bis(6-mercaptopurinato)mercury (II), for instance.

Registry No. Dichlorobis(6-mercaptopurine)mercury(II), 56995-00-7.

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

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Synthesis and Properties of Cobalt and Nickel Complexes with the Tripod Ligand Tris(2-diphenylarsinoethyl)amine. Structural Characterization of a σ-Phenyl Complex of Nickel(II) with the Same Ligand

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The "tripod" ligand tris(2-diphenylarsinoethyl)amine, nas$_3$, reacts with cobalt(II) and nickel(II) salts in the presence of sodium borohydride to give complexes of cobalt(I) and nickel(I) having the general formula [MX(nas$_3$)] (M = Co, X = Cl, Br, I; M = Ni, X = Cl, Br, I, NCS, NO$_3$). These compounds are assigned a trigonal-bipyramidal structure. The cobalt(I) complexes are high spin. A trigonal-pyramidal structure is suggested for the ionic compound [Ni(nas$_3$)]BF$_4$. A bound halide ion can be replaced by carbon monoxide yielding cations isolated as the salts [M(CO)(nas$_3$)]BPh$_4$ (M = Co, Ni); the cobalt(I) compound is low spin. The product of the reaction of nickel(II) chloride and sodium tetraphenylborate has the formula [Ni(C$_6$H$_5$)(nas$_3$)]BPh$_4$. In this reaction a phenyl group is transferred from the boron to the nickel atom. An x-ray structural analysis has shown that the complex has a trigonal-bipyramidal structure with a phenyl group σ-bonded in the axial position. Analogous σ-phenyl complexes are formed with other polydentate arsenical ligands.

Introduction

Some years ago we found that the reaction of NiBr$_2$ and NiI$_2$ with the tetradentate ligand tris(2-diphenylarsinoethyl)amine, nas$_3$, in the presence of NaBPh$_4$, yields five-coordinate complexes of the formula [NiX(nas$_3$)]BPh$_4$.[1] The salt NiCl$_2$ yielded a different, chloride-free complex which has now been fully characterized as a five-coordinate nickel(II) complex containing a σ-bonded phenyl group. Analogous compounds incorporating a nickel–carbon σ bond can be obtained if nas$_3$ is replaced by other polydentate ligands containing arsenic donor atoms.

Using NaBH$_4$ two series of five-coordinate cobalt(I) and nickel(I) complexes were obtained having the general formula [MX(nas$_3$)] (M = Co, X = Cl, Br, I; M = Ni, X = Cl, Br, I, NCS, NO$_3$) and the two carbonyl derivatives [M(CO)(nas$_3$)]BPh$_4$ (M = Co, Ni). The nickel(II) tetrafluoroborate gave the complex [Ni(nas$_3$)]BF$_4$, which has been attributed a trigonal-pyramidal geometry.

All the compounds were characterized and their physical properties studied by the usual methods. A complete x-ray determination of the complex [Ni(C$_6$H$_5$)(nas$_3$)]BPh$_4$ has been carried out. Preliminary results of this structure have already appeared.[2]

Experimental Section

All solvents were purified by standard methods. Electronic and infrared spectra, molar conductivities, and other physical measurements were performed using methods described elsewhere.[3]

Synthesis of Ligands. The ligands nas$_3$, tris(*o*-diphenylarsinophenyl)arsine, QAS, and *o*-phenylenebis(dimethylarsine), DAS, were synthetized by published methods.[4]

Tris(2-dimethylarsinoethyl)amine, Me$_6$nas$_3$, was prepared as follows. N(CH$_2$CH$_2$Cl)$_3$[5] (0.124 mol) in anhydrous tetrahydrofuran (50 ml) was added with stirring to NaAsMe$_2$[6] (0.37 mol) in tetrahydrofuran (300 ml). The resulting mixture was heated under reflux for 3 hr and the solvent then removed under reduced pressure. The residue was dissolved in ether, washed with water, and dried over Na$_2$SO$_4$, and the ether was then removed under reduced pressure. The ligand distills at 130°C and 0.5 Torr. The ligand was prepared and stored under nitrogen; yield 43%. Anal. Calcd for C$_{12}$H$_{30}$As$_3$N: C, 34.9; H, 7.3; N, 3.4; As, 54.9. Found: C, 34.9; H, 7.4; N, 3.6; As, 54.8.

Preparation of Complexes. All complexes were prepared and manipulated under dry nitrogen unless otherwise stated.

[NiX(nas$_3$)], X = Cl, Br, I, NO$_3$, BF$_4$. The ligand (1 mmol) in methylene chloride (20 ml) was added to a hot solution of NiX$_2$ (1 mmol) in ethanol (15 ml). NaBH$_4$ (1 mmol) in ethanol (15 ml) was then added to the resulting mixture. The crystals obtained by concentrating the solution were washed with ethanol and light petroleum.

X = NCS. The complex was prepared at room temperature.

[Ni(CO)(nas$_3$)]BPh$_4$. Carbon monoxide was bubbled for 30 min through a suspension of [NiBr(nas$_3$)] (1 mmol) in dry tetrahydrofuran (20 ml). NaBPh$_4$ (1 mmol) in ethanol (10 ml) was then added. The violet-brown product which crystallized on evaporation of the solvent was filtered and washed with ethanol and petroleum ether.

[Ni(C$_6$H$_5$)(nas$_3$)]BPh$_4$. A solution of NaBPh$_4$ (2 mmol) in butanol (15 ml) was added in air to a mixture of NiCl$_2$ (1 mmol) and nas$_3$ (1 mmol) in boiling butanol (50 ml). After partial boil off of the solvent, cherry red crystals formed and were filtered hot, washed with

Table I. Positional Parameters ($\times 10^4$), Anisotropic Temperature Factors[a] ($\times 10^3$), and Estimated Standard Deviations in Parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	2743 (1)	2442 (2)	2316 (2)	49 (2)	51 (2)	35 (2)	−2 (1)	−20 (1)	4 (1)
As(1)	2308 (1)	2022 (1)	914 (1)	58 (2)	54 (2)	40 (1)	−4 (1)	−27 (1)	3 (1)
As(2)	3189 (1)	1029 (1)	3259 (1)	64 (2)	58 (2)	43 (1)	−4 (1)	−26 (1)	12 (1)
As(3)	2513 (1)	4002 (1)	2958 (1)	59 (2)	53 (2)	40 (1)	−2 (1)	−19 (1)	0 (1)
N	1653 (7)	2087 (10)	3322 (10)	73 (11)	48 (10)	61 (10)	−23 (8)	−43 (9)	26 (8)

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

hot butanol, and then recrystallized from methylene chloride and butanol.

Reaction of $[\mathrm{NiBr(nas_3)}]\mathrm{BPh_4}$ with $\mathrm{NaBPh_4}$. The compound (2 mmol) in anhydrous tetrahydrofuran (40 ml) was boiled under reflux for 1 hr. After vacuum distillation of the solvent, a white crystalline sublimate was obtained at 70°C and 0.5 Torr. This air-sensitive product was identified by elemental analysis and infrared spectra as triphenylboron.[7] The sublimation residue was extracted with water and silver halide was precipitated by the addition of silver nitrate. The resulting slurry was extracted with 30 ml of tetrahydrofuran to which was added more $\mathrm{NaBPh_4}$ (2 mmol) in cold ethanol. Crystals of $[\mathrm{Ni(C_6H_5)(nas_3)}]\mathrm{BPh_4}$ (1.5 mmol) appeared and were recrystallized from methylene chloride and butanol.

$[\mathrm{Ni(C_6H_5)(QAS)}]\mathrm{BPh_4}$. The brick red compound was prepared as the previous compound, starting from $[\mathrm{NiCl(QAS)}]\mathrm{BPh_4}$[8] in dimethylformamide.

$[\mathrm{Ni(C_6H_5)(DAS)_2}]\mathrm{BPh_4}$. The complex $[\mathrm{NiCl(DAS)_2}]\mathrm{BPh_4}$[9] (1 mmol) in butanol (30 ml) was boiled under reflux in air for 30 min. Addition of $\mathrm{NaBPh_4}$ (1 mmol in 15 ml of ethanol) and evaporation of the solvent gave orange crystals, which were recrystallized from tetrahydrofuran and butanol.

$[\mathrm{Ni(C_6H_5)(Me_6nas_3)}]\mathrm{BPh_4}$. This cherry red compound was prepared as $[\mathrm{Ni(C_6H_5)(nas_3)}]\mathrm{BPh_4}$ with the ligand dissolved in tetrahydrofuran.

$[\mathrm{CoX(nas_3)}]$, X = Cl, Br, I. These compounds were prepared in a way similar to the preparation of the nickel analogues, with the ligand dissolved in acetone or tetrahydrofuran.

$[\mathrm{Co(CO)(nas_3)}]\mathrm{BPh_4}$. This compound was prepared in a fashion similar to the preparation of the nickel derivative.

Collection and Reduction of X-Ray Intensity Data. The cherry red crystals of $[\mathrm{Ni(C_6H_5)(nas_3)}]\mathrm{BPh_4}$ have a parallelepiped shape. The unit cell is triclinic, space group $P\bar{1}$, as confirmed by successfull refinement of the structure, with $a = 18.132$ (3) Å, $b = 13.377$ (2) Å, $c = 13.162$ (2) Å, $\alpha = 84.65$ (2)°, $\beta = 73.80$ (2)°, $\gamma = 86.93$ (2)°, $V = 3051.1$ Å^3, d_{measd} (by flotation) = 1.34 g cm^{-3}, $Z = 2$, mol wt 1240.55, and $d_{\mathrm{calcd}} = 1.35$ g cm^{-3}. Cell parameters were determined by carefully measuring the setting angles of 20 reflections at room temperature (about 22°C), using the Mo Kα radiation monochromatized by a flat graphite crystal (λ 0.70926 Å), collected on a four-circle Philips automatic diffractometer. The intensity data were also collected on this diffractometer using the same wavelength radiation. The crystal used for the data collection had dimensions 0.50 × 0.15 × 0.05 mm. Data were collected with equatorial geometry using the θ–ω scan technique, with a takeoff angle of 2.0°. The scan across the peak was 1° (for ω) measured in 14 sec; background was counted for 7 sec on each side of the peak. The integrated intensities were calculated by the expression $I = P - (B_1 + B_2)$, where P is the peak count and B_1 and B_2 are the background counts. Three standard reflections were counted periodically every 100 measurements and, on the basis of the variations of the intensity of these standard reflections during the collection, all reflections have been rescaled (no systematic loss of intensity was noticed during the automatic collection). The standard deviations on the intensities were calculated by use of the expression $\sigma(I) = [P + (B_1 + B_2) + (0.02I)^2]^{1/2}$.[10] The 3008 reflections having $I \geq 3\sigma(I)$, in the range $6° < 2\theta < 40°$, on a total of 6035 measured reflections, were considered observed and were used in the structure analysis. These reflections were corrected for absorption by numerical methods ($\mu = 34.34$ cm^{-1}):[11] transmission factors varied between 0.70 and 0.89. The intensities were then corrected for Lorentz and polarization effects. Scattering factors for nonhydrogen atoms (all in the neutral state) were taken from ref 12 and for hydrogen atoms (in the neutral state) from ref 13.

Solution and Refinement of the Structure. A three-dimensional Patterson synthesis yielded the positional parameters of the nickel and arsenic atoms. The other nonhydrogen atoms were located from successive three-dimensional Fourier maps. These calculations were performed on an IBM 1130 computer.[14] At this point the R factor, defined as $\sum||F_o| - |F_c||/\sum|F_o|$, was about 0.20. Refinement was then undertaken on a CII 10070 computer by use of the full-matrix least-squares program of Busing and Levy adapted by Stewart.[15] The function minimized was $\sum w(|F_o| - |F_c|)^2$, in which w is the weight assigned to the F_o values according to the expression $w = 1/\sigma^2(F_o)$, where the $\sigma(F_o)$ values are obtained from the $\sigma(I)$ values. The hydrogen atoms were introduced in calculated positions (C–H distances of 0.9 Å) with an overall B temperature factor of 6 Å^2 and were not refined. Several cycles were carried out with anisotropic temperature factors for nickel, arsenic, and nitrogen atoms and isotropic factors for the carbon and boron atoms. The final conventional R factor was 0.069, and the weighted R factor, defined as $[\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$, was 0.068. A final difference Fourier synthesis showed no remarkable features. The final values of the parameters and their standard deviations, as estimated from the inverse matrix, are reported in Tables I and II.

Results and Discussion

Analytical, magnetic, and conductometric data are set out in Table III. All the complexes possessing $\mathrm{BX_4^-}$ (X = Ph, F) as counterion behave as 1:1 electrolytes in organic solvents.

$[\mathrm{MX(nas_3)}]$, M = Ni, X = Cl, Br, I, NCS, NO$_3$; M = Co, X = Cl, Br, I. Both series of compounds are fairly air stable in the solid state but undergo rapid decomposition in solution, even in an inert atmosphere. Magnetic moments of the nickel complexes are in the region expected for a nickel(I) d^9 ion. Cobalt moments falling in the range 3.30–3.40 BM confirm the presence of high-spin cobalt(I) d^8. Without exception the reflectance spectra for the nickel complexes are representative of other five-coordinated d^9 systems,[16] consisting of two bands at 9–12 and 20–27 kK. Figure 1 shows the virtual superimposability of the $[\mathrm{NiCl(nas_3)}]$ and the $[\mathrm{NiCl(np_3)}]$ spectra, and it is interesting to note the close resemblance between these and the spectrum of $[\mathrm{NiI(np_3)}]$ which has been established by x-ray analysis to have a trigonal-bipyramidal geometry.[16]

The fact that all these complexes incorporate a halide directly coordinated to the metal can be inferred from the spectrochemical shift observed in passing from chloride to iodide. Similarly infrared spectra of the nickel(I) thiocyanate and nitrate show stretching frequencies consistent with a metal–N-bonded thiocyanate (2095 cm^{-1})[17] and a nitrate ligand coordinated to the nickel via an oxygen atom (two N–O stretches at 1288 and 1045 cm^{-1}).[18]

Reflectance spectra for the green crystalline cobalt(I) complexes (Table IV) consisting of four transitions at 8.3–8.9, 10.4–10.8, 12.9–13.8, and 15.5–17.4 kK are comparable with those of the high-spin trigonal-bipyramidal phosphorous analogues $[\mathrm{CoX(np_3)}]$[16] (Figure 2).

$[\mathrm{Ni(nas_3)}]\mathrm{BF_4}$. This light tan compound is fairly soluble in polar organic solvents and has the magnetic properties of a typical d^9 ion. Reflectance and solution spectra show a broad band at 8 kK and a shoulder at ca. 25 kK, though the spectra are more clearly resolved at 110 K (Figure 1). The fact that the main features of these spectra closely resemble those of the complex $[\mathrm{NiH_{0.04}(np_3)}]\mathrm{BF_4}$,[19] also shown in Figure 1 and known to consist mainly of trigonal-pyramidal $[\mathrm{Ni(np_3)}]\mathrm{BF_4}$ species, is strong evidence for the assignment of a similar stereochemistry to the cation $[\mathrm{Ni(nas_3)}]^+$.

In contrast to np$_3$, the nas$_3$ ligand does not seem able to form

Table II. Positional Parameters ($\times 10^4$), Isotropic Temperature Factors ($\times 10^3$), and Estimated Standard Deviations in Parentheses

Atom	*x/a*	*y/b*	*z/c*	*U*, Å^2
C(1)	3671 (10)	2914 (13)	1406 (13)	58 (6)
C(2)	3726 (10)	3597 (13)	550 (14)	55 (5)
C(3)	4446 (11)	3938 (14)	−116 (14)	71 (6)
C(4)	5118 (11)	3603 (15)	70 (16)	82 (7)
C(5)	5125 (12)	2922 (15)	899 (16)	85 (7)
C(6)	4408 (12)	2590 (14)	1568 (15)	73 (6)
C(7)	1199 (10)	1449 (14)	2799 (14)	68 (6)
C(8)	1249 (10)	1833 (13)	1652 (13)	62 (6)
C(9)	1671 (11)	1378 (15)	4316 (15)	82 (7)
C(10)	2222 (10)	528 (13)	4085 (13)	57 (5)
C(11)	1179 (11)	3025 (15)	3678 (15)	93 (7)
C(12)	1570 (9)	3742 (12)	4063 (12)	55 (5)
C(13)	2642 (10)	788 (12)	308 (13)	57 (5)
C(14)	2168 (10)	292 (14)	−235 (14)	74 (6)
C(15)	2443 (12)	−592 (14)	−729 (14)	76 (6)
C(16)	3130 (13)	−964 (16)	−710 (16)	95 (7)
C(17)	3613 (11)	−545 (16)	−189 (16)	86 (7)
C(18)	3329 (11)	350 (14)	300 (14)	65 (6)
C(19)	2287 (10)	2950 (13)	−330 (14)	57 (5)
C(20)	2734 (12)	2731 (16)	−1320 (18)	100 (7)
C(21)	2800 (14)	3535 (20)	−2226 (19)	125 (9)
C(22)	2294 (13)	4278 (16)	−1963 (17)	94 (7)
C(23)	1894 (12)	4609 (16)	−999 (19)	104 (8)
C(24)	1883 (11)	3822 (16)	−140 (16)	87 (7)
C(25)	3673 (9)	1350 (12)	4340 (12)	51 (5)
C(26)	3903 (10)	527 (14)	4992 (15)	76 (6)
C(27)	4230 (11)	809 (14)	5775 (15)	81 (7)
C(28)	4284 (10)	1745 (14)	5974 (15)	73 (6)
C(29)	4069 (11)	2526 (15)	5330 (16)	88 (7)
C(30)	3760 (10)	2313 (13)	4477 (14)	75 (6)
C(31)	3750 (11)	−184 (13)	2756 (13)	58 (5)
C(32)	4464 (13)	−166 (16)	2219 (16)	88 (7)
C(33)	4885 (13)	−1075 (19)	1828 (17)	102 (8)
C(34)	4494 (14)	−1921 (18)	2085 (17)	102 (8)
C(35)	3791 (15)	−1975 (18)	2639 (19)	118 (9)
C(36)	3362 (12)	−1039 (18)	2980 (16)	95 (7)
C(37)	3189 (9)	4651 (11)	3563 (13)	42 (5)
C(38)	2920 (10)	5055 (14)	4562 (15)	72 (6)
C(39)	3409 (11)	5552 (13)	5017 (14)	63 (6)
C(40)	4114 (12)	5609 (14)	4503 (15)	72 (6)
C(41)	4441 (11)	5183 (14)	3550 (15)	77 (6)
C(42)	3933 (11)	4731 (13)	3097 (13)	63 (6)
C(43)	2255 (11)	5183 (13)	2117 (14)	66 (6)
C(44)	2798 (11)	5798 (16)	1601 (16)	81 (7)
C(45)	2596 (14)	6689 (18)	1009 (18)	118 (9)
C(46)	1865 (14)	6743 (16)	891 (17)	101 (8)
C(47)	1300 (13)	6160 (18)	1447 (18)	111 (8)
C(48)	1496 (14)	5296 (18)	2093 (18)	112 (8)
C(49)	−1324 (10)	1825 (14)	4263 (14)	60 (6)
C(50)	−825 (10)	1175 (13)	4668 (14)	58 (5)
C(51)	−663 (10)	1292 (14)	5643 (15)	67 (6)
C(52)	−1007 (13)	2090 (18)	6225 (17)	106 (8)
C(53)	−1518 (16)	2762 (20)	5858 (23)	148 (11)
C(54)	−1680 (13)	2597 (18)	4879 (20)	116 (9)
C(55)	−1387 (10)	503 (12)	2880 (12)	49 (5)
C(56)	−1991 (9)	−118 (13)	3060 (12)	49 (5)
C(57)	−1899 (11)	−1136 (15)	2899 (14)	77 (6)
C(58)	−1146 (13)	−1538 (15)	2586 (15)	86 (7)
C(59)	−531 (12)	−958 (17)	2336 (16)	93 (7)
C(60)	−664 (12)	41 (16)	2516 (15)	80 (7)
C(61)	−2359 (10)	2132 (12)	3141 (13)	52 (5)
C(62)	−2510 (10)	2794 (13)	2311 (13)	64 (6)
C(63)	−3281 (11)	3134 (13)	2356 (14)	69 (6)
C(64)	−3891 (11)	2839 (15)	3185 (16)	79 (6)
C(65)	−3746 (11)	2154 (15)	3990 (15)	80 (6)
C(66)	−2991 (11)	1833 (13)	3973 (14)	66 (6)
C(67)	−876 (11)	2415 (16)	2129 (16)	83 (7)
C(68)	−638 (12)	1986 (16)	1102 (18)	101 (8)
C(69)	−127 (14)	2703 (20)	198 (19)	124 (9)
C(70)	−35 (12)	3564 (18)	526 (18)	104 (8)
C(71)	−186 (13)	4006 (17)	1428 (20)	116 (8)
C(72)	−668 (14)	3305 (20)	2320 (19)	122 (9)
B	−1484 (12)	1666 (16)	3089 (16)	58 (7)

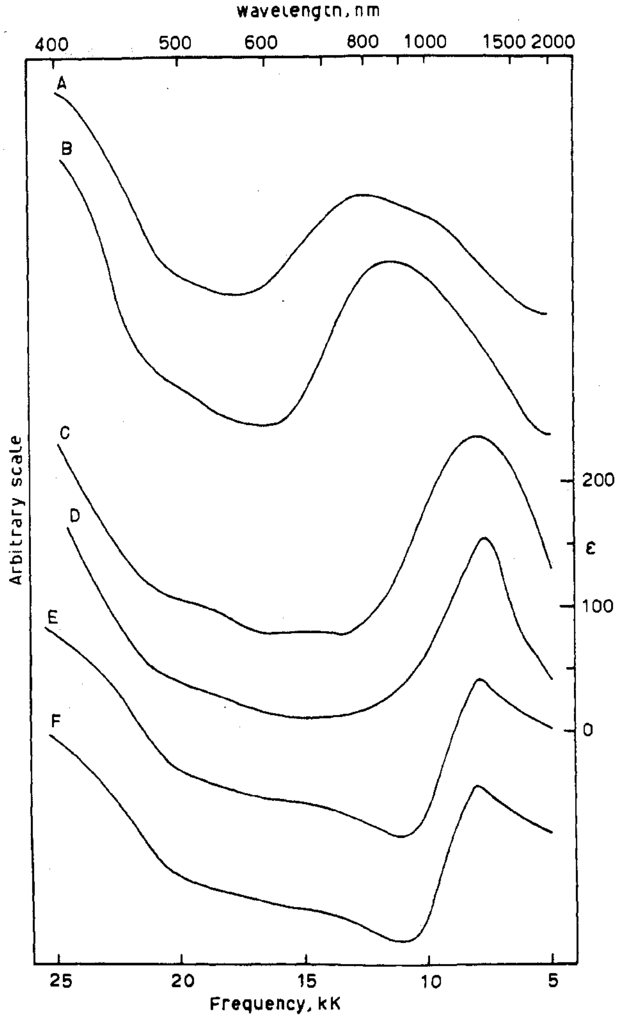

Figure 1. Reflectance spectra of [NiCl(np$_3$)] (A), [NiCl(nas$_3$)] (B), and [Ni(nas$_3$)]BF$_4$ at room temperature (C) and at 110 K (E), and [NiH$_{0.04}$(np$_3$)]BF$_4$ (F). Absorption spectrum of [Ni(nas$_3$)]BF$_4$ in 1,2-dichloroethane (D).

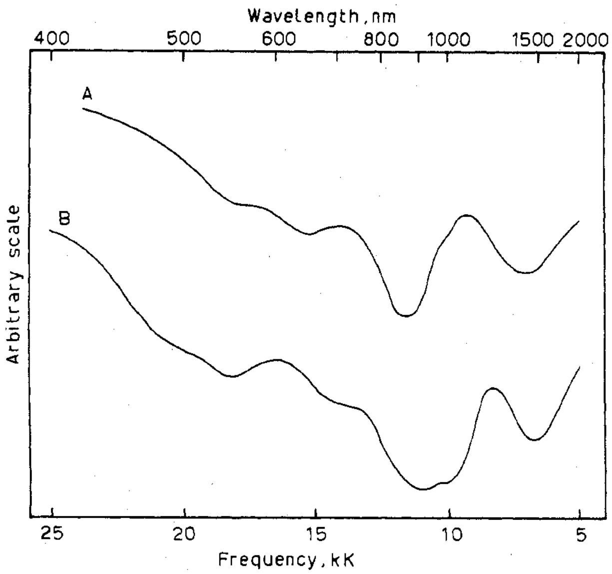

Figure 2. Reflectance spectra of [CoI(np$_3$)] (A) and [CoI(nas$_3$)] (B).

hydride nickel(II) complexes; on reaction of [Ni(H$_2$O)$_6$](BF$_4$)$_2$ with nas$_3$ only the tetracoordinate [Ni(nas$_3$)]$^+$ cation is formed, while both the hydride [NiH(np$_3$)]$^+$ and the tetracoordinate [Ni(np$_3$)]$^+$ are obtained with the phosphorus ligand.

Table III. Physical Constants and Analytical Data

		Λ_M,[a] cm^2 ohm^{-1} mol^{-1}		Anal., %								μ_{eff} (293 K), BM
				Calcd				Found				
Compd	Color	A	B	C	H	N	M	C	H	N	M	
$[NiCl(nas_3)]$[b]	Yellow			57.3	4.8	1.6	6.7	57.5	4.9	1.7	6.6	2.06
$[NiBr(nas_3)]$[c]	Green-yellow			54.6	4.6	1.5	6.3	54.5	4.8	1.6	6.3	2.03
$[NiI(nas_3)]$	Yellow			51.9	4.3	1.4	6.0	51.5	4.4	1.3	6.0	2.09
$[NiNCS(nas_3)]$	Brown			57.2	4.7	3.1	6.5	57.1	4.8	3.2	6.6	2.02
$[NiNO_3(nas_3)]$	Beige			55.7	4.7	3.1	6.5	55.5	4.5	2.9	6.5	2.23
$[Ni(nas_3)]BF_4$	Light tan	21		54.2	4.5	1.5	6.3	54.2	4.7	1.4	6.3	2.17
$[Ni(CO)(nas_3)]BPh_4$	Purple-brown	20		67.5	5.2	1.2	4.9	67.6	5.4	1.1	4.7	2.07
$[Ni(C_6H_5)(nas_3)]BPh_4$[d]	Cherry red	21	50	69.7	5.4	1.1	4.7	69.6	5.6	1.1	4.7	Diam
$[Ni(C_6H_5)(Me_6nas_3)]BPh_4$[e]	Cherry red	25	53	58.1	6.4	1.6	6.8	58.3	6.6	1.6	6.6	Diam
$[Ni(C_6H_5)(DAS)_2]BPh_4$[f]	Orange	26	50	58.5	5.6		5.7	58.5	5.8		5.5	Diam
$[Ni(C_6H_5)(QAS)]BPh_4$[g]	Brick red	26	49	68.8	4.7		4.1	68.8	4.8		3.9	Diam
$[CoCl(nas_3)]$[h]	Yellow-green			57.3	4.8	1.6	6.7	57.0	4.8	1.6	6.7	3.45
$[CoBr(nas_3)]$[i]	Green			54.6	4.6	1.5	6.4	54.3	4.8	1.5	6.3	3.36
$[CoI(nas_3)]$	Green			51.9	4.4	1.4	6.1	51.7	4.5	1.4	5.9	3.33
$[Co(CO)(nas_3)]BPh_4$[j]	Magenta	23		67.5	5.2	1.2	4.9	67.7	5.4	1.1	4.7	Diam

[a] Molar conductance of an ca. 10^{-3} *M* solution in (A) 1,2-dichloroethane and (B) nitroethane at 20°C. [b] Calcd: Cl, 4.0. Found: Cl, 4.1. [c] Calcd: Br, 8.6. Found: Br, 8.7. [d] Calcd: As, 18.1. Found: As, 18.2. [e] Calcd: As, 25.9. Found: As, 25.7. [f] Calcd: As, 29.2. Found: As, 29.3. [g] Calcd: As, 20.7. Found: As, 20.4. [h] Calcd: Cl, 4.0. Found: Cl, 4.1. [i] Calcd: Br, 8.6. Found: Br, 8.5. [j] Calcd: As, 18.9. Found: As, 18.5.

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

Compd	State[a]	Absorption max, kK (ϵ_M for soln)
$[NiCl(nas_3)]$	a	11.7, 27.0 sh
$[NiBr(nas_3)]$	a	11.4, 25.0 sh
$[NiI(nas_3)]$	a	9.4, 25.0 sh
$[NiNCS(nas_3)]$	a	10.3, 20.0 sh
$[NiNO_3(nas_3)]$	a	10.5, 20.0 sh
$[Ni(nas_3)]BF_4$	a	8.0, 25.0 sh
	a′	8.0, 9.1, 20.0 sh
	b	7.7 (158), 20.0 sh
$[Ni(CO)(nas_3)]BPh_4$	a	12.7, 21.1
	b	13.6 (210), 20.0 (1095)
$[Ni(C_6H_5)(nas_3)]BPh_4$	a	20.0
	b	19.6 (3706)
$[Ni(C_6H_5)(Me_6nas_3)]BPh_4$	a	21.7
	a′	21.7, 24.4 sh
	b	21.1 (2400)
$[Ni(C_6H_5)(DAS)_2]BPh_4$	a	20.0 sh, 25.0 sh
	b	20.0 sh, 25.0 (1500)
$[Ni(C_6H_5)(QAS)]BPh_4$	a	21.7
	b	21.6 (1900)
$[CoCl(nas_3)]$	a	<5.0, 8.5, 10.7 sh, 13.1, 17.4
$[CoBr(nas_3)]$	a	<5.0, 8.6, 10.8, 13.5, 16.7
$[CoI(nas_3)]$	a	<5.0, 8.4, 10.5, 13.9, 16.7
$[Co(CO)(nas_3)]BPh_4$	a	19.7
	b	19.7 (3045)

[a] Key: a, diffuse reflectance spectrum at room temperature; a′, diffuse reflectance spectrum at ca. 110 K; b, 1,2-dichloroethane solution.

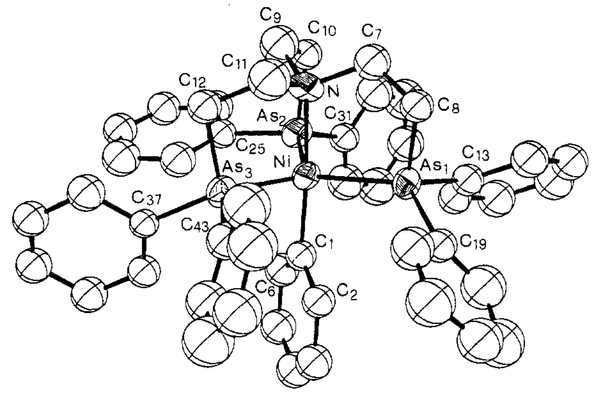

Figure 3. ORTEP diagram of the $[Ni(C_6H_5)(nas_3)]^+$ cation.

$[M(CO)(nas_3)]BPh_4$, M = Co, Ni. These magenta (Co) and purple (Ni) complexes are reasonably air stable as solids and can be dissolved unchanged under anaerobic conditions in polar solvents. The cobalt derivative is diamagnetic, being a low-spin d^8 compound, and shows a C–O stretching vibration at 1850 cm^{-1}. The reflectance and solution spectra show a band at ca. 19.7 kK (Table IV) which is comparable both in frequency and in intensity with the trigonal-bipyramidal d^8 complex $[Ni(C_6H_5)(nas_3)]BPh_4$ (see below). It is reasonable therefore to assign the same stereochemistry to this compound, with the carbonyl group in the axial position.

The magnetic moment of the nickel carbonyl derivative is in accord with a d^9 ion. A carbonyl stretching frequency is observed at 2000 cm^{-1}, while the reflectance spectra comprise two bands at 13 and 20 kK. Assuming the ligand nas_3 used all four potential donor atoms, the effective atomic number of the nickel would be 37. Such a value is clearly untenable and, though there is no direct evidence, it is likely that one donor atom, probably the apical nitrogen, remains uncoordinated, thus constraining the nickel atom to adopt a tetrahedral geometry.

$[Ni(C_6H_5)(L)]BPh_4$, L = nas_3, QAS, $(DAS)_2$, Me_6nas_3. When $NiCl_2$ is treated with nas_3 and $NaBPh_4$ in butanol, there is obtained a cherry red diamagnetic product, which contains no chloride. Under forcing conditions, boiling butanol or tetrahydrofuran, $[NiX(nas_3)]BPh_4$ complexes (X = Br, I) are also converted into the same product, $[Ni(C_6H_5)(nas_3)]BPh_4$. The x-ray analysis of this compound shows that it consists of the ions $[Ni(C_6H_5)(nas_3)]^+$ and BPh_4^-. The nickel atom is pentacoordinate, being bound to the four donor atoms of the ligand nas_3 and to a carbon atom of the phenyl ring. A perspective view of the cation is shown in Figure 3, and selected distances and angles are given in Table V. The phenyl rings in nas_3 and BPh_4^- show no unexpected features. The coordination polyhedron is a distorted trigonal bipyramid with arsenic atoms in the equatorial plane and carbon and nitrogen atoms at the apices. The nickel atom lies 0.16 Å below the equatorial plane (on the carbon side). The distance Ni–As(2) is significantly longer than Ni–As(1) and Ni–As(3). The most probable cause of this is repulsion between the phenyl ring attached to the metal and the phenyl groups attached to As(2). In favor of this hypothesis are the short contact distances H(6)···H(30) (2.73 Å) and H(6)···H(32) (2.35 Å), where the hydrogen atoms are given the same numbers as the carbon atom to which they are attached.

Values of σ-phenyl C–Ni bond length (1.88 and 1.91 Å) based on the sum of covalent radii for an sp^2 carbon (0.73 Å)

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

(A) Selected Bond Lengths

Ni–As(1)	2.323 (3)	N–C(9)	1.55 (2)
Ni–As(2)	2.393 (3)	N–C(11)	1.52 (2)
Ni–As(3)	2.298 (3)	C(1)–C(2)	1.37 (2)
Ni–N	2.099 (11)	C(1)–C(6)	1.45 (3)
Ni–C(1)	1.874 (16)	C(2)–C(3)	1.43 (2)
		C(3)–C(4)	1.35 (3)
As(1)–C(8)	1.91 (2)	C(4)–C(5)	1.36 (3)
As(1)-C(13)	1.90 (2)	C(5)–C(6)	1.42 (3)
As(1)–C(19)	1.97 (2)	B–C(49)	1.68 (3)
As(2)–C(10)	1.91 (2)	B–C(55)	1.60 (3)
As(2)–C(25)	1.96 (2)	B–C(61)	1.66 (3)
As(2)–C(31)	1.94 (2)	B–C(67)	1.71 (3)
As(3)–C(12)	1.93 (1)	C(7)–C(8)	1.53 (3)
As(3)–C(37)	1.92 (2)	C(9)–C(10)	1.47 (3)
As(3)–C(43)	1.96 (2)	C(11)–C(12)	1.43 (3)
N–C(7)	1.54 (3)		

(B) Selected Bond Angles

As(1)–Ni–As(2)	113.8 (1)	Ni–As(2)–C(31)	130.8 (5)
As(1)–Ni–As(3)	122.3 (1)	C(10)–As(2)–C(25)	102.8 (7)
As(1)–Ni–N	87.6 (4)	C(10)–As(2)–C(31)	102.4 (7)
As(1)–Ni–C(1)	92.6 (6)	C(25)–As(2)–C(31)	102.2 (8)
As(2)–Ni–As(3)	122.6 (1)	Ni–As(3)–C(12)	99.3 (5)
As(2)–Ni–N	84.9 (4)	Ni–As(3)–C(37)	124.7 (4)
As(2)–Ni–C(1)	101.1 (6)	Ni–As(3)–C(43)	122.2 (6)
As(3)–Ni–N	85.9 (4)	C(12)–As(3)–C(37)	107.8 (7)
As(3)–Ni–C(1)	88.3 (5)	C(12)–As(3)–C(43)	103.9 (7)
N–Ni–C(1)	173.3 (7)	C(37)–As(3)–C(43)	97.0 (8)
		Ni–N–C(7)	112.4 (9)
Ni–As(1)–C(8)	99.1 (6)	Ni–N–C(9)	114.2 (10)
Ni–As(1)–C(13)	119.4 (6)	Ni–N–C(11)	111.6 (10)
Ni–As(1)–C(19)	124.0 (6)	C(7)–N–C(9)	100.3 (13)
C(8)–As(1)–C(13)	104.3 (7)	C(7)–N–C(11)	109.0 (13)
C(8)–As(1)–C(19)	104.5 (7)	C(9)–N–C(11)	108.8 (12)
C(13)–As(1)–C(19)	102.9 (7)	Ni–C(1)–C(2)	124.4 (14)
Ni–As(2)–C(10)	99.0 (5)	Ni–C(1)–C(6)	122.0 (12)
Ni–As(2)–C(25)	115.5 (5)	C(2)–C(1)–C(6)	113.5 (15)

and a nickel atom (1.15 and 1.18 Å)[20,21] agree remarkably well with the observed value of 1.87 (2) Å.

In the σ-phenyl group the CCC angle, 113.5 (15)°, with the donor atom at the apex is considerably less than 120°. This distortion from the ideal sp^2 value has been found also in the two above-mentioned complexes containing Ni–C(aryl) bonds, and it has been attributed to the existence of a bond order higher than 1 in the linkage between the metal atom and the phenyl ring.

Analogous σ-phenyl derivatives can be obtained from $[NiCl(DAS)_2]^+$ and $[NiCl(QAS)]^+$ in the presence of excess BPh_4^- under forcing conditions. All compounds of the type $[Ni(C_6H_5)(L)]BPh_4$ are 1:1 electrolytes in dichloroethane and nitroethane and their reflectance and solution spectra show a band between 20 and 25 kK which is typical of five-coordinate nickel(II).

In these reactions tetraphenylborate has been unambiguously confirmed as the source of the phenyl groups coordinated to the metal by the preparation of the complex $[Ni(C_6H_5)(Me_6nas_3)]BPh_4$ in which the ligand does not possess a phenyl group. The mode of formation of these compounds can therefore be summarized by

$$2[NiX(L)BPh_4 \rightarrow [Ni(C_6H_5)(L)]BPh_4 + BPh_3 + NiX_2 + L$$

(X = halogen)

$$NiCl_2 + L + 2NaBPh_4 \rightarrow [Ni(C_6H_5)(L)]BPh_4 + 2NaCl + BPh_3$$

where L represents a poly(tertiary arsine) or two DAS ligands. Both BPh_3 and free halide have been confirmed in the reaction mixtures. It is a peculiar feature of these reactions that if nas_3 is replaced by the phosphorus analogue np_3, no reaction occurs with the BPh_4^- ion. All of the above-mentioned σ-phenyl complexes were also obtained from the reaction of phenylmagnesium bromide with the bromo complexes $[NiBr(L)]BPh_4$ in tetrahydrofuran.

This series of reactions highlights a new aspect of the nature of the BPh_4^- ion, (i) acting as an orthodox reducing agent as, for example, in the formation of $[Ni_2(NN)_4Br_2]BPh_4$ from nickel(II) salts (NN = 1,8-naphthyridine)[23] and (ii) acting, under suitable conditions as a provider of phenyl groups to transition metal ions.

Interestingly this mode of behavior closely parallels that of the BH_4^- ion. The analogy between the reactions of BPh_4^- and BH_4^- can be expressed schematically as

$$2BH_4^- \rightarrow B_2H_6 + 2H^- \qquad (1)$$

$$2BH_4^- \rightarrow B_2H_6 + H_2 + 2e^- \qquad (2)$$

$$2BPh_4^- \rightarrow 2BPh_3 + 2Ph^- \qquad (3)$$

$$2BPh_4^- \rightarrow 2BPh_3 + Ph_2 + 2e^- \qquad (4)$$

in which Ph_2 signifies diphenyl.

Transfer of a phenyl group from BPh_4^- to mercury,[24] platinum,[25] and ruthenium[26] has already been reported, as has its reducing action on copper(II) to give copper(I). However, this is the first time that behavior of BPh_4^- and BH_4^- toward 3d metal ions has been systematically correlated.

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Registry No. $[NiCl(nas_3)]$, 57215-16-4; $[NiBr(nas_3)]$, 57287-14-6; $[NiI(nas_3)]$, 57287-15-7; $[NiNCS(nas_3)]$, 57215-17-5; $[NiNO_3(nas_3)]$, 57215-18-6; $[Ni(nas_3)]BF_4$, 57215-20-0; $[Ni(CO)(nas_3)]BPh_4$, 57215-22-2; $[Ni(C_6H_5)(nas_3)]BPh_4$, 53450-18-3; $[Ni(C_6H_5)(Me_6nas_3)]BPh_4$, 57215-24-4; $[Ni(C_6H_5)(DAS)_2]BPh_4$, 57215-26-6; $[Ni(C_6H_5)(QAS)]BPh_4$, 57215-28-8; $[CoCl(nas_3)]$, 57215-29-9; $[CoBr(nas_3)]$, 57215-30-2; $[CoI(nas_3)]$, 57215-31-3; $[Co(CO)(nas_3)]BPh_4$, 57215-33-5; BPh_4^-, 4358-26-3; Me_6nas_3, 57214-93-4; $N(CH_2CH_2Cl)_3$, 555-77-1; $NaAsMe_2$, 13787-40-1; $[NiBr(nas_3)]BPh_4$, 15051-12-4; $[NiCl(DAS)_2]BPh_4$, 57215-34-6; $[NiCl(QAS)]BPh_4$, 33774-40-2.

Supplementary Material Available: Listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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