complexes with trans[26] and cis[27] configurations, respectively. In the cis complex $Ni(VII)I_2$ the nickel–oxygen distances, 2.25 and 2.18 Å, and the nickel–nitrogen distances, 2.06 and 2.03 Å, are significantly longer than in the trans complex and compare more closely with the analogous cobalt bonds in Co(*O*-en-*N*-tn)$(NCS)_2$.

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Registry No. II, 62375-57-9; III, 62375-56-8; IV, 25440-16-8; [Co(*O*-en-*N*-tn)Cl]ClO_4, 62393-00-4; [Co(*O*-en-*N*-tn)Br]ClO_4, 62392-98-7; [Co(*O*-en-*N*-tn)I]ClO_4, 62431-04-3; Co(*O*-en-*N*-tn)I_2, 62392-96-5; *trans*-Co(*O*-en-*N*-tn)$(NCS)_2$, 62445-35-6; *cis*-Co(*O*-en-*N*-tn)$(NCS)_2$, 62392-95-4; Co(Cl_2Ph_2-*O*-en-*N*-en)Cl_2, 62392-94-3; Co(Cl_2Ph_2-*O*-en-*N*-en)Br_2, 62392-93-2; Co(Cl_2Ph_2-*O*-en-*N*-pn)I_2, 62448-24-2.

Supplementary Material Available: Listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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Synthesis, Properties, and X-Ray Structural Characterization of Cationic Five-Coordinate σ-Alkylnickel(II) Compounds with Poly(tertiary phosphines and arsines)

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Cationic five-coordinate nickel(II) compounds containing a nickel–carbon σ bond with the general formula $[NiR(L)]BPh_4$ (L = tris(2-diphenylphosphinoethyl)amine, np_3; tris(2-diphenylarsinoethyl)amine, nas_3; tris(2-diphenylphospinoethyl)phosphine, pp_3; R = CH_3, C_2H_5, or $CH_2C_6H_5$) were synthesized by reaction of the five-coordinate complexes $[NiX(L)]BPh_4$ (X = halogen) with the appropriate Grignard reagents. The structure of the $[Ni(CH_3)(np_3)]BPh_4 \cdot CH_3COCH_3$ derivative was determined by x-ray analysis using diffractometric data. The crystals are monoclinic, space group $P2_1/c$ with cell dimensions $a = 12.514$ (2) Å, $b = 20.234$ (3) Å, $c = 24.214$ (4) Å, $\beta = 103.23$ (2)°. The structure was solved by three-dimensional Patterson and Fourier syntheses and refined by least-squares techniques to a final conventional R factor of 0.061 over the 1738 independent observed reflections. The structure consists of $[Ni(CH_3)(np_3)]^+$ cations, of tetraphenylborate anions, and of interposed acetone molecules. The chromophore is a distorted trigonal bipyramid with the methyl group linked to the nickel in an axial position, the Ni–C distance being 2.02 (2) Å. An analogous trigonal-bipyramidal geometry is assigned to all of the σ-carbon-bonded complexes on the basis of physical data.

Introduction

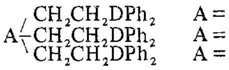
Most of the alkyl- and arylnickel(II) complexes so far described are four-[1] or six-coordinate.[2] Apart from the cyclopentadienyl derivatives,[3] which only formally can be considered as five-coordinate, only two five-coordinate organonickel complexes have been reported, namely, $[((CH_3)_3P)_4Ni(CH_3)]^+$,[2] and $[Ni(C_6H_5)(nas_3)]^+$,[4] where nas_3 is the tripod tetradentate ligand tris(2-diphenylarsino-

Table I. Positional Parameters (× 10^4), Anisotropic Temperature Factors[a] (×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	−327 (2)	3178 (1)	4673 (1)	47 (2)	33 (2)	32 (2)	1 (2)	10 (1)	−3 (2)
P(1)	1074 (4)	3125 (3)	5442 (2)	47 (4)	40 (4)	34 (4)	3 (4)	1 (3)	−3 (4)
P(2)	7 (4)	3450 (3)	3842 (2)	51 (4)	41 (4)	37 (4)	−1 (3)	2 (3)	−1 (3)
P(3)	−1951 (4)	2796 (3)	4765 (2)	49 (4)	44 (4)	48 (4)	−8 (4)	7 (3)	−2 (3)
N	49 (10)	2193 (6)	4505 (5)	43 (11)	62 (12)	44 (11)	−11 (9)	26 (9)	6 (9)
C(1)	−731 (14)	4122 (8)	4810 (7)	63 (18)	45 (14)	32 (14)	0 (12)	0 (12)	14 (11)

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

ethyl)amine. The particular ability shown by the nas_3 ligand in stabilizing five-coordinate cationic organonickel compounds prompted us to attempt to synthesize σ-alkyl derivatives of this metal using as coligands the same ligands nas_3 and the analogous tripodlike poly(tertiary phosphines) tris(2-diphenylphosphinoethyl)amine, np_3, and tris(2-diphenylphosphinoethyl)phosphine, pp_3.


$$A\begin{cases} CH_2CH_2DPh_2 \\ CH_2CH_2DPh_2 \\ CH_2CH_2DPh_2 \end{cases}$$

A = N D = P L = np_3
A = N D = As L = nas_3
A = P D = P L = pp_3

Thus we found that the five-coordinate nickel derivatives having the general formula $[NiX(L)]BPh_4$ (L = np_3, nas_3, pp_3; X = halogen) react easily with alkyl Grignards to form alkyl cationic complexes with the general formula $[NiR(L)]BPh_4$ (R = CH_3, C_2H_5, $CH_2C_6H_5$). In these complexes the alkyl group is σ-bonded to the nickel atom which therefore is really pentacoordinate. All of the compounds, which are quite air stable in the solid state, were characterized by conductivity, ^1H NMR, and spectroscopic measurements. The structure of $[Ni(CH_3)(np_3)]BPh_4 \cdot CH_3COCH_3$ has been determined by a complete x-ray analysis.

Experimental Section

The solvents were dried by standard methods. All reactions were run under a nitrogen atmosphere in a small Schlenk-type flask containing a magnetic stirring bar. The ligands np_3 and nas_3 were prepared by previously described techniques,[5] and the ligand pp_3 was obtained from Pressure Chemical Co..

Physical Measurements. Magnetic, conductometric, and spectrophotometric (both visible and infrared) measurements were carried out using methods already described.[6] Proton magnetic resonance spectra were recorded with a Varian CFT 20 spectrometer equipped with a ^1H probe. The peaks were calibrated with the internal-lock technique on deuterium. The solutions in C^2HCl_3 and $(C^2H_3)CO$ were prepared under nitrogen and then poured into the sample tube which was sealed.

Synthesis of the Complexes. $[NiR(L)]BPh_4$ (L = np_3, R = CH_3; L = nas_3, R = CH_3, C_2H_5; L = pp_3, R = CH_3, C_2H_5, $CH_2C_6H_5$). A solution of the appropriate bromide Grignard reagent (1 mmol) in ether was slowly added at 0 °C to the complex $[NiX(L)]BPh_4$ (1 mmol) dissolved in tetrahydrofuran (30 mL). The resulting solution was stirred for 15 min and then hydrolyzed with a few drops of water and filtered; the crystalline products were obtained by concentration under vacuum and by addition of absolute ethanol. The compounds were filtered and then washed with absolute ethanol and petroleum ether. The compounds were recrystallized from acetone or chloroform and absolute ethanol.

$[NiR(L)]BPh_4$ (L = np_3, R = C_2H_5, $CH_2C_6H_5$; L = nas_3, R = $CH_2C_6H_5$). The stoichiometric amount of the Grignard reagent in ether was slowly added at 0 °C to a suspension of the complex $[NiX(L)]BPh_4$ in ether (40 mL); the resulting slurry was stirred for 30 min. The ether was then removed under vacuum and the residue was dissolved in tetrahydrofuran (30 mL); the solution was filtered. Crystals were obtained by concentration under vacuum. The products were filtered, washed with absolute ethanol and petroleum ether, and dried under nitrogen.

Collection and Reduction of X-Ray Intensity Data. The red crystals of $[Ni(CH_3)(np_3)]BPh_4 \cdot CH_3COCH_3$, which are air stable, are parallelepipeds. The crystal used for the data collection had dimensions 0.3 × 0.1 × 0.1 mm. The unit cell is monoclinic, space group $P2_1/c$, with a = 12.514 (2) Å, b = 20.234 (3) Å, c = 24.214 (4) Å, β = 103.23 (2)°, V = 5968.4 Å^3, d_{measd} = 1.22 g cm^{-3}, Z = 4, mol wt 1104.72, and d_{calcd} = 1.23 g cm^{-3}. Cell parameters were determined by least-squares refinement of 20 reflections centered on a four-circle Philips PW 1100 automatic diffractometer at about 22 °C using the Mo Kα radiation (λ 0.7107 Å). The intensity data were collected, again on this Philips diffractometer, in the range $4° \leq 2\theta \leq 40°$ using the Mo Kα radiation monochromatized by a flat graphite crystal. The method used was the θ–ω scan technique: scans of 0.7° in 10 s were taken across the peaks (background was counted for 5 s on each side of the peak). On the basis of the intensities of three standard reflections, which were measured periodically during the data collection, the intensities of all reflections were automatically rescaled (no systematic loss of intensity was noticed during the collection). The standard deviations on the intensities were calculated by the expression $\sigma(I) = [P - 0.25(B_1 + B_2)(T_p/T_b) + (0.02I)^2]^{1/2}$,[7] where P is the peak count, B_1 and B_2 are the counts, T_p and T_b are the count times on the peak and background, respectively, and I is the intensity itself.

The 1738 reflections having $I \geq 2\sigma(I)$ were considered observed and were used in the structure analysis (about 30% of the collected reflections). An absorption correction (μ = 4.5 cm^{-1}) was applied by a numerical method:[8] transmission factors varied between 0.94 and 0.96. The intensities were corrected for Lorentz and polarization effects. Atomic scattering factors for nickel, phosphorus, oxygen, nitrogen, carbon, and boron atoms were taken from ref 9 (all in the neutral state); those for hydrogen atoms, from ref 10 (in the neutral state).

Solution and Refinement of the Structure. The position of the nickel and phosphorus atoms were obtained from a three-dimensional Patterson synthesis. Two three-dimensional Fourier syntheses showed the positions of all nonhydrogen atoms of the structure. Refinement was performed with the full-matrix least-squares program of Busing and Levy, adapted by Stewart.[11] The minimized function was $\sum w(|F_o| - |F_c|)^2$, where w is the weight assigned to the F_o values, according to the expression $w = 1/\sigma^2(F_o)$. Anisotropic temperature factors were used for nickel, for nitrogen atoms, and for the carbon atom linked to the nickel atom; isotropic temperature factors were used for the other atoms. The hydrogen atoms of the np_3 ligand and of the tetraphenylborate group were introduced in calculated positions (C–H = 0.95 Å) with temperature factors $B_H = 1 + B_{C(attached)}$. A ΔF Fourier synthesis calculated in the final stage of the refinement showed the three hydrogen atoms of the methyl group linked to the nickel atom (the heights of these peaks are 0.47, 0.38, and 0.35 e Å^{-3}). In the last refinement cycle these hydrogen atoms were also introduced in the ΔF Fourier positions and were not refined. The final conventional R factor was 0.061, and the R_w factor, defined as $\sum[w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, was 0.062. The positional and thermal parameters of the atoms are reported in Tables I and II.

Results and Discussion

The complexes here reported are formed by substituting an alkyl group from the appropriate Grignard reagent for the halogen of the five-coordinate complexes $[NiX(L)]BPh_4$ (L = np_3, nas_3, pp_3). This is the first example of formation of cationic σ-alkylmetal complexes by reaction of Grignard reagents with cationic halo compounds. In fact the few cationic aryl and alkyl compounds of d^8 metals[2,12] so far described are obtained either by extracting a coordinated anionic ligand from a metal complex or by replacing such a ligand with a neutral one. The substitution reaction for the pp_3 derivatives may be carried out at room temperature, while for the np_3 and nas_3 derivatives the temperature must be kept at 0 °C; higher temperatures lead to the formation of nick-

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(2)	1227 (14)	2045 (8)	4778 (7)	53 (6)
C(3)	1517 (13)	2260 (8)	5415 (7)	49 (6)
C(4)	−88 (15)	2101 (9)	3866 (7)	60 (6)
C(5)	385 (13)	2648 (8)	3602 (7)	46 (6)
C(6)	−663 (14)	1717 (9)	4720 (7)	55 (6)
C(7)	−1848 (15)	1914 (9)	4592 (7)	67 (7)
C(8)	924 (14)	3207 (9)	6168 (7)	56 (6)
C(9)	162 (16)	3639 (9)	6292 (8)	65 (7)
C(10)	73 (16)	3743 (10)	6865 (9)	80 (7)
C(11)	821 (17)	3412 (10)	7286 (9)	89 (8)
C(12)	1576 (18)	3028 (11)	7177 (10)	97 (8)
C(13)	1702 (16)	2897 (10)	6614 (9)	89 (8)
C(14)	2319 (15)	3627 (9)	5475 (7)	48 (6)
C(15)	3204 (21)	3405 (11)	5260 (9)	100 (9)
C(16)	4126 (21)	3792 (14)	5265 (10)	113 (10)
C(17)	4133 (19)	4388 (12)	5515 (9)	86 (8)
C(18)	3304 (19)	4644 (10)	5730 (8)	80 (7)
C(19)	2369 (15)	4241 (10)	5709 (8)	63 (7)
C(20)	1080 (15)	4000 (9)	3722 (9)	55 (6)
C(21)	1313 (16)	4036 (9)	3184 (8)	63 (7)
C(22)	2132 (17)	4436 (10)	3090 (9)	69 (7)
C(23)	2703 (17)	4812 (10)	3500 (10)	78 (7)
C(24)	2477 (17)	4824 (10)	4053 (9)	79 (7)
C(25)	1670 (17)	4394 (10)	4157 (9)	71 (7)
C(26)	−1155 (14)	3752 (8)	3290 (7)	54 (6)
C(27)	−1372 (15)	4410 (9)	3247 (8)	52 (6)
C(28)	−2312 (17)	4646 (10)	2851 (9)	70 (7)
C(29)	−2989 (17)	4198 (12)	2519 (9)	74 (7)
C(30)	−2810 (18)	3560 (11)	2548 (9)	83 (7)
C(31)	−1877 (15)	3306 (9)	2943 (8)	69 (7)
C(32)	−3302 (13)	3032 (8)	4328 (7)	53 (6)
C(33)	−3412 (16)	3506 (9)	3935 (8)	56 (7)
C(34)	−4481 (17)	3657 (10)	3587 (9)	83 (8)
C(35)	−5368 (16)	3304 (10)	3645 (8)	80 (7)
C(36)	−5264 (18)	2826 (11)	4040 (9)	96 (8)
C(37)	−4222 (17)	2664 (10)	4377 (8)	74 (7)
C(38)	−2236 (15)	2808 (10)	5474 (8)	51 (6)
C(39)	−2794 (16)	3347 (10)	5642 (9)	69 (7)
C(40)	−2953 (17)	3373 (10)	6206 (10)	75 (7)
C(41)	−2542 (17)	2907 (11)	6582 (9)	76 (8)
C(42)	−2009 (18)	2380 (12)	6426 (10)	90 (8)
C(43)	−1850 (15)	2330 (10)	5869 (9)	67 (7)
C(44)	3638 (13)	4061 (8)	1407 (8)	43 (6)
C(45)	4199 (15)	3836 (9)	1002 (8)	50 (6)
C(46)	4766 (15)	3235 (11)	1047 (8)	72 (6)
C(47)	4768 (14)	2847 (9)	1503 (8)	58 (6)
C(48)	4250 (15)	3042 (9)	1902 (7)	54 (6)
C(49)	3670 (14)	3638 (9)	1849 (7)	52 (6)
C(50)	1783 (13)	4694 (9)	1517 (7)	45 (6)
C(51)	1215 (14)	4103 (9)	1496 (7)	56 (6)
C(52)	183 (17)	4009 (10)	1654 (9)	84 (8)
C(53)	−273 (16)	4574 (11)	1793 (8)	65 (7)
C(54)	186 (18)	5141 (10)	1823 (8)	71 (7)
C(55)	1195 (16)	5221 (9)	1675 (8)	68 (7)
C(56)	3671 (14)	5322 (9)	1782 (7)	50 (6)
C(57)	3684 (16)	6012 (11)	1694 (9)	83 (8)
C(58)	4197 (20)	6481 (12)	2083 (11)	107 (9)
C(59)	4868 (19)	6278 (12)	2578 (10)	91 (3)
C(60)	4894 (16)	5618 (10)	2715 (8)	74 (7)
C(61)	4328 (13)	5146 (8)	2321 (7)	45 (6)
C(62)	2706 (16)	5033 (8)	687 (7)	42 (6)
C(63)	1704 (17)	4942 (9)	285 (9)	66 (7)
C(64)	1552 (16)	5168 (9)	−287 (8)	60 (7)
C(65)	2369 (17)	5452 (9)	−457 (8)	53 (6)
C(66)	3406 (16)	5545 (9)	−98 (9)	62 (7)
C(67)	3550 (14)	5336 (9)	464 (8)	56 (6)
B	2957 (16)	4786 (10)	1350 (9)	42 (7)
O[a]	2450 (11)	1669 (7)	3686 (6)	101 (5)
C(68)	3094 (18)	1215 (12)	3825 (10)	90 (8)
C(69)	3227 (16)	691 (10)	3423 (9)	85 (8)
C(70)	3708 (14)	1193 (8)	4457 (8)	56 (6)
H(1)[b]	−0.125	0.432	0.446	
H(2)	−0.117	0.400	0.510	
H(3)	−0.027	0.452	0.500	

[a] Atoms of the acetone. [b] H atoms of the CH_3 group linked to the nickel. These positions are those of the ΔF synthesis.

el(I)–halo complexes,[13] probably through a reductive elimination of the type

$$2[NiR(L)]^+ + 2X^- \rightarrow R_2 + 2[NiX(L)]$$

Analytical data for the compounds are reported in Table III. These alkyl derivatives are fairly air stable and diamagnetic in the solid state; they are readily soluble in polar organic solvents without decomposition under inert atmosphere and behave as 1:1 electrolytes in 1,2-dichloroethane and nitroethane solutions (Table III); such solutions quickly decompose in the air.

Spectral data for the solid compounds and their solutions in 1,2-dichloroethane and nitroethane are shown in Table IV. The electronic spectra of the complexes both in the solid state and in solution show an intense band in the range 2.02–2.42 μm^{-1} (ϵ 1800–4500); some compounds show also another weak band (ϵ <100) between 1.03 and 1.72 μm^{-1} which is probably due to some impurity. The frequency of the first band for the various compounds is shifted in accordance with the relative position of the donor atoms of the ancillary ligands in the spectrochemical series N < As < P. For each series of complexes with the same tripod ligand the frequency of such bands decreases in the order $CH_3 > C_2H_5 > CH_2C_6H_5$. These spectra can be correlated with those of the corresponding trigonal-bipyramidal nickel(II) complexes with the formula $[NiX(L)]BPh_4$[14] where X = halogen and L = np_3, nas_3, or pp_3. Although the symmetry of the complexes is lower than D_{3h}, it is still reasonable to use the splitting scheme for d orbitals in D_{3h} symmetry;[15] in this case the intense band shown by these compounds 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 $[NiX(L)]BPh_4$ by the presence of the alkyl radicals, probably masks the expected band of the $(a_1')^2 \rightarrow a_1'e''$ transition.

Nuclear magnetic resonance spectra of the alkyl radical of the complexes are reported in Table V. The assignments were made by comparing the spectra of the complexes with different alkyl radicals bonded to the metal. A quartet is observed in the spectrum of $[Ni(CH_3)(np_3)]BPh_4$, suggesting an equivalence of the three phosphorus atoms of the ligand and, therefore, a trigonal-bipyramidal geometry for the compound. The doublet of quartets shown by the methyl derivative of the pp_3 ligand suggests that this complex too has a trigonal-bipyramidal geometry with the three equatorial phosphorus atoms being nonequivalent to the apical phosphorus atom. The same trigonal-bipyramidal geometry must be assigned also to the other complexes even if the fine structure of their resonance is not resolved.

A complete x-ray structural analysis has been carried out on the acetone adduct of the methyl derivative $[Ni(CH_3)(np_3)]BPh_4$. The structure of the compound consists of $[Ni(CH_3)(np_3)]^+$ cations and of tetraphenylborate anions with interposed acetone molecules. The nickel atom is five-coordinate, linked to the four donor atoms of the np_3 ligand and to the carbon atom of the methyl group. The geometry of the coordination polyhedron can be considered as a distorted trigonal bipyramid with the three phosphorus atoms in the equatorial plane and the nitrogen and carbon atoms in apical positions (Figure 1). Table VI lists selected intramolecular distances and angles with their estimated standard deviations. The Ni–C distance, 2.02 (2) Å, is quite reasonable, being just a little longer than the Ni–C(methyl) distances found in other four-coordinate nickel complexes (1.97 and 1.94 Å).[16,17] On the other hand this distance is larger by 0.15 Å than the Ni–C(phenyl) distance, 1.87 Å, found in the five-coordinate trigonal-bipyramidal $[Ni(C_6H_5)(nas_3)]BPh_4$ complex.[4] This difference may be ascribed only partially to the difference between the covalent radii of sp^3- and sp^2-hybridized carbon atoms in the two complexes, 0.04 Å.[3] The trans effect cannot

Table III. Physical Constants and Analytical Data

		Λ_M,[a] cm^2 Ω^{-1} mol^{-1}		Anal, %							
				Calcd				Found			
Compd	Color	A	B	C	H	N	M	C	H	N	M
[Ni(CH$_3$)(np$_3$)]BPh$_4$·CH$_3$COCH$_3$	Brick red	22	48	76.1	6.5	1.3	5.3	76.1	6.5	1.2	5.1
[Ni(C$_2$H$_5$)(np$_3$)]BPh$_4$[b]	Brick red	23	48	77.0	6.4	1.3	5.5	76.7	6.4	1.3	5.4
[Ni(CH$_2$C$_6$H$_5$)(np$_3$)]BPh$_4$	Purple	23	42	78.1	6.2	1.2	5.2	77.6	6.2	1.2	5.0
[Ni(CH$_3$)(nas$_3$)]BPh$_4$[c]	Brick red	24	45	68.3	5.6	1.2	5.0	68.3	5.5	1.2	5.0
[Ni(C$_2$H$_5$)(nas$_3$)]BPh$_4$	Brick red	26	49	68.5	5.7	1.2	4.9	68.2	5.9	1.2	4.8
[Ni(CH$_2$C$_6$H$_5$)(nas$_3$)]BPh$_4$[d]	Purple	24	42	69.9	5.5	1.1	4.7	70.0	5.7	1.0	4.7
[Ni(CH$_3$)(pp$_3$)]BPh$_4$[e]	Green	24	45	75.6	6.2		5.5	75.1	6.1		5.4
[Ni(C$_2$H$_5$)(pp$_3$)]BPh$_4$	Green	23	45	75.7	6.4		5.4	75.1	6.1		5.2
[Ni(CH$_2$C$_6$H$_5$)(pp$_3$)]BPh$_4$	Brown	24	46	76.9	6.1		5.1	76.3	6.2		5.0

[a] Molar conductance of a ca. 10^{-3} M solution in (A) 1,2-dichloroethane and (B) nitroethane at 20 °C. [b] Calcd: P, 8.8. Found: P, 8.6. [c] Calcd: As, 19.1. Found: As, 18.8. [d] Calcd: As, 17.9. Found: As, 17.6. [e] Calcd: P, 11.6. Found: P, 11.4.

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

Compd	State[a]	Absorption max, μm^{-1} (ϵ_{molar} for soln)
[Ni(CH$_3$)(np$_3$)]BPh$_4$·CH$_3$COCH$_3$	a	1.38, 2.22
	b	1.33 (86), 2.20 (4300)
	c	1.41 (80), 2.20 (3500)
[Ni(C$_2$H$_5$)(np$_3$)]BPh$_4$	a	1.32, 2.17
	b	1.33 (60), 2.15 (4200)
	c	1.33 (70), 2.15 (3800)
[Ni(CH$_2$C$_6$H$_5$)(np$_3$)]BPh$_4$	a	1.28 sh, 1.96
	b	1.31 sh, 1.96 (2580)
	c	1.96 (2880)
[Ni(CH$_3$)(nas$_3$)]BPh$_4$	a	1.16, 2.10
	b	2.06 (3750)
	c	2.06 (3460)
[Ni(C$_2$H$_5$)(nas$_3$)]BPh$_4$	a	1.33, 2.04
	b	1.38 (85), 2.02 (3220)
[Ni(CH$_2$C$_6$H$_5$)(nas$_3$)]BPh$_4$	a	1.89
	b	1.89 (3000)
	c	1.89 (2950)
[Ni(CH$_3$)(pp$_3$)]BPh$_4$	a	1.72, 2.44
	b	1.72 (90), 2.44 (4480)
[Ni(C$_2$H$_5$)(pp$_3$)]BPh$_4$	a	1.69, 2.31
	b	1.68 (60), 2.31 (4100)
[Ni(CH$_2$C$_6$H$_5$)(pp$_3$)]BPh$_4$	a	2.07
	b	2.06 (2850)

[a] Key: a, diffuse reflectance spectrum at room temperature; b, 1,2-dichloroethane solution; c, nitroethane solution.

Table V. ^{1}H NMR Resonance for the Alkyl Group of the [NiR(L)]BPh$_4$ Complexes

Compd	Resonance, τ[a]	Coupling constant[b]
[Ni(CH$_3$)(np$_3$)]BPh$_4$· CH$_3$COCH$_3$[c]	9.30 q	J(P-H) = 10
[Ni(CH$_3$)(nas$_3$)]BPh$_4$[c]	9.63 s	
[Ni(CH$_3$)(pp$_3$)]BPh$_4$	9.17 q	$J(P_{eq}\text{-}H) = 10$ $J(P_{ap}\text{-}H) = 4.2$
[Ni(C$_2$H$_5$)(np$_3$)]BPh$_4$[c]	8.69 m	
	8.38 t	$J(H_{CH_3}\text{-}H_{CH_2}) = 8.0$
[Ni(C$_2$H$_5$)(nas$_3$)]BPh$_4$[d]	8.70 q	$J(H_{CH_2}\text{-}H_{CH_3}) = 8.0$
	9.38 t	$J(H_{CH_3}\text{-}H_{CH_2}) = 8.0$
[Ni(C$_2$H$_5$)(pp$_3$)]BPh$_4$[d]	8.37 m	
[Ni(CH$_2$C$_6$H$_5$)(np$_3$)]BPh$_4$[d]	6.79 q	J(P-H) = 8.1
[Ni(CH$_2$C$_6$H$_5$)(nas$_3$)]BPh$_4$[d]	6.99 s	
[Ni(CH$_2$C$_6$H$_5$)(pp$_3$)]BPh$_4$[d]	6.71 m	

[a] Chemical shifts are relative to TMS = τ 10.00. Key: s, singlet; t, triplet; q, quartet; m, multiplet. [b] Coupling constants in Hz. [c] In C^{2}HCl$_3$ solution. [d] In (C^{2}H$_3$)$_2$CO solution.

be invoked to account for this difference, as the Ni–N(apical) distances are equal (2.10 Å) in both compounds. We prefer to attribute this difference to some overlap between the π system of the phenyl ring and the appropriate orbital of the metal.

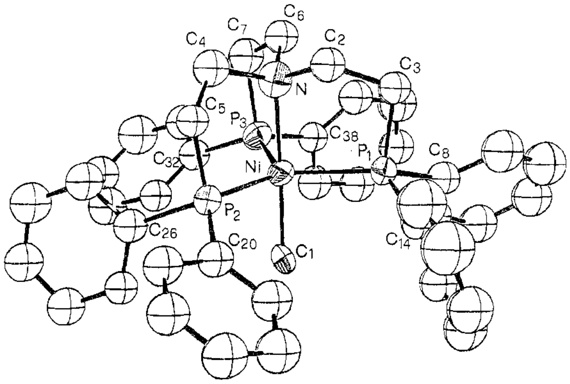


Figure 1. Perspective view of the [Ni(CH$_3$)(np$_3$)]$^+$ cation.

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

	(A) Selected Bond Lengths		
Ni-P(1)	2.250 (5)	P(3)-C(32)	1.84 (2)
Ni-P(2)	2.216 (6)	P(3)-C(38)	1.83 (2)
Ni-P(3)	2.232 (6)	N-C(2)	1.50 (2)
Ni-N	2.11 (1)	N-C(4)	1.53 (2)
Ni-C(1)	2.02 (2)	N-C(6)	1.48 (2)
P(1)-C(3)	1.84 (2)	C(2)-C(3)	1.56 (2)
P(1)-C(8)	1.82 (2)	C(4)-C(5)	1.47 (3)
P(1)-C(14)	1.85 (2)	C(6)-C(7)	1.50 (3)
P(2)-C(5)	1.82 (2)	B-C(44)	1.69 (3)
P(2)-C(20)	1.82 (2)	B-C(50)	1.62 (3)
P(2)-C(26)	1.84 (2)	B-C(56)	1.62 (3)
P(3)-C(7)	1.84 (2)	B-C(62)	1.64 (3)
	(B) Selected Bond Angles		
P(1)-Ni-P(2)	119.4 (2)	C(5)-P(2)-C(26)	106.5 (7)
P(1)-Ni-P(3)	117.1 (2)	C(20)-P(2)-C(26)	99.8 (8)
P(1)-Ni-N	87.0 (3)	Ni-P(3)-C(7)	101.6 (7)
P(1)-Ni-C(1)	94.9 (4)	Ni-P(3)-C(32)	126.2 (6)
P(2)-Ni-P(3)	122.8 (2)	Ni-P(3)-C(38)	117.7 (6)
P(2)-Ni-N	87.9 (4)	C(7)-P(3)-C(32)	103.0 (8)
P(2)-Ni-C(1)	91.2 (5)	C(7)-P(3)-C(38)	105.3 (9)
P(3)-Ni-N	86.5 (4)	C(32)-P(3)-C(38)	100.6 (8)
P(3)-Ni-C(1)	92.5 (5)	Ni-N-C(2)	110.1 (9)
N-Ni-C(1)	178.1 (4)	Ni-N-C(4)	109.3 (9)
Ni-P(1)-C(3)	101.5 (5)	Ni-N-C(6)	111.5 (11)
Ni-P(1)-C(8)	124.3 (6)	C(2)-N-C(4)	107.0 (13)
Ni-P(1)-C(14)	119.9 (6)	C(2)-N-C(6)	109.0 (12)
C(3)-P(1)-C(8)	102.7 (8)	C(4)-N-C(6)	109.8 (12)
C(3)-P(1)-C(14)	105.4 (8)	N-C(2)-C(3)	111.2 (14)
C(8)-P(1)-C(14)	100.5 (8)	P(1)-C(3)-C(2)	107.3 (10)
Ni-P(2)-C(5)	100.7 (6)	N-C(4)-C(5)	112.7 (13)
Ni-P(2)-C(20)	126.6 (7)	P(2)-C(5)-C(4)	111.9 (13)
Ni-P(2)-C(26)	117.4 (7)	N-C(6)-C(7)	113.7 (14)
C(5)-P(2)-C(20)	103.8 (9)	P(3)-C(7)-C(6)	109.1 (12)

The appreciable stability of these complexes can be ascribed to the particular shape of the tripod ligand which forms as a "nest" around the nickel atom. The hypothesis that the tripod shape of the ligands may confer some degree of kinetic shielding upon the complexes is supported both by the fluxional behavior of the trigonal-bipyramidal isoelectronic complexes

$[((CH_3)_3P)_4Ni(CH_3)]^+$[2] and $[((CH_3)_3P)_4Co(CH_3)]$[18] and by the fact that the five-coordinate organonickel compounds which bear as coligands monodentate tertiary phosphines have low stability.[19]

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Registry No. $[Ni(CH_3)(np_3)]BPh_4{\cdot}CH_3COCH_3$, 62561-25-5; $[Ni(C_2H_5)(np_3)]BPh_4$, 62520-84-7; $[Ni(CH_2C_6H_5)(np_3)]BPh_4$, 62520-86-9; $[Ni(CH_3)(nas_3)]BPh_4$, 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; $[Ni(CH_3)(pp_3)]BPh_4$, 62520-75-6; $[Ni(C_2H_5)(pp_3)]BPh_4$, 62520-77-8; $[Ni(CH_2C_6H_5)(pp_3)]BPh_4$, 62520-78-9.

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

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Trimethylamine–Isocyanoborane. Reactions and Derivatives

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The reactions of trimethylamine–isocyanoborane with Lewis acids like BCl_3 and BH_3 result in the formation of the corresponding adducts. Boronium cations are easily formed by the boryl isocyanide displacement of the iodide from $4\text{-}CH_3C_5H_4N{\cdot}BH_2I$ and $(CH_3)_3N{\cdot}BH_2NC{\cdot}B_2I$. The salts $[(CH_3)_3NBH_2NCBH_2NC_5H_5]^+X^-$ and $[(CH_3)_3NBH_2NCBH_2NC_5H_5CH_3]^+X^-$ ($X^- = I^-, PF_6^-$), as well as $[(CH_3)_3NBH_2NC]_2BH_2^+I^-$, have been characterized. Acid isomerization, methylation by $(CH_3)_3OBF_4$, CH_3FSO_3, and CH_3I, and the reactions of $(CH_3)_3N{\cdot}BH_2NC{\cdot}AgCN$ with B_2H_6 are also reported. The chemistry of trimethylamine–isocyanoborane is quite similar to that of alkyl isocyanides, although a distinctive behavior of boryl isocyanides is shown by some of the reported reactions.

Introduction

While little attention has been given to pseudohalogenated boranes, extensive studies of amine–haloboranes have been conducted.[1] Recently, there has been considerable interest in cyanoborohydride anion[2,3] in addition to limited studies of amine–cyanoboranes.[4-10] The feasibility of isolating boron isocyanides was implied by the existence of carbon isocyanides and the similarity between boron and carbon chemistry. The extensive chemistry of analogous isocyanide species[11] and the possibility of investigating any preference for B–CN vs. B–NC bonding prompted our interest in amine–isocyanoborane species. The synthesis of trimethylamine–isocyanoborane[12,13] and some of its reactions[14,15] showed the remarkable similarity between the chemistry of boryl and carbon isocyanides. We describe here other results obtained by studying the chemistry of the first tetrahedral isocyanoboron species reported.

Experimental Section

Details concerning the preparation of trimethylamine–isocyanoborane, solvents, products, and spectroscopic studies are similar to those reported elsewhere.[14] Analyses of the compounds isolated in this work were done by Galbraith Microanalytical Laboratories, Nashville, Tenn. All of the work was done in absence of air, either by working in a drybox or with Schlenk techniques. Proton NMR chemical shifts, δ, are reported in ppm downfield of tetramethylsilane used as standard.

Reaction of Trimethylamine–Isocyanoborane with 4-Methylpyridine–Iodoborane. A solution of 4-methylpyridine–iodoborane (0.96 g, 4.10 mmol), prepared according to Nainan,[16] in 10 mL of benzene was slowly added to a solution of trimethylamine–isocyanoborane (0.40 g, 4.08 mmol) in 10 mL of the solvent. A yellow oil was formed immediately after mixing. The solvent was decanted, and the oil was washed with fresh benzene and vacuum-dried. The product was dissolved in water and precipitated with ammonium hexafluorophosphate solution. The precipitate (1.21 g, 91% yield), mp 41–43 °C, had an elemental analysis as expected for $[(CH_3)_3NBH_2NCBH_2NC_6H_7][PF_6]$. Anal. Calcd: C, 35.87; H, 6.02; N, 8.37; B, 6.46; P, 9.25; F, 34.04. Found: C, 34.69; H, 5.79; N, 11.86; B, 6.12; P, 8.89; F, 32.44.

Reaction of Trimethylamine–Isocyanoborane with Trimethylamine–Isocyanoborane–Iodoborane. Trimethylamine–isocyanoborane–iodoborane was prepared by the reaction of trimethylamine–borane–isocyanoborane (0.26 g, 2.32 mmol) with iodine (0.23 g, 0.91 mmol) in 30 mL of benzene, with the halogen added in very small amounts at a time. Trimethylamine–isocyanoborane (0.23 g, 2.35 mmol) was added to the solution after the decoloration was complete. A finely divided solid precipitated and the mixture was stirred for another 1 h. The solid was removed by filtration, washed with fresh solvent, and vacuum-dried. The product (0.61 g, 100% yield), mp 141–143 °C, had a composition in agreement with that of $[(CH_3)_3NBH_2NC]_2BH_2I$. Anal. Calcd: C, 28.62; H, 7.21; N, 16.70; B, 9.66; I, 37.82. Found: C, 28.48; H, 7.33; N, 16.61; B, 9.69; I, 37.69.

Reaction of Trimethylamine–Isocyanoborane with Boron Trichloride. Trimethylamine–isocyanoborane (0.50 g, 5.10 mmol) was dissolved in 20 mL of benzene in a 100-mL single-neck round-bottom flask provided with a vacuum stopcock that was attached to a vacuum line. Boron trichloride (5.19 mmol) was measured in the line and condensed into the previously evacuated vessel. The brown color which developed upon contact of both reagents turned yellow overnight. Vacuum

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