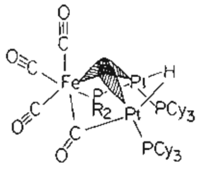
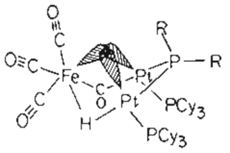


II



III

group, which in III is on the same side of the $FePt_2$ ring as the "$FePt_2$ bond" (in contrast to the case for II). The strength of the hypothesis that the addition of further "$Pt(PCy_3)$" units requires the prior reorganization of "FePt" and "$FePt_2$" systems to conformations containing an exposed, sterically accessible $FePt_x$ bond is its ability to account for the observed reaction sequences shown in Scheme I. The above correlations are the first definitive mechanistic results with respect to delineating a platinum cluster assembly process.

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Articles

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Further Synthetic Studies of $B_9H_{11}NH$. The Crystal Structure of $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}1,2\text{-}CoNHB_9H_9$

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Received June 3, 1988

The synthesis of $B_9H_{11}NH$ has been improved. The first closo metallaazaborane, $1\text{-}(\eta^5\text{-}C_5H_5)\text{-}1,2\text{-}CoNHB_9H_9$ (space group $P2_1/n$, $a = 15.035$ (28) Å, $b = 12.042$ (25) Å, $c = 14.017$ (27) Å, $\beta = 110.54$ (2)°, $Z = 8$), has been prepared and characterized, including a single-crystal X-ray structure determination. Two-dimensional ^{11}B–^{11}B NMR and ^{14}N NMR studies of certain azaborane derivatives have been completed.

Introduction

Since the discovery of nitrogen-containing boranes in 1967,[1] the development of the chemistry of azaboranes has been slow. While several azaboranes have been synthesized by various methods,[1-3] the most useful synthetic procedure at present is reaction of decaborane(14) with sodium nitrite.[3-6] Recently, we described our initial studies in this area, which included the synthesis of the first closo azaborane, B_9H_9NH.[6] We report here some NMR studies of these azaboranes, as well as the synthesis and structure of the first closo metallaazaborane.

Experimental Section

Physical Measurements. Boron (^{11}B) NMR spectra were obtained at 115.8 MHz with a Nicolet NT-360 spectrometer and were externally referenced to $BF_3{\cdot}OEt_2$ (positive values downfield). Proton (^1H) NMR spectra were obtained on the same instrument and were referenced by using the proton solvent impurities. Nitrogen (^{14}N) NMR spectra were obtained at 26.1 MHz on the same instrument and were externally referenced to neat nitromethane ($\delta = 0$ ppm; positive values downfield). Two-dimensional NMR spectra (^{11}B–^{11}B) were obtained on the same instrument. Broad-band ^1H decoupling (3W) was continuously used. High-resolution mass spectra data were recorded on a Kratos MS-80 instrument. Infrared data were obtained by using KBr disks with a Perkin-Elmer 283 spectrometer. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratories.

Materials. All reactions were carried out under an atmosphere of nitrogen. Tetrahydrofuran (THF), benzene, and pentane were distilled from sodium benzophenone ketyl. Acetonitrile and methylene chloride were dried over calcium hydride and distilled before use. Anhydrous cobalt chloride was prepared from the hexahydrate according to the method of King.[7] All other commercially available reagents were used as received. Decaborane(14) was sublimed before use.

$B_9H_{11}NH$. After $NaNO_2$ (3.70 g, 54.7 mmol) was heated in a three-neck, 500-mL round-bottom flask under vacuum for 2 h at 100 °C to remove any water present, 100 mL of THF was added and the mixture cooled by using a room-temperature water bath. A solution of $B_{10}H_{14}$ (5.05 g, 41.3 mmol) in 100 mL of THF was added dropwise over 6 h, stirred for an additional 3 h, and then filtered to remove unreacted $NaNO_2$ (0.84 g; identity confirmed by infrared spectroscopy). Analysis of the homogeneous filtrate by ^{11}B NMR spectroscopy indicated the presence of $B_9H_{12}NH^-$ and $B_{10}H_{15}^-$ in a ratio of 80:20. The THF was removed under vacuum and the resulting yellow powder dissolved in 300 mL of CH_3CN (gas evolution was observed). Iodine (6.3 g, 24.8 mmol) was dissolved in 250 mL of CH_3CN and added dropwise to the above solution over 4 h. A jacketed tube was attached to the flask and filled with an ice/water mix, and CH_3CN was removed under vacuum at 60 °C, giving a yellow powder. The ice/water mix was replaced by a dry ice/acetone slush bath, and pure $B_9H_{11}NH$ (2.91 g, 57% based on $B_{10}H_{14}$) sublimed over several hours. The ^{11}B NMR spectrum of this product was identical with that previously reported.[6] The high-resolution mass spectrum of this compound contained a parent ion peak at *m/e* 125.1807 (calcd for $^{11}B_9{}^1H_{12}{}^{14}N$ *m/e* 125.1806).

$(C_5H_5)Co(B_9H_9NH)$. Into an "H-reactor" was placed 2.0 g of NaH (approximately 42 mmol) as an oil dispersion. An H-reactor consists of two flasks joined by a glass frit, forming a vessel in the shape of an H. The frit is in the bridge of the "H", and both sides of the H-reactor have two ground-glass joints for introduction of reagents and an inert atmosphere. Under an atmosphere of nitrogen, the NaH was washed with several portions of pentane to remove the oil and then 30 mL of THF was added. Freshly cracked cyclopentadiene (1.0 g, 15.1 mmol) and $B_9H_{11}NH$ (1.0 g, 8.1 mmol) were added to the THF slurry, and the mixture was stirred for 1 h. Gas evolution was observed. The reaction mixture was filtered through the glass frit of the H-reactor and the resulting

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Table I. ^{11}B NMR Data for $(C_5H_5)Co(B_9H_9NH)$ and Related Compounds

compd			chem shift, ppm (*J*, Hz)
$(C_5H_5)Co(B_9H_9NH)$	*a*	1:1:2:1:4	67.0 (156), 21.6 (140), 0.1 (156), −15.7 (161), −19.5 (139)
$(C_5H_5)Co(B_9H_9N)^-$	*b*	1:1:2:1:4	53.3 (127), 16.7 (131), 1.8 (147), −15.6 (134), −19.1 (132)
$(C_5H_5)Co(B_9H_9NCH_3)$	*b*	1:1:2:1:2:2	65.3 (162), 20.4 (144), 3.8 (155), −7.6 (166), −19.5, −20.3
$(C_5H_5)Co(B_9H_9CNH_3)$	*c*	1:1:2:1:2:2	53.3 (130), 11.9 (126), −6.1 (132), −10.7 (147), −21.1 (137), −23.7 (130)
$(NMe_4)(C_5H_5)Co(B_9H_9CNH_2)$	*c*	1:1:1:2:2:2	46.1 (130), 8.8 (133), −4.8 (130), −7.3 (139), −22.5, −26.2 (133)
$(C_5H_5)Co(B_9H_9CN(CH_3)_2H)$	*c*	1:1:2:1:4	53.1; 13.4 (136); −6.9 (136), −14.0 (144), −22.8

[a] Acetone solvent. [b] THF solvent. [c] Reference 25.

solution added to a solution of $CoCl_2$ (5.2 g, 40.0 mmol) in 30 mL of THF at room temperature. The reaction mixture turned dark, and after 12 h of stirring at room temperature, a dark precipitate was noted. The mixture was filtered, giving a dark green solution. Most of the solvent was removed by evaporation under vacuum. The residue was chromatographed on a silica gel column (100–200 mesh) using CH_2Cl_2 as the eluant. The first band was green in color and consisted of a small amount of material containing $B_8H_{12}NH$, as indicated by ^{11}B NMR spectroscopy. The second band was violet and contained a major portion of the product. After removal of CH_2Cl_2 under vacuum, the resulting powder was crystallized from CH_2Cl_2/pentane to give small violet needles (0.9 g, 45% yield based on $B_9H_{11}NH$). The ^1H NMR spectrum in acetone-d_6 contains resonances at 5.55 ppm (C_5H_5) and 3.10 ppm (NH). The ^{11}B NMR spectra data for this compound and other azaborane derivatives reported here are presented in Table I.

$(C_5H_5)Co(B_9H_9NCH_3)$. In an H-reactor, 1 g of NaH as an oil dispersion was prepared as described above in the $(C_5H_5)Co(B_9H_9NH)$ synthesis. A solution of $(C_5H_5)Co(B_9H_9NH)$ (0.5 g, 2.0 mmol) in 10 mL of THF was added rapidly to the NaH/THF slurry. Vigorous gas evolution was observed. The reaction mixture was stirred for 1 h and then filtered from the excess sodium hydride to yield a green solution. Analysis of this air-sensitive solution (assumed to be $[Na][(C_5H_5)Co(B_9H_9N)]$) by ^{11}B NMR spectroscopy is presented in Table I. Methyl iodide (1 mL) was added to the green solution, resulting in an immediate color change to violet. The volatiles were removed under vacuum, leaving a violet powder, which was crystallized from CH_2Cl_2/pentane (0.45 g, 85% yield). The high-resolution mass spectrum contained a peak at m/e = 261.1540, corresponding to the $^{11}B_9{}^{12}C_6{}^{59}Co{}^1H_{17}{}^{14}N^+$ ion (calcd m/e = 261.1543). The ^1H NMR spectrum in acetone-d_6 contains resonances at 5.6 ppm (C_5H_5) and 4.8 ppm (NCH_3). Anal. Calcd for $B_9C_6CoH_{17}N$: C, 27.6; H, 6.6. Found: C, 27.5; H, 6.8.

Crystallography of $1\text{-}(C_5H_5)\text{-}1,2\text{-}CoNHB_9H_9$. A bluish single crystal was grown by slow diffusion of a dichloromethane/pentane mixture. The crystal chosen for data collection of dimensions 0.18 × 0.18 × 0.20 mm was mounted on a previously described goniostat[8] and cooled to −155 °C. Lattice parameters were determined from a least-squares fit of angular data from 36 reflections, centered by using automated top/bottom-left/right slit assemblies.

The structure was solved by direct methods and Fourier techniques and refined by full-matrix least-squares techniques. A summary of crystal data and intensity information is given in Table VI. Atomic coordinates and isotropic thermal parameters are presented in Table VII.

Results and Discussion

Further Observations on the Reaction of $B_{10}H_{14}$ with $NaNO_2$. Recently, we reported that the reaction of $B_{10}H_{14}$ with $NaNO_2$ in THF formed a mixture of $B_9H_{12}NH^-$, $B_9H_{14}^-$, and $B_{10}H_{15}^-$, in which the azaborane anion was the major product.[6] This anion mixture, when treated with H_2SO_4 in pentane, gave a moderate yield of $B_9H_{11}NH$, which, unfortunately, was contaminated with a small amount of $B_{10}H_{14}$ derived from protonation of $B_{10}H_{15}^-$ followed by H_2 elimination. Rather tedious methods were devised to obtain pure $B_9H_{11}NH$, but at the expense of this neutral azaborane's yield.

We have found that reaction of the crude sodium salt mixture from the sodium nitrite reaction with I_2 in acetonitrile forms a mixture of the adducts $B_9H_{11}NH{\cdot}NCCH_3$ and $B_{10}H_{12}{\cdot}2NCCH_3$. It is known[4] that some $B_9H_{11}NH{\cdot}$(Lewis base) adducts dissociate easily upon mild heating. The $B_{10}H_{12}{\cdot}2NCCH_3$ compound does not dissociate as easily and is thus relatively nonvolatile. This then constitutes a simple method to purify $B_9H_{11}NH$. It appears, from qualitative observations, that purified $B_9H_{11}NH$ is much less susceptible to hydrolysis by moisture than previously reported.[5,6]

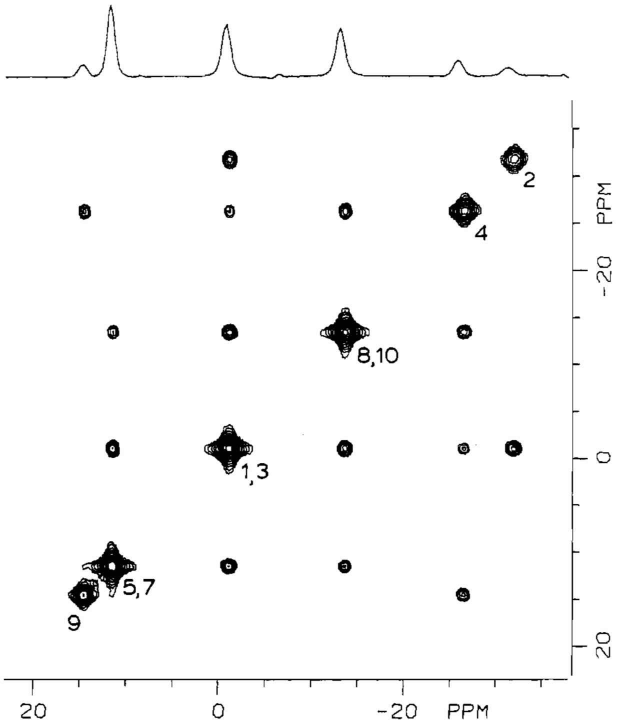

Figure 1. 115.8-MHz $^{11}B\{^1H\}$ 1-D and 2-D NMR spectra of $B_9H_{11}NH$.

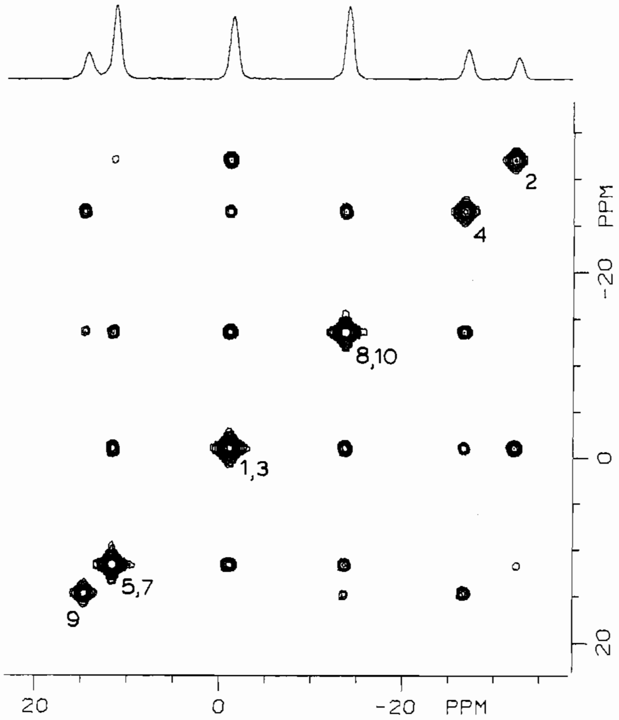

Figure 2. 115.8-MHz $^{11}B\{^1H\}$ 1-D and 2-D NMR spectra of $B_9H_{11}NH$.

Two-Dimensional ^{11}B–^{11}B NMR Spectroscopy of Some Azaborane Derivatives. Boron-11 NMR spectra have been useful for the characterization of many polyhedral cage structures.[9] More

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Table II. Assignments of ^{11}B NMR Resonances (ppm)

compd		B(4)	B(5,7)	B(2)	B(9)	B(8,10)	B(1,3)
$B_9H_{11}NH$	*a*	−27.2	11.8	−32.8	14.9	−13.9	−1.2
$NaB_9H_{12}NH$	*b*	−1.0	−12.5	−20.1	−23.8	−41.8	−41.0
py·$B_9H_{11}NH$	*c*	2.2	−11.7	−19.4	−11.2	−38.0	−41.3
$CH_3CN·B_9H_{11}NH$	*d*	2.8	−11.5	−17.6	−23.0	−37.1	−40.9

compd		B(9)	B(4,7)	B(8)	B(3)	B(5,6)	B(10,11)
$(C_5H_5)Co(B_9H_9NH)$	*e*	21.9	0.1	−15.7	67.0	−19.5	−19.5
$(C_5H_5)Co(B_9H_9N)^-$	*b*	16.7	1.8	−15.6	53.3	−19.1	−19.1
$(C_5H_5)Co(B_9H_9NCH_3)$	*b*	20.4	3.8	−7.6	65.3	−20.3	−19.5
$(C_5H_5)Co(B_9H_9C{-}NH_3)$	*e*	11.9	−6.8	−10.7	53.3	−21.1	−23.7
$[Me_4N][(C_5H_5)Co(B_9H_9C{-}NH_2)]$	*e*	8.8	−4.8	−7.3	46.1	−22.5	−26.2
$(C_5H_5)Co(B_9H_9C{-}N(CH_3)_2H)$	*e*	13.4	−6.9	−14.0	53.1	−22.8	−22.8

[a] C_6H_6 solvent. [b] THF solvent. [c] CH_2Cl_2 solvent. [d] CH_3CN solvent. [e] Acetone solvent; ref 25 (tentatively assigned).

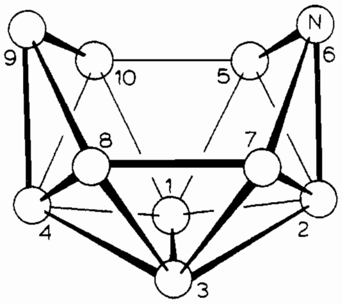

Figure 3. Numbering system for $B_9H_{11}NH$ and related compounds.

recently, when two-dimensional ^{11}B–^{11}B NMR methods were introduced, correlation between ^{11}B chemical shifts and specific boron sites in a given molecule became possible.[10,11] The general technique of 2-D NMR spectroscopy has been previously described,[12] and there have been many publications using 2-D ^{11}B–^{11}B NMR data for structural assignments.[13]

The 2-D COSY spectrum of $B_9H_{11}NH$ is shown in Figures 1 and 2, along with the conventional 1-D spectrum. Figure 1 differs from Figure 2 only by the number of acquisitions taken in each of the 128 experiments, 16 vs 64, respectively. This results in doubling the signal-to-noise ratio, allowing smaller peaks to be observed. Assignments of the individual boron resonances are presented in Table II. The numbering of $B_9H_{11}NH$ is given in Figure 3.

In Figure 1, no cross peak is seen between the resonances of B(8,10) and B(9) or between those of B(5,7) and B(2). Hydrogen-bridged boron nuclei [i.e., B(8,10)–B(9)] generally do not show cross-correlation peaks. This is consistent with theoretical calculations[14] which show that the electron density between hydrogen-bridged boron nuclei is lower than most directly bonded boron nuclei, and this leads to very small, difficult-to-observe coupling between the bridged boron nuclei.[15] One might then expect an absence of a cross peak between all hydrogen-bridged boron nuclei. This, however, is not the case.[13b-d] By simply increasing the signal-to-noise ratio (by taking more scans and/or increasing the concentration of the sample), we can observe small cross peaks, as is evident in Figure 2, between hydrogen-bridged boron nuclei. We do not deny, however, that the low electron density between the hydrogen-bridged boron nuclei results in a small cross peak.

Table III. ^{14}N Chemical Shift Values of Azaboranes

compd		chem shift, ppm
$NaB_9H_{12}NH$	*a*	−358
py·$B_9H_{11}NH$	*b*	−354, −144
$CH_3CN·B_9H_{11}NH$	*c*	−351, −205
$B_9H_{11}NH$	*b*	−241 ($J_{^{14}N-^{1}H}$ = 40 Hz)
$(C_5H_5)Co(B_9H_9NH)$	*d*	−401
$(C_5H_5)Co(B_9H_9NCH_3)$	*d*	−386

[a] THF solvent. [b] CH_2Cl_2 solvent. [c] CH_3CN solvent. [d] Acetone solvent.

Table IV. Selected Intramolecular Distances (Å) for 1-(η^5-C_5H_5)Co(η^6-2-NB_9H_{10})

Co(1)–N(2)	1.942 (7)	B(5)–B(9)	1.787 (14)
Co(1)–B(3)	2.040 (10)	B(5)–B(10)	1.798 (14)
Co(1)–B(4)	2.309 (10)	B(6)–B(7)	1.825 (14)
Co(1)–B(5)	2.263 (11)	B(6)–B(9)	1.832 (14)
Co(1)–B(6)	2.252 (11)	B(6)–B(11)	1.779 (13)
Co(1)–B(7)	2.314 (10)	B(7)–B(8)	1.828 (13)
Co(1)–C(12–16)	2.053 (9) (av)	B(7)–B(11)	1.743 (13)
N(2)–B(4)	1.543 (13)	B(8)–B(10)	1.739 (15)
N(2)–B(7)	1.510 (13)	B(8)–B(11)	1.739 (15)
N(2)–B(8)	1.674 (11)	B(9)–B(10)	1.778 (15)
B(3)–B(5)	1.722 (15)	B(9)–B(11)	1.773 (14)
B(3)–B(6)	1.725 (15)	B(10)–B(11)	1.849 (14)
B(3)–B(9)	1.708 (13)		
B(4)–B(5)	1.859 (15)		
B(4)–B(8)	1.846 (13)		
B(4)–B(10)	1.762 (15)		

In Figure 2, there is also a small cross peak between the B(5,7) and B(2) peaks that is not present in Figure 1. This peak is even smaller than the cross peak between the hydrogen-bridged boron nuclei.[16] The lack of a strong cross peak in the ^{11}B–^{11}B COSY spectra of metallathiaborane derivatives has been reported recently.[17] We are investigating this specific lack of strong coupling in B–B sites bridged by a four-electron-donor heteroatom in more detail and will publish our results soon.[18]

^{14}N NMR Spectra. Several ^{15}N NMR studies of compounds containing N–B bonds have been published.[19] It was not obvious that ^{14}N NMR chemical shifts could be observed in the higher cage azaboranes due to the quadrupolar nature of not only ^{14}N but ^{11}B as well. (There are three boron atoms bonded to nitrogen, possibly resulting in very broad ^{14}N resonances.) It was a pleasant

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(16) The cross-correlation peak between the B(5,7) and B(2) peaks is 1.7% of the highest peak while the peak between those of B(8,10) and B(9) is 2.2% of the highest peak.

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(18) Kester, J. G. Todd, L. J. Unpublished results.

(19) All references in this section can be found in: (a) *Annu. Rep. NMR Spectrosc.* 1977, *7*. (b) *Ibid.* **1981**, *11B*. (c) *Ibid.* **1987**, *18*.

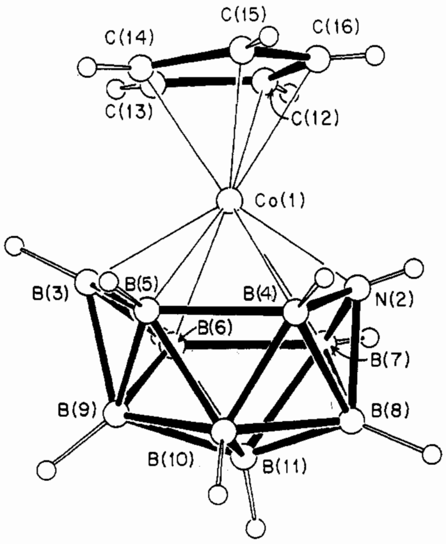

Figure 4. Structure of 1-(η^5-C_5H_5)-1,2-$CoNHB_9H_9$.

Table V. Boron–Nitrogen Intramolecular Distances (Å)

compd	N(6)–B(2)	N(6)–B(5)	N(6)–B(7)
$B_9H_{11}NH{\cdot}CN(C_6H_{11})$	1.557 (4)	1.525 (5)	1.525 (4)
$B_8H_{12}NH$	1.585 (3)	1.517 (3)	1.520 (3)
compd	N(2)–B(8)	N(2)–B(7)	N(2)–B(4)
$(C_5H_5)CoB_9H_9NH$	1.674 (11)	1.543 (13)	1.510 (13)

(column headers under "bond dist (esd)")

surprise that ^{14}N NMR signals were observed and at fairly low concentrations. (A lower limit of 0.2 M samples was used.) Specifically for $B_9H_{11}NH$, even $^1J_{^{14}N-^1H}$ = 40 Hz was observed.[20] This coupling constant is usually only observed for species such as ammonium ions and protonated isonitriles in which the electric field gradient about the nitrogen nucleus is very symmetric. This result suggests that there is also a fairly symmetric electronic environment about the nitrogen nucleus of $B_9H_{11}NH$. In other words, the lone pair of electrons on nitrogen is delocalized into boron cage orbitals, making this nitrogen atom more like that of NH_4^+ in character.

The ^{14}N chemical shift value of $B_9H_{11}NH$ is conspicuously deshielded relative to the other values given in Table III. This suggests that the boron cage of *nido*-$B_9H_{11}NH$ is relatively electron withdrawing in nature. An increase in the electron density in the azaborane framework in *arachno*-$B_9H_{12}NH^-$ or its closely related neutral Lewis base complexes substantially increases the shielding of the ^{14}N nucleus, resulting in a 110 ppm upfield change in the ^{14}N chemical shift. The ^{14}N chemical shift values of the azaboranes occurs in a region where alkylamines (−300 to −400 ppm) and arylamines (−270 to −370 ppm) are found.[19]

Structure Determination of 1-(η^5-C_5H_5)Co(2-NB_9H_{10}). A single-crystal X-ray structure study of the first closo metallaazaborane, $(C_5H_5)Co(B_9H_9NH)$, has been completed, and a view of the molecule with the numbering system is presented in Figure 4. Selected intramolecular distances are listed in Table IV. The structure of this compound is similar to several closo 11-atom cages[21] and is nearly identical with that of $[(H_3C)_4N][(C_5H_5)Fe(2\text{-}CB_9H_{10})]$.[21a] The related boron–nitrogen distances of $(C_5H_5)Co(B_9H_9NH)$, $B_8H_{12}NH$,[3] and the isocyanide adduct $B_9H_{11}NH{\cdot}CN(C_6H_{11})$[6] are given in Table V. The largest change in distance occurs between the nitrogen and the base boron (B(8)), which lengthens approximately 0.1 Å to a value of 1.674 Å. This length is longer than the single-bond B–N distances of $H_3B{\cdot}NH_3$,[22] $H_6B_3N_3Me_6$,[23] and $H_3N{\cdot}B_3H_7$,[24] which are 1.56 (4), 1.59 (3), and 1.58 Å, respectively.

Table VI. Summary of Crystal Data and Intensity Information for 1-(C_5H_5)-1,2-$CoNHB_9H_9$

empirical formula	$CoC_5H_{15}NB_9$
color of cryst	bluish
cryst dimens	0.18 × 0.18 × 0.20 mm
space group	$P2_1/n$
cell dimens (at −155 °C, 36 reflcns)	
a	15.035 (28) Å
b	12.042 (25) Å
c	14.017 (27) Å
β	110.54 (2)°
Z	8
V	2376.60 Å^3
dens (calcd)	1.372 g/cm^3
wavelength	0.71069 Å
mol wt	245.40
linear abs coeff	13.973 cm^{-1}
detector to sample dist	22.5 cm
sample to source dist	23.5 cm
takeoff angle	2.0°
av ω-scan width at half-height	0.25°
scan speed	4.0°/min
scan width	2.0° + dispersion
single bkgd time at extremes of scan	8 s
limits of data collcn: min 2θ; max 2θ	6°; 45°
total no. of reflcns collcd	3861
no. of unique intensities	3085
no. with $F > 0.0$	2707
no. with $F > 2.33\sigma(F)$	1750
final residuals: $R(F)$; $R_w(F)$	0.0460; 0.0451
goodness of fit for last cycle	0.885
max Δ/σ for last cycle	0.05

Table VII. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10)

atom	*x*	*y*	*z*	B_{iso}[a]
Co(1)	7021 (1)	2993 (1)	6312 (1)	13
N(2)	7862 (5)	4017 (6)	7286 (5)	17
B(3)	7524 (7)	1408 (8)	6397 (7)	17
B(4)	8532 (7)	3711 (9)	6708 (7)	15
B(5)	8377 (7)	2258 (9)	6228 (8)	19
B(6)	7562 (7)	1770 (9)	7602 (8)	18
B(7)	7749 (6)	3202 (9)	8055 (7)	15
B(8)	8929 (6)	3650 (9)	8111 (7)	16
B(9)	8624 (7)	1387 (9)	7323 (8)	18
B(10)	9271 (7)	2643 (9)	7419 (7)	15
B(11)	8703 (7)	2282 (8)	8354 (8)	18
C(12)	6306 (6)	3750 (9)	4929 (6)	24
C(13)	6121 (6)	2602 (9)	4907 (7)	28
C(14)	5716 (6)	2349 (9)	5620 (7)	25
C(15)	5604 (6)	3322 (8)	6114 (7)	17
C(16)	5969 (6)	4171 (8)	5671 (8)	24

[a] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

The crystal contains two independent molecules related by a translation of 0, 0, $^1/_2$, but there is no obvious supercell. These

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(20) Nitrogen coupling constants are usually reported as $J_{^{15}N-X}$, where $J_{^{15}N-X}$ = −1.4027$J_{^{14}N-X}$. Therefore, $^1J_{^{15}N-^1H}$ = 56 Hz.

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two molecules are virtually identical, implying the structure found is a true energy minimum. In the solid state, $(C_5H_5)Co(B_9H_9NH)$ possesses a molecular mirror plane through Co(1), N(2), B(3), B(8), and B(9). The cobalt, however, is not over the idealized C_2 axis of the azaborane, being slightly closer to N(2) than to B(3). This asymmetry is also seen in the Co(1)–B(4,7) bond lengths when compared to the Co(1)–B(5,6) bond lengths, being slightly shorter in the latter.

Upon coordination of the $(C_5H_5)Co^{2+}$ group to the azaborane, several bond changes occur as compared to the case for B_9H_{11}-$NH{\cdot}CN(C_6H_{11})$. The nitrogen-basal boron length increases, but the N(2)–B(4,7) bond lengths stay the same. The B(3)–B(5,6) bond lengths decrease nearly 0.1 Å. These two changes are probably interrelated since the cobalt would rather share electrons with the negatively charged nitrogen[28,29] than with the electron-withdrawing B(3). Loss of electron density from the cage due to nitrogen electron density delocalization should be balanced by decreasing the B(3)–B(5,6) bond lengths and increasing the sharing of electrons. Molecular orbital studies are needed to investigate the bonding in this complex.

$(C_5H_5)Co(B_9H_9NH)$, Related Compounds, and Their NMR Spectra. The synthesis of $(C_5H_5)Co(B_9H_9NCH_3)$ is analogous to the synthesis of $B_9H_9NCH_3$ from B_9H_9NH. In both cases, NaH is used to remove the acidic hydrogen, forming H_2. Methyl iodide is then added to form the corresponding methylated derivative. The COSY 2-D spectra of $(C_5H_5)Co(B_9H_9NH)$ and (C_5H_5)-$Co(B_9H_9NCH_3)$ have been obtained and the results listed in Table II. The ^{14}N NMR chemical shifts can be found in Table III. The ^{14}N chemical shift of $(C_5H_5)Co(B_9H_9NH)$, –401 ppm, represents the most upfield shift of any nitrogen–boron compound, and its nitrogen is one of the most shielded nitrogens presently known (screening constant of gaseous NH_3 is –399.9 ± 0.2 ppm).[19a] The significance of this physical property is not yet apparent. The ^{11}B NMR spectrum of $(C_5H_5)Co(B_9H_9NH)$ is very similar to that of the isoelectronic $(C_5H_5)Co(B_9H_9CNH_3)$[25] (Table I), and the structural assignments for the metallocarborane can easily be made (Table II). As was observed with several of the other azaboranes, $(C_5H_5)Co(B_9H_9NH)$ exhibits no cross peak between the resonances of B(8) and B(4,7). Further studies of this and other closo metallaazaboranes are planned. It should also be noted that several of the closo 11-atom cyclopentadienyl first-row metallaheteroboranes are blue or violet.[25-27] The significance of this physical property is not yet apparent.

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Supplementary Material Available: Tables containing complete atomic coordinates with isotropic thermal parameters, anisotropic thermal parameters, and complete bond distances and angles (6 pages). Ordering information is given on any current masthead page.

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Alkoxides of the Hexanuclear Niobium and Tantalum Cluster Units $[M_6X_{12}](OMe)_2{\cdot}4MeOH$ and $M'_2[Ta_6Cl_{12}](OMe)_6{\cdot}6MeOH$ (M = Nb, Ta; X = Cl, Br; M′ = Alkali Metal)

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In an inert atmosphere, the diamagnetic, mixed halide–methoxide clusters of the composition $[M_6X_{12}](OCH_3)_2{\cdot}4CH_3OH$ (M = Nb, Ta; X = Cl, Br) are prepared by the exchange reaction of the terminal halides in the clusters $[M_6X_{12}]X_2{\cdot}8H_2O$ by methoxide groups. The mixed halide–methoxide clusters are not soluble in methanol, but from suspensions in this solvent they dissolve slowly with further addition of alkali-metal methoxides. From concentrated alkaline solution in an oxygen-containing atmosphere a series of diamagnetic compounds $M'_2[Ta_6Cl_{12}](OCH_3)_6{\cdot}6CH_3OH$ (M′ = alkali metal) having all six terminal positions of the cluster units occupied by methoxide groups are isolated and their properties described.

Introduction

The outer halogen atoms (X^a) of the cluster units $[M_6X^i_{12}]^{n+}X^a_nL_{6-n}$, where M = Nb or Ta, X = Cl or Br, n = 2–4, i = inner, and a = outer, are easily replaceable by other halogens[1-5] or anions such as BF_4^- or OH^-.[1-3,6] A series of mixed-ligand clusters of the type $[M_6X^i_{12}]X^a_2$ (X^i = Cl, Br; X^a = Cl, Br, I, OH) has been described,[5,7] and the members have been classified into five structural groups according to their X-ray diffraction patterns. Only another halogen could be introduced into the inner (X^i) positions of the $[M_6X^i_{12}]^{n+}$ cluster units without destruction of the whole cluster unit.[8] Transition-metal alkoxides have been studied extensively and their relation to metal oxide systems discussed.[9,10] Cluster alkoxides of molybdenum and tungsten having two to six metal atoms in one cluster unit and having various bond orders between metal atoms have been widely investigated from preparative, structural, and theoretical points of view.[11,12] Although the cluster alkoxides of the molybdenum hexanuclear cluster units, namely, $Na_2[Mo_6X_8](OR)_6$, with X = Cl or Br and R = Me or Et, and $Na_2[Mo_6(OMe)_8](OMe)_6$, were prepared as early as two decades ago,[13] and their crystal structures solved more recently,[14] so far no results have been reported for

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