5)	1006 (14)	3169 (15)	695 (107)
C(68)	4320 (5)	1088 (14)	1998 (15)	693 (102)
C(19)	4001 (6)	2768 (8)	−309 (21)	601 (101)
C(29)	3717 (6)	3228 (8)	124 (21)	718 (107)
C(39)	3686 (6)	4013 (8)	−96 (21)	865 (121)
C(49)	3942 (6)	4370 (8)	−770 (21)	981 (136)
C(59)	4227 (6)	3953 (8)	−1220 (21)	1030 (139)
C(69)	4253 (6)	3169 (8)	−989 (21)	859 (120)
C(110)	4271 (5)	1382 (11)	−1120 (20)	581 (101)
C(210)	4577 (5)	876 (11)	−895 (20)	544 (96)
C(310)	4761 (5)	527 (11)	−1818 (20)	622 (107)
C(410)	4643 (5)	676 (11)	−3019 (20)	667 (100)
C(510)	4346 (5)	1166 (11)	−3302 (20)	876 (113)
C(610)	4165 (5)	1509 (11)	−2365 (20)	522 (94)

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

Compound	State^a	Absorption max, μm^{-1} (ϵ molar for soln)
[$Ni(COCH_3)(nas_3)$]BPh_4	a	1.28, 2.10
	b	1.28 (270), 210 (2650)
[$Ni(COC_2H_5)(nas_3)$]BPh_4·THF	a	2.08
	c	2.08 (2450)
[$Ni(COCH_2C_6H_5)(nas_3)$]BPh_4	a	2.08
	b	2.08 (2850)
	c	2.08 (2990)
[$Ni(COCH_3)(np_3)$]BPh_4·2.5THF	a	2.13
	b	2.17 (3300)
	c	2.13 (3370)
[$Ni(COC_2H_5)(np_3)$]BPh_4·THF	a	2.17
	c	2.17 (2975)
[$Ni(COCH_2C_6H_5)(np_3)$]BPh·THF	a	2.13
	c	2.13 (2840)
[0.5 {$Ni(COCH_3)(np_3)$}·0.5{$Ni(CO)(np_3)$}] BPh_4·2THF	a	1.37 sh, 2.13
	b	1.37 (290), 2.17 (2680)
	c	1.38 (335), 2.15 (2950)
[0.5 {$Ni(COC_2H_5)(np_3)$}·0.5 {$Ni(CO)(np_3)$}]BPh_4	a	1.37 sh, 2.13
	b	1.37 (330), 2.11 (3020)
	c	1.38 (360), 2.11 (3120)
[0.5 {$Ni(COCH_2C_6H_5)(np_3)$}·0.5 {$Ni(CO)(np_3)$}]BPh_4	a	1.39, 2.14
	c	1.40 (280), 2.15 (2600)
[$Co(CH_3)(np_3)$]	a	2.30
	d	2.32 (6700)
[$Co(CH_3)(pp_3)$]	a	2.38
	d	2.38 (10700)
[$Co(C_6H_5)(np_3)$]	a	2.35
	b	2.35 (4300)
[$Co(C_6H_5)(pp_3)$]	a	2.38
	d	2.35 (10800)
[$Co(CH_3)(np_3)$]BPh_4	a	0.76, 1.00 sh, 2.00, 2.63 sh
	c	0.85 (115), 1.00 sh, 2.00 (655)
[$Co(CH_2C_6H_5)(np_3)$]BPh_4·THF	a	0.75, 1.00 sh, 1.82, 2.22
	c	0.67 (85), 1.04 (81), 1.89 sh
[$Co(COCH_3)(np_3)$]BPh_4·THF	a	0.84, 1.43 sh, 1.82, 2.17
	c	0.79 (145), 1.43 (30), 1.82 (206), 2.17 (852)

^{a} Key: a, diffuse reflectance spectrum at room temperature; b, 1,1-dichloroethane solution; c, nitroethane solution; d, benzene solution.

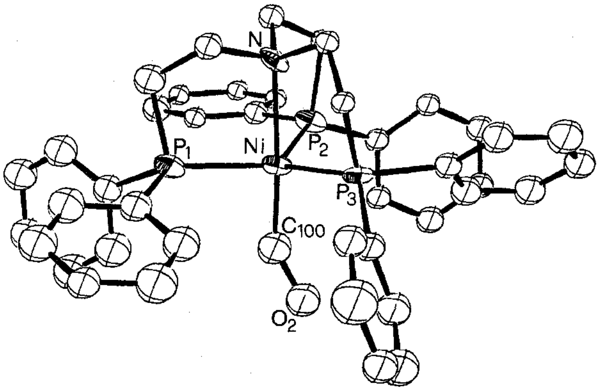


Figure 4. Perspective view of the [$Ni(CO)(np_3)$]$^+$ cation in structure II.

metal atom is bound to the four donor atoms of the ligand and to a carbon atom of the acetyl group or the carbonyl group, giving a distorted trigonal-bipyramidal geometry. The only difference in these two cations thus lies in one of the axial ligands, which is carbonyl in one case and acetyl in the other. The Ni–N distance (2.31 (2) Å) and the three Ni–P distances (2.29 Å (av)) are close to those found in the pure acetyl derivative. Regarding the Ni–C distance (1.90 (5) Å), it is necessary to note that this value is not at all significant because of the lack of resolution of the two positions of the carbon of the carbonyl and that of the acetyl group. This lack in resolution achieves some indetermination also for distances and angles both in carbonyl and acetyl groups; the angle Ni–C–O(carbonyl) is 147.5 (44)°.

The electronic and infrared spectra and the magnetic data are consistent with the presence of the two cations. The two absorption bands shown by the compound in the region of ν(CO) (1988 and 1650 cm^{-1}) coincide respectively with the

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

Selected Bond Lengths

Compound I		Compound II	
Ni-P(1)	2.27 (1)	Ni-P(1)	2.28 (1)
Ni-P(2)	2.29 (2)	Ni-P(2)	2.29 (1)
Ni-P(3)	2.31 (2)	Ni-P(3)	2.30 (1)
Ni-N	2.31 (3)	Ni-N	2.31 (2)
Ni-C(100)	1.97 (6)	Ni-C(100)	1.90 (5)
C(100)-O(1)	1.36 (8)	C(100)-O(1)	1.27 (7)
C(100)-C(101)	1.44 (8)	C(100)-C(101)	1.42 (15)
P(1)-C(2)	1.77 (3)	C(100)-O(2)	1.28 (8)
P(2)-C(4)	1.80 (4)	P(1)-C(2)	1.84 (4)
P(3)-C(6)	1.83 (3)	P(2)-C(4)	1.88 (3)
N-C(1)	1.45 (5)	P(3)-C(6)	1.76 (3)
N-C(3)	1.52 (6)	N-C(1)	1.53 (4)
N-C(5)	1.47 (5)	N-C(3)	1.55 (4)
C(1)-C(2)	1.52 (6)	N-C(5)	1.43 (4)
C(3)-C(4)	1.51 (6)	C(1)-C(2)	1.54 (5)
C(5)-C(6)	1.53 (5)	C(3)-C(4)	1.46 (4)
		C(5)-C(6)	1.57 (4)

Selected Bond Angles

Compound I		Compound II	
P(1)-Ni-P(2)	126.2 (6)	P(1)-Ni-P(2)	122.3 (4)
P(1)-Ni-P(3)	113.8 (6)	P(1)-Ni-P(3)	119.4 (3)
P(1)-Ni-N	84.4 (8)	P(1)-Ni-N	83.9 (8)
P(1)-Ni-C(100)	94.1 (20)	P(1)-Ni-C(100)	93.3 (15)
P(2)-Ni-P(3)	116.8 (6)	P(2)-Ni-P(3)	114.4 (4)
P(2)-Ni-N	84.1 (9)	P(2)-Ni-N	83.8 (7)
P(2)-Ni-C(100)	92.1 (21)	P(2)-Ni-C(100)	96.1 (13)
P(3)-Ni-N	83.7 (8)	P(3)-Ni-N	82.2 (8)
P(3)-Ni-C(100)	102.3 (20)	P(3)-Ni-C(100)	100.9 (16)
N-Ni-C(100)	173.9 (22)	N-Ni-C(100)	176.6 (17)
Ni-C(100)-O(1)	124.3 (42)	Ni-C(100)-O(1)	122.2 (40)
Ni-C(100)-C(101)	105.9 (40)	Ni-C(100)-C(101)	94.2 (58)
O(1)-C(100)-C(101)	124.0 (53)	O(1)-C(100)-C(101)	133.7 (70)
Ni-P(1)-C(2)	101.3 (13)	Ni-C(100)-O(2)	147.5 (44)
Ni-P(2)-C(4)	100.6 (15)	Ni-P(1)-C(2)	102.9 (11)
Ni-P(3)-C(6)	99.3 (13)	Ni-P(2)-C(4)	98.6 (9)
Ni-N-C(1)	106.0 (20)	Ni-P(3)-C(6)	100.6 (11)
Ni-N-C(3)	107.7 (20)	Ni-N-C(1)	109.2 (17)
Ni-N-C(5)	110.6 (21)	Ni-N-C(3)	110.0 (16)
		Ni-N-C(5)	113.2 (21)

ν(CO) values for the carbonyl derivative $[Ni(CO)(np_3)]BPh_4$[17] and with the ν(CO) of the acetyl derivative $[Ni(COCH_3)(np_3)]BPh_4$. Furthermore the relative intensity of each band when compared to one taken as internal standard (e.g., the band at 1620 cm^{-1} present in both compounds) appears at about half the intensity of the corresponding band in either of the two compounds. This is in agreement with the 1:1 ratio found for cations by structural analysis. Electronic spectra, both in the solid state and in 1,2-dichloroethane solutions, have two maxima at 1.37 and 2.13 μm^{-1}. The band with the lower frequency corresponds to the one at 1.25 μm^{-1} reported for the chromophore $[Ni(CO)(np_3)]^+$,[17] while the absorption at higher frequency coincides with that found for the pure acetyl derivative $[Ni(COCH_3)(np_3)]BPh_4$ (Table XI) at 2.13 μm^{-1}. In Figure 5 are reported the reflectance spectra of the compounds $[Ni(CO)(np_3)]BPh_4$ (A) and $[Ni(COCH_3)(np_3)]BPh_4$ (C) and of the solid solution (B). One can see that the spectrum of the solid solution is intermediate between the spectra of the two pure compounds. The compound II is slightly paramagnetic. The value of the magnetic moment, calculated for the formula $[\{Ni(CO)(np_3)\}\cdot\{Ni(COCH_3)(np_3)\}](BPh_4)_2\cdot 4THF$ is 2.1 μ_B. This value, consistent with the presence of one unpaired electron for every two nickel atoms is reasonable in view of the value of μ_{eff} which has been found for $[Ni(CO)(np_3)]BPh_4$ (1.87 μ_B).[17]

Also the products formed from the reaction of $[Ni(C_2H_5)(np_3)]BPh_4$ and $[Ni(CH_2C_6H_5)(np_3)]BPh_4$ show two infrared bands in the CO stretching region, are slightly paramagnetic, and have electronic spectra, both in the solid state and in 1,2-dichloroethane solution, which are similar to those of the solid solution II; it appears, therefore, that these crystalline precipitates are also solid solutions containing acyl and carbonyl derivatives.

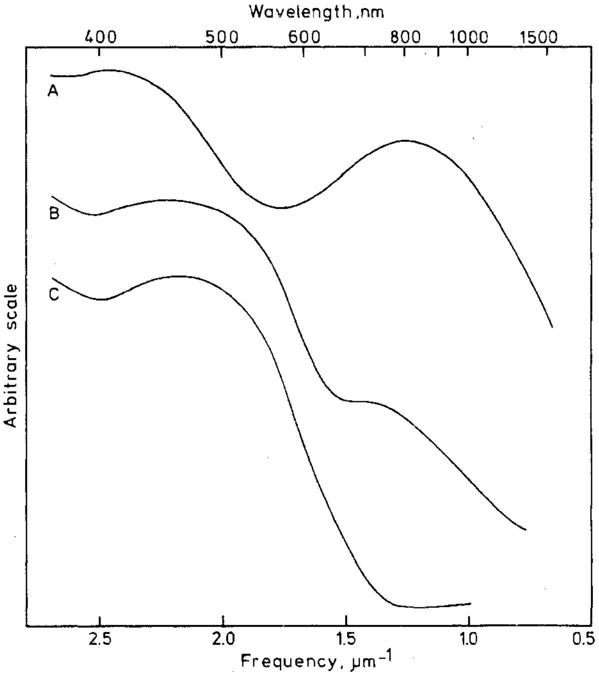
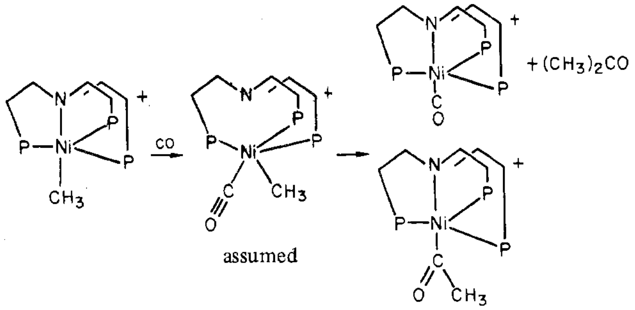


Figure 5. Reflectance spectra of $[Ni(CO)(np_3)]BPh_4$ (A), $[0.5\{Ni(COCH_3)(np_3)\}\cdot 0.5\{Ni(CO)(np_3)\}]BPh_4\cdot 2THF$ (B), and $[Ni(COCH_3)(np_3)]BPh_4\cdot 2.5THF$ (C).

The acetyl derivative spontaneously loses carbon monoxide on exposure to air re-forming the original methyl complex and does not react further with carbon monoxide. This behavior rules out the idea that the carbonyl species in the solid solution is formed subsequent to the decomposition[18] or reductive elimination[19] undergone by the acetyl group. One must therefore postulate that the carbon monoxide is precoordinated to the metal forming an intermediate compound containing a carbonyl and methyl group bound to the metal. The 50:50 composition of the solid solution suggests that half of the methyl radicals migrate to the carbon atom of the carbon monoxide giving the acetyl derivative, while the remaining 50% is cleaved from the metal leaving the carbonyl derivative. The migration of the alkyl group has already been suggested[2] for the insertion reaction of carbon monoxide into M–C σ bonds but has been verified only in the cases of complexes of Mn(I).[20] The hypothesis that the formation of the assumed intermediate involves a nitrogen atom not bound to the metal is supported by the fact that the original methyl derivative is fully coordinated, with the consequence that before the carbon monoxide can coordinate, it is necessary for a coordination site to become available on the nickel. The ability of the ligand np_3 to bind to a metal ion by means only of the three phosphorus atoms



has already been demonstrated from the structure of several nitrosyl and carbonyl derivatives of cobalt[21] and nickel[22] with np_3, in which an apical nitrogen atom is not coordinated to the metal. Further corroboration comes from the fact that for the alkyl derivatives of the ligand pp_3, which differs from np_3 by the presence of a phosphorus in the place of the apical nitrogen, and for whose derivatives no evidence has been found for compounds with the apical donor atom noncoordinated, no carbon monoxide insertion takes place.

Cobalt Complexes. The cobalt(I) five-coordinate complexes having formula $[CoBr(L)]$ (L = np_3, pp_3) react with the stoichiometric amount of the appropriate lithium salt to give crystalline compounds with formula $[CoR(L)]$ (L = np_3, pp_3; R = CH_3, C_6H_5). Analytical data of these complexes are reported in Table I. These cobalt organo complexes are slightly soluble in tetrahydrofuran, benzene, and nitroethane. The solutions of these complexes are stable under nitrogen but decompose quickly in air; in the solid state the compounds are reasonably air-stable. Reflectance spectra are identical with those in solution and show an intense band at ca. 2.25 μm^{-1} (Table XI). All the complexes are diamagnetic, being low-spin d^8 compounds. A trigonal-bipyramidal geometry is assigned to the cobalt.

The five-coordinate cobalt(II) complexes having the general formula $[CoBr(np_3)]BPh_4$ react with Grignard reagents (CH_3MgI and $C_6H_5CH_2MgBr$) to give compounds with formula $[CoR(np_3)]BPh_4$ (R = CH_3, $CH_2C_6H_5$). In Table I analytical data of the complexes are reported; they behave as 1:1 electrolytes in nitroethane solution. The complexes have a μ_{eff} of ca. 2.1 μ_B corresponding to d^7 low spin (Table I). Electronic spectra both in the solid state and in solution show two bands at 7.6 and 2.00 μm^{-1} and two shoulders at ca. 1.00 and 2.63 μm^{-1}, respectively. The features of the spectra are similar to those of cobalt(II) five-coordinate complexes.[23]

The methyl derivative reacts with carbon monoxide to give the corresponding acetyl derivative $[Co(COCH_3)(np_3)]BPh_4$. The C═O stretching vibration is at 1604 cm^{-1}. The compound has a μ_{eff} of 2.18 μ_B (Table I).

The benzyl derivative reacts with carbon monoxide to give the carbonyl derivative $[Co(CO)(np_3)]BPh_4$, previously described. The complex probably reacts in the same way as $(CH_2C_6H_5)_2TiCp_2$.[19]

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Registry No. I, 60790-37-6; II, 65045-69-4; $[Ni(COCH_3)(nas_3)]BPh_4$, 65027-75-0; $[Ni(COC_2H_5)(nas_3)]BPh_4$, 65027-77-2; $[Ni(COCH_2C_6H_5)(nas_3)]BPh_4$, 65027-79-4; $[Ni(COC_2H_5)(np_3)]BPh_4$, 65027-81-8; $[Ni(COCH_2C_6H_5)(np_3)]BPh_4$, 65027-83-0; $[0.5\{Ni(COC_2H_5)(np_3)\}\cdot 0.5\{Ni(CO)(np_3)\}]BPh_4$, 65027-85-2; $[0.5\{Ni(COCH_2C_6H_5)(np_3)\}\cdot 0.5\{Ni(CO)(np_3)\}]BPh_4$, 65027-86-3; $Co(CH_3)(np_3)$, 65027-87-4; $Co(CH_3)(pp_3)$, 65027-72-7; $Co(C_6H_5)(np_3)$, 65027-73-8; $Co(C_6H_5)(pp_3)$, 65036-10-4; $[Co(CH_3)(np_3)]BPh_4$, 65036-12-6; $[Co(CH_2C_6H_5)(np_3)]BPh_4$, 65036-14-8; $[Co(COCH_3)(np_3)]BPh_4$, 65036-16-0; $[Ni(CH_3)(nas_3)]BPh_4$, 62520-88-1; $[Ni(C_2H_5)(nas_3)]BPh_4$, 62520-90-5; $[Ni(CH_2C_6H_5)(nas_3)]BPh_4$, 62520-92-7; $[Ni(CH_3)(np_3)]BPh_4$, 60790-34-3; $[Ni(C_2H_5)(np_3)]BPh_4$, 62520-84-7; $[Ni(CH_2C_6H_5)(np_3)]BPh_4$, 62520-86-9; $[CoBr(np_3)]BPh_4$, 65036-18-2; CO, 630-08-0.

Supplementary Material Available: A listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Stereochemistry of Bis(1,10-phenanthroline) Complexes of Cobalt(III) with *meso*-Tartrate or D-(−)-Malate Ion

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The *meso*-tartratobis(1,10-phenanthroline)cobalt(III) complex has been prepared, and four possible isomers, Δ-LD (Δ isomer containing an L-asymmetric carbon in the chelate ring), Λ-LD, Δ-DL (Δ isomer containing a D-asymmetric carbon in the chelate ring), and Λ-DL, have been separated by column chromatography on SP-Sephadex and CM-Sephadex. These complexes have been characterized by absorption, circular dichroism, infrared, and ^1H NMR spectra. The chromatographic behavior and the formation ratios of these isomers are discussed in comparison with the case of L-(+)- or D-(−)-tartrato complexes. The isolation and spectroscopic data of the two diastereoisomers of the analogous bis(phenanthroline) complexes containing D-(−)-malic acid are also reported.

Introduction

Recently, we have reported the study on the configurationally optically active isomers of $[Co(tart)(phen\ or\ bpy)_2]^+$, where tart is the dinegative L-(+)- or D-(−)-tartrate anion and phen and bpy are 1,10-phenanthroline and 2,2′-bipyridine, respectively.[1] Furthermore, an extension to chromium(III)

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