can adopt a conformation with all four nitrogen donor atoms in a distorted square-planar array. In contrast, models of $2_N.2_O.2_O$ show that only one bridgehead nitrogen and two bridge nitrogens can readily coordinate to a metal ion with square-planar or tetragonal geometry. Further evidence in support of this hypothesis is provided by the crystal structure of $Cu(2_S.2_O.2_O)^{2+}$, where the cupric ion is coordinated to only one of the bridgehead nitrogen atoms, to the two sulfur atoms in one bridge, and to one oxygen atom adjacent to the coordinated nitrogen in each of the other two bridges. The sixth coordination site of Cu(II) is occupied by a water molecule.[42]

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Chemical and Structural Studies of Azaboranes

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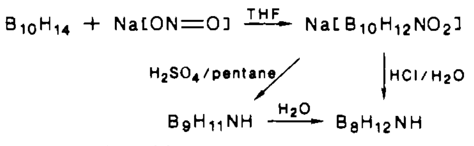
Reaction of $B_{10}H_{14}$ with sodium nitrite in THF at room temperature forms $Na[B_9H_{12}NH]$, $Na[B_9H_{14}]$, and $Na[B_{10}H_{15}]$ as the major products. A single-crystal X-ray structure study of the Lewis base adduct $B_9H_{11}NH{\cdot}CN(C_6H_{11})$ has been completed. The arachno open cage structure of this azaborane derivative is very similar to that previously reported for the isoelectronic compound 9-$N(C_2H_5)_3$-6-SB_9H_{11}. Slow passage of $B_9H_{11}NH$ through an evacuated hot tube (400 °C) formed *closo*-B_9H_9NH and H_2. Some of the chemical and spectral properties of this first *closo*-azaborane are described.

In the last two decades there has been considerable progress in understanding the chemistry of thiaboranes,[1-10,17] as well as the chemistry of selenium and tellurium analogues.[11-14] While the initial syntheses of azaboranes were reported in the same paper as those of the first thiaboranes,[1] progress with the nitrogen-containing boranes has been very slow. Decaborane was found to react with (thionitroso)dimethylamine, $(CH_3)_2NN{=}S$, to give both $B_{10}H_{11}S^-$ and $B_9H_{12}NN(CH_3)_2^-$.[1] The yield of the azaborane anion was low, which precluded any extensive study of its chemistry.

Even so, some derivative chemistry was reported.[1] The $B_9H_{12}NN(CH_3)_2^-$ ion reacted with methyl iodide to form the inner salt $B_9H_{12}NN(CH_3)_3$. The N–N bond of $B_9H_{12}NN(CH_3)_2^-$ was broken by reaction with excess sodium in tetrahydrofuran to form $Na[B_9H_{12}NH]$. Salts of $B_9H_{12}NH^-$ are stable enough to survive recrystallization from hot aqueous or ethanol solutions. Bromine oxidation of $B_9H_{12}NH^-$ in acetonitrile solution formed $CH_3CN{\cdot}B_9H_{11}NH$. Treatment of the acetonitrile complex with either lithium aluminum hydride or lithium borohydride re-formed the $B_9H_{12}NH^-$ ion.

At a later date it was reported that sodium nitrite reacted with decaborane in tetrahydrofuran to give an intermediate assumed to be $B_{10}H_{12}NO_2^-$. Treatment of this product with 4 M HCl, with a layer of hexane present, formed the neutral azaborane, $B_8H_{12}NH$.[15] An X-ray structure determination of this compound has been reported.[15] The structure can be described as that of the *arachno*-borane, *i*-B_9H_{15}, in which a BH unit and two bridge hydrogen atoms have been replaced by an NH unit (Figure 1). Subsequently it was reported that treatment of the proposed $B_{10}H_{12}NO_2^-$ intermediate with concentrated sulfuric acid, with a layer of hexane present, formed $B_9H_{11}NH$.[16]

Controlled hydrolysis of $B_9H_{11}NH$ produced $B_8H_{12}NH$ in good yield. This azaborane chemistry is summarized in eq 1.



(1)

We report herein additional details of the sodium nitrite–decaborane reaction and related chemistry, as well as the synthesis and chemistry of the first *closo*-azaborane.

Results and Discussion

Observations Concerning the Reaction of $B_{10}H_{14}$ with $NaNO_2$ with THF as Solvent. As soon as decaborane was added to the $NaNO_2$/THF slurry, a yellow color developed. This may be due to the formation of $NaB_{10}H_{13}$ and nitrous acid. While $NaB_{10}H_{12}NO_2$ may form as a transient intermediate in the reaction of $B_{10}H_{14}$ with $NaNO_2$ in THF, it is not one of the major final products of this complex reaction. The ^{11}B NMR spectrum of the products, after the reaction mixture was stirred for 3 days at room temperature, showed the presence of $B_9H_{12}NH^-$, $B_9H_{14}^-$,

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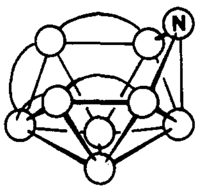

Figure 1. Structure of $B_8H_{12}NH$. The curved lines represent B–H–B bridge hydrogen atoms.

Table I. Boron-11 NMR Data of $B_9H_{11}NH$ and Related Derivatives

compd (area ratio)	^{11}B chem shift, ppm (J_{B-H}, Hz)
$PPN[B_9H_{12}NH]^a$ (1:2:1:1:4)	−1.2 (127), −12.6 (156), −20.4, −22.3 (119), −42
$B_9H_{11}NH^b$ (1:2:2:2:1:1)	15.2 (162), 11.8 (160), −1.5 (140), −14.5 (149), −27.4 (156), −33.0 (176)
$B_9H_{11}NH{\cdot}CN(t\text{-}C_4H_9)^a$ (1:3:2:1:2)	4.6 (136), −12.7 (142), −36.1 (137), −38, −40.5 (144)
$B_9H_{11}NH{\cdot}CN(C_6H_{11})^a$ (1:3:3:2)	5.1 (131), −11.8, −36.0 (151), −39.7 (143)
$B_9H_{11}NH{\cdot}py^c$ (1:3:1:2:2)	2.4 (127), −11.4 (121), −19.5 (143), −38.1 (121), −40.8 (140)

[a] CH_2Cl_2 solvent. [b] $CHCl_3$ solvent. [c] THF solvent.

Table II. Proposed Assignments for ^{11}B NMR Resonances of Selected $B_9H_{11}E{\cdot}L$ Compounds (E = NH, S, Se)

	^{11}B chem shift, ppm					
compd	B(4)	B(5,7)	B(2)	B(9)	B(8,10)	B(1,3)
$CsB_9H_{12}S^a$	−4.0	−7.9	−11.6	−15.0	−33.4	−36.6
$PPN(B_9H_{12}NH)^b$	−1.2	−12.6	−20.4	−22.3	−42	−42
$B_9H_{11}Se{\cdot}N(C_2H_5)_3{}^b$	2.6	−8.8	−8.8	−4.0	−29.8	−38.1

[a] Acetonitrile solvent. [b] Methylene chloride solvent.

$B_{10}H_{15}^-$, and borates as the major products as well as a smaller amount of $B_9H_{12}^-$. The amount of $B_{10}H_{15}^-$ in the mixture was large during the first few hours of the reaction, but after 3 days, the amount of this anion diminished considerably. Apparently some of the $B_{10}H_{15}^-$ was converted to $B_9H_{12}NH^-$ or $B_9H_{14}^-$ after a long reaction period. The $B_{10}H_{15}^-$ was probably formed by hydride ion transfer from one or more reaction intermediates to excess $B_{10}H_{14}$, which was present during the early stages of the reaction. We assume that the $B_9H_{12}NH^-$ and $B_9H_{14}^-$ ions were formed from one or more types of B_{10}–nitrite intermediates. The tenth boron atom of the decarborane reagent is used to reduce the nitrite ion. Obviously a considerable amount of chemistry takes place before the observed boron anions are formed. Other studies are in progress to further elucidate this interesting reaction.

$B_9H_{11}NH$ and $B_9H_{11}NH{\cdot}L$ (L = Ligand) Derivatives. The solvent-free sodium salts from the nitrite reaction when treated with concentrated sulfuric acid under a layer of dry pentane formed mainly $B_9H_{11}NH$ and $B_{10}H_{14}$ as illustrated in eq 2 and 3. This neutral azaborane was very susceptible to hydrolysis.

$$2NaB_9H_{12}NH + H_2SO_4 \rightarrow 2B_9H_{11}NH + Na_2SO_4 \quad (2)$$

$$2NaB_{10}H_{15} + H_2SO_4 \rightarrow 2B_{10}H_{14} + 2H_2 + Na_2SO_4 \quad (3)$$

The presence of $B_8H_{12}NH$ in the product mixture (as observed by ^{11}B NMR) was a good indication that attack of the $B_9H_{11}NH$ by moisture had occurred. Suitable Lewis base adducts of $B_9H_{11}NH$ were very effective in protecting the azaborane from attack by water or air.

The $B_9H_{12}NH^-$ ion (a $B_9H_{11}NH$ base adduct with H^- as the base) was isolated from the $B_{10}H_{14}$–sodium nitrite reaction as the $Ph_3P{=}N{=}PPh_3^+$ salt. This salt was recrystallized from methylene chloride–hexanes and was stable to air as a solid for months. The ^{11}B NMR spectrum (115.8 MHz) of this anion is quite similar to that of the isoelectronic thiaborane analogue $B_9H_{12}S^-$ (see Tables I and II).

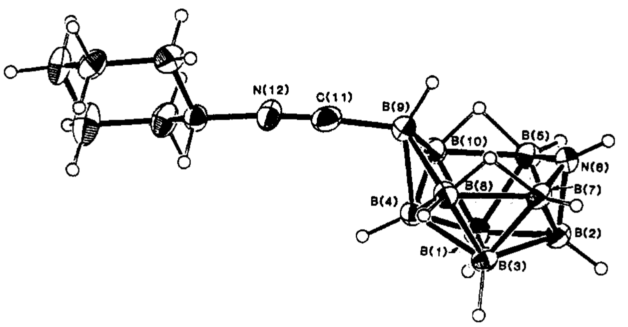

Figure 2. ORTEP diagram of 9-[$(C_6H_{11})NC$]-6-NHB_9H_{11}.

Table III. Selected Intramolecular Distances (Å) for 9-[$(C_6H_{11})NC$]-6-NHB_9H_{11}

A	B	dist	A	B	dist
N(6)	B(2)	1.557 (4)	B(2)	B(5)	1.872 (5)
N(6)	B(5)	1.525 (5)	B(2)	B(7)	1.872 (5)
N(6)	B(7)	1.525 (4)	B(3)	B(4)	1.772 (5)
N(12)	C(11)	1.146 (4)	B(3)	B(8)	1.800 (5)
N(12)	C(13)	1.448 (4)	B(3)	B(7)	1.799 (5)
C(11)	B(9)	1.552 (5)	B(4)	B(8)	1.758 (5)
B(1)	B(2)	1.758 (5)	B(4)	B(9)	1.748 (5)
B(1)	B(3)	1.811 (5)	B(4)	B(10)	1.762 (5)
B(1)	B(4)	1.767 (5)	B(8)	B(9)	1.879 (5)
B(1)	B(10)	1.801 (5)	B(8)	B(7)	1.846 (5)
B(1)	B(5)	1.803 (5)	B(9)	B(10)	1.880 (5)
B(2)	B(3)	1.765 (5)	B(10)	B(5)	1.852 (5)

Table IV. Boron–Nitrogen Intramolecular Distances (Å) of Two Azaboranes

	bond dist (esd)		
compd	N(6)–B(2)	N(6)–B(5)	N(6)–B(7)
$L{\cdot}NHB_9H_{11}$ (L = $C_6H_{11}NC$)	1.557 (4)	1.525 (5)	1.525 (4)
$B_8H_{12}NH$	1.585 (3)	1.517 (3)	1.520 (3)

The triplet resonance for the BH_2 group is clearly observed at −22.3 ppm ($J_{^{11}B-H}$ = 119 Hz). A previous ^{11}B NMR study at 64.18 MHz with line narrowing had indicated that the triplet resonance was located within the highest field multiplet of area 4 at −42 ppm.[16] In most of the $B_9H_{11}E{\cdot}L$ derivatives (E = S, Se, Te, NH; L = H^-, NR_3, CH_3CN, CNR) a high-field resonance of area 2 assigned to B(8,10) shows observable bridge hydrogen coupling. This B(8,10) bridge hydrogen coupling, which might be observed with line narrowing, may be the cause of the mistaken BH_2 group assignment for $B_9H_{12}NH^-$.

The $B_9H_{11}NH$ molecule can also be stabilized against atmospheric attack by simple mixing and complexation with strong neutral Lewis bases such as tertiary amines and alkyl isocyanides. In the solid state, these compounds are stable to the atmosphere for months. The ^{11}B NMR spectra of these $B_9H_{11}NH{\cdot}L$ derivatives were found to be quite similar to the spectra observed for other $B_9H_{11}E{\cdot}L$ compounds (E = S, Se or Te) (see Tables I and II). The ^{11}B NMR spectrum of $CsB_9H_{12}S$ was previously assigned by using selectively labeled derivatives.[3] Proposed assignments for other $B_9H_{11}E{\cdot}L$ compounds are included in Table II (see Figure 2 for the cage numbering system). Two-dimensional ^{11}B–^{11}B NMR experiments will probably strengthen these assignments, and such studies are planned.[18,19] The mass spectra of the $B_9H_{11}NH{\cdot}L$ derivatives generally show the most abundant ion to be that derived from $B_9H_{11}NH$. This suggests that at 80–120 °C the ligand complexes may be dissociating.

Structure Determination of 9-[$(C_6H_{11})NC$]-6-NHB_9H_{11}. A single-crystal X-ray structure study of the isocyanide Lewis base adduct $B_9H_{11}NH{\cdot}CN(C_6H_{11})$ has been completed, and a view of the molecule with the numbering system is presented in Figure

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Table V. ^{11}B NMR Data for B_9H_9NH and Its Derivatives

	^{11}B chem shift, ppm (J_{BH}, Hz)		
compd	B(10)	B(2,3,4,5)	B(6,7,8,9)
B_9H_9NH[a]	+61 (165)	-6.1 (175)	-21.5 (153)
$(CH_3)_4N[B_9H_9N]$[b]	+50 (149)	-8.3 (161)	-18.3 (140)
$B_9H_9NCH_3$[c]	+59.1 (168)	-1.5 (175)	-20.8 (150)

[a] $CHCl_3$ solvent. [b] Acetone solvent. [c] THF solvent.

Table VI. ^1H NMR Data for B_9H_9NH and Its Derivatives

	^1H chem shift, ppm (J_{BH}, Hz)			
compd	B_{10}	$B_{2,3,4,5}$	$B_{6,7,8,9}$	other
B_9H_9NH[a]	+7.5 (165)	+2.7 (170)	+1.2 (153)	+6.1 [br singlet; NH group]
$(CH_3)_4N[B_9H_9N]$[b]	+6.5 (149)	+1.8	+0.8	+3.5 [singlet; $(CH_3)_4N$]
$B_9H_9NCH_3$[a]	+7.5 (167)	+2.7 (174)	+1.2 (156)	+4.6 [singlet; NCH_3]

[a] $CDCl_3$ solvent. [b] Acetone-d_6 solvent.

2. Selected interatomic distances are listed in Table III. The geometry of the azaborane derivative is very similar to that of the isoelectronic thiaborane analogue *arachno*-$B_9H_{11}S{\cdot}N(C_2H_5)_3$, whose structure was reported a few years ago.[20] The cyclohexyl isocyanide ligand occupies an exo position to the azaborane cage on B(9). This is analogous to the ligand attachment found for 9-$N(C_2H_5)_3$-6-SB_9H_{11}.[20] The related boron–nitrogen distances of the isocyanide adduct and of $B_8H_{12}NH$[15] are given in Table IV.

These two *arachno*-azaboranes are closely related. Removal of B(9) with its attached substituents from the isocyanide adduct and capping of the open boron orbitals of the remaining eight-boron-atom fragment with two bridge hydrogens forms the $B_8H_{12}NH$ structure (see Figure 1). The similarity in boron–nitrogen bond distances of these two azaboranes is in accord with this relationship. The boron–nitrogen bond lengths of the azaboranes are similar to single-bond distances observed in several previous studies. The single-bond B–N distances of $H_3B{\cdot}NH_3$,[21] $H_6B_3N_3Me_6$,[22] and $NH_3{\cdot}B_3H_7$[23] are 1.56 ± 0.04, 1.59 ± 0.03, and 1.58 Å, respectively. It is interesting to note that the nitrogen atoms of both azaboranes are four-coordinate. The bonds to this nitrogen atom could all be considered as localized single bonds.

The bridging hydrogen atoms of the isonitrile complex are asymmetrically bound across atoms B(5) and B(10) and atoms B(7) and B(8). The bridging hydrogen distances were found to be 1.35 (3) and 1.23 (3) Å for B(5)–Hμ and B(10)–Hμ respectively and 1.32 (3) and 1.16 (3) Å for B(7)–Hμ and B(6)–Hμ respectively. Similar asymmetry with the bridge hydrogens being closer to B(9) was observed in the structure of 9-$N(C_2H_5)_3$-6-SB_9H_{11}.[20]

Synthesis and Properties of B_9H_9NH and Its Derivatives. Slow passage of $B_9H_{11}NH$ through an evacuated hot (375–400 °C) tube forms B_9H_9NH and H_2 gas. This is the same procedure used to prepare B_9H_9S from $B_9H_{11}S$.[2] This is the first *closo*-azaborane to be synthesized. The ^{11}B NMR spectrum (see Table V) consists of three very sharp doublets of areas 1:4:4. The area 1 signal is quite deshielded (+61 ppm) as is also the area 1 signal of 1-B_9H_9S (+74.5 ppm).[2] The ^1H NMR spectrum consists of three quartet signals in a 1:4:4 area ratio and a broad singlet signal at +6.1 ppm assigned to the NH group (see Table VI). These data are consistent with an axial placement of the NH unit in the bicapped Archimediam antiprism structure of C_{4v} symmetry illustrated in Figure 3. Treatment of 1-B_9H_9NH with sodium hydride in THF or with KOH in ethanol, formed the $B_9H_9N^-$ ion, which was isolated and characterized as the tetramethylammonium salt. The ^{11}B and ^1H NMR data are consistent with simple proton removal from the nitrogen atom in this chemical reaction. The azaborane anion reacts readily with methyl iodide in THF to form $B_9H_9NCH_3$. The ^1H NMR spectrum of this methylated derivative has a singlet signal at +4.6 ppm assigned to the $N(CH_3)$ group and three broad but well-resolved quartets in a 1:4:4 area ratio as illustrated in Table VI. The *N*-methyl protons of this azaborane are relatively deshielded when compared with those of other methylamine derivatives (see Table VII). The NH proton signal of B_9H_9NH found at 6.1 ppm is also very deshielded relative to NH resonances of alkyl- and phenylamines. We conclude from this limited information that the B_9H_9N group is very electron-withdrawing at the nitrogen atom.

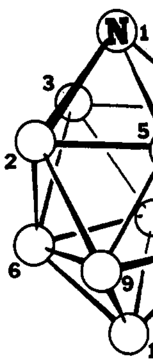
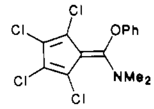


Figure 3. Structure of 1-B_9H_9NH.

Table VII. N–CH_3 ^1H NMR Chemical Shift Values for Selected Compounds

compd	^1H chem shift for ppm N–CH_3, ppm	ref
$N(CH_3)_3$	2.1	25
$C_6H_5N(CH_3)_2$	2.9	25
$CH_3NC_2B_8H_{12}$	2.8	26
	3.55	27
1-B_9H_9N–CH_3	4.6	this work

Treatment of 1-B_9H_9NMe with KOH in refluxing ethanol formed $K[B_9H_9N]$ as the major product, which is consistent with the weak Lewis base properties of the nitrogen function. These chemical transformations of the *closo*-azaborane are summarized in eq 4. Further studies of these interesting *closo*-azaborane derivatives are in progress.

$$B_9H_9NH \xrightarrow{\text{KOH/EtOH}} K[B_9H_9N] \underset{\substack{\text{KOH/EtOH} \\ (-CH_3OH)}}{\overset{CH_3I}{\rightleftarrows}} B_9H_9NCH_3 \quad (4)$$

Experimental Section

Physical Measurements. Boron (^{11}B) NMR spectra (Table I) 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 recorded on the same instrument. Infrared data were obtained by using KBr disks with a Perkin-Elmer 283 spectrometer. High-resolution mass spectra were obtained on a KRATOS MS80 spectrometer. Melting points were obtained in sealed evacuated capillaries and are uncorrected.

Materials. All reactions were performed under an atmosphere of prepurified nitrogen. Tetrahydrofuran (THF) and benzene were freshly distilled from sodium benzophenone ketyl. Triethylamine was dried over and distilled from sodium hydroxide. All other solvents were dried over calcium hydride and distilled just before use. Decaborane-14 was sublimed before use.

$Ph_3P{=}N{=}PPh_3[B_9H_{12}NH]$. To a suspension of $NaNO_2$ (0.97 g, 0.014 mol) in 100 mL of tetrahydrofuran was added dropwise a tetrahydrofuran solution of $B_{10}H_{14}$ (1.22 g, 0.01 mol) in 50 mL of the ether.

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The reaction was run at room temperature, and the decaborane-14 was added over a 3-h period. The mixture was stirred at room temperature overnight. NMR analysis (^{11}B) of the product mixture indicated the presence of $B_9H_{12}NH^-$, $B_9H_{14}^-$, and $B_{10}H_{15}^-$ in a 77:14:9 ratio, respectively. The ether was removed under vacuum and benzene (50 mL) added to the residue. Cyclohexyl-15-crown-5 (1 mL) was added to the benzene slurry and the mixture stirred overnight, at which point much of the residue had dissolved in the benzene. The solution was filtered and the benzene removed under vacuum. The residue was dissolved in CH_2Cl_2 (100 mL) and an excess of $[Ph_3P{=}N{=}PPh_3]Cl$ added to the solution. The solvent was slowly reduced in volume on a rotary evaporator to give 1.9 g (29% yield) of white crystalline product. The ^{11}B NMR data are presented in Table I. The proton NMR spectrum (360 MHz, acetone-d_6) contains a complex multiplet at δ 7.6–7.8 (phenyl protons) and broad resonances at δ 3.1 (NH) and −2.5 (bridge protons). The IR spectrum includes absorptions at 3000–3600 (br), 2560 (s), 2500 (s), 2200 (w), 2020 (w), 1900 (m), 1830 (m), 1620 (s), 1580 (s), 1480 (s), 1435 (s), 1395 (s), 1225 (s), 1190 (s), 1115 (s), and 1020 (s) cm^{-1}.

$B_9H_{11}NH$. Pentane (100 mL) was added to the residue of $NaB_9H_{12}NH$ prepared above. Concentrated sulfuric acid (50 mL) was added dropwise from a dropping funnel. After the addition, the mixture was stirred for 1 h and the pentane layer was removed. Another 100 mL of pentane was used to extract more product. The pentane was removed from the combined extracts under vacuum. The crude white residue was purified by sublimation (40–50 °C (0.01 mm)) on to a dry-ice cold finger. This procedure gave a 60% yield of $B_9H_{11}NH$. The proton NMR spectrum (360 MHz, $CDCl_3$) contains broad resonances at δ 4 (1 H, NH) and −2.2 (2 H, bridge protons).

$B_9H_{11}NH{\cdot}CN(t\text{-}C_4H_9)$. Freshly sublimed $B_9H_{11}NH$ (1.0 g, 8 mmol) was dissolved in 100 mL of pentane in a 250-mL flask fitted with a magnetic stirrer and a nitrogen inlet. *tert*-Butyl isocyanide (0.6 mL, 7.8 mmol) was added and the mixture stirred at room temperature for 2 h. The white precipitate formed was removed by filtration in the open air. The product was crystallized from methylene chloride–hexane on a rotary evaporator to give 1.5 g (90% yield) of $B_9H_{11}NH{\cdot}CN(t\text{-}C_4H_9)$, mp 126–128 °C. The proton NMR spectrum (360 MHz, $CDCl_3$) contains resonances at δ 3.0 (1 H, broad, NH), 1.6 (9 H, singlet, t-C_4H_9) and −2.2 (2 H, broad, bridge protons). The mass spectrum of the parent ion peak was found at m/z 208.2551 (calcd for $^{11}B_9{}^1H_{21}{}^{12}C_5{}^{14}N_2$, 208.2540). The IR spectrum includes absorptions at 3385 (m), 2980 (m), 2560 (s), 2540 (s), 2260 (s), 1370 (m), 1250 (s), 1140 (s), 1020 (s), and 990 (s) cm^{-1}.

$B_9H_{11}NH{\cdot}CN(C_6H_{11})$. This compound was prepared by using the same procedure described above for $B_9H_{11}NH{\cdot}CN(t\text{-}C_4H_9)$. The product was crystallized from methylene chloride–hexane; mp 115–117 °C. The proton NMR spectrum (360 MHz, $CDCl_3$) contains resonances at δ 3.1 (1 H, broad, NH), 1–2.8 (complex pattern; C_6H_{11}), and −2.2 (2 H, broad, bridge protons). The IR spectrum includes absorptions at 3500 (m), 3070 (m), 3040 (m), 2925 (s), 2540 (s), 2500 (sh), 2250 (s), 1550 (s), 1470 (s), 1430 (s), 1300 (br), 1250 (s), and 1140 (s) cm^{-1}.

$B_9H_{11}NH{\cdot}py$. This compound was prepared by using the procedure described above for $B_9H_{11}NH{\cdot}CN(t\text{-}C_4H_9)$. The product was crystallized from methylene chloride–hexane, giving yellow plates, mp 122–123 °C. The proton NMR spectrum (360 MHz, $CDCl_3$) contains resonances at δ 8.8, 8.1, and 7.6 (2 H, 1 H, 2H, respectively, pyridine protons), 3.1 (1 H, broad, NH), and −2.3 (2 H, bridge protons). The IR spectrum includes absorptions at 3380 (m), 3100 (w), 3060 (w), 2510 (s), 1610 (m), 1480 (w), 1450 (m), 1400 (w), 1340 (m), 1255 (w), 1210 (m), 1140 (m), 1120 (m), and 1010 (m) cm^{-1}.

B_9H_9NH. The flow-through reactor system used for pyrolysis was similar to that described previously for the synthesis of 1-SB_9H_9 with slight modification. A borosilicate glass tube (24 mm o.d. and 1 m long) fitted with a male 24/40 standard taper joint at both ends was used. One end was connected to a flask containing $B_9H_{11}NH$, and the other end was connected through an L-shaped tube to a vacuum sublimer. Degreased glass wool was loosely packed in the middle region of the tube. A furnace (50 cm long) was placed around the tube in the region of the glass wool (25 cm from both ends). Heating tape was wrapped around the flask with the $B_9H_{11}NH$, and the end of the pyrolysis tube before the pyrolysis zone, to gently sublime the $B_9H_{11}NH$. The entire apparatus was evacuated through the sublimer and the furnace was heated to 375–400 °C. The system was continuously evacuated during the entire pyrolysis while the sublimer cold finger was maintained at −78 °C (dry ice). After 5 h, the heating was stopped and the system backfilled with nitrogen. In a typical pyrolysis, 2.0 g of $B_9H_{11}NH{\cdot}CH_3CN$ (12 mmol) was placed in the flask. Crude B_9H_9NH was recovered from the cold finger and from the pyrolysis tube just after the pyrolysis zone. The compound was purified by sublimation at 55–70 °C (0.01 Torr) onto a dry-ice finger to give 0.8 g (54% yield) of B_9H_9NH, mp 155–157 °C. The ^{11}B and proton NMR data are given in Tables V and VI, respectively. The mass spectrum of the parent ion peak was found at m/z 123.1649 (calcd for $^{11}B_9{}^1H_{10}{}^{14}N_1$, 123.1651). The IR spectrum includes absorptions at 3300 (m), 2560 (s), 1190 (s), 1130 (m), 1011 (w), 972 (m), and 958 (m) cm^{-1}.

Table VIII. Summary of Crystal Data and Intensity Information for 9-[$(C_6H_{11})NC$]-6-NHB_9H_{11}

empirical formula	$B_9H_{23}N_2C_7$
color of cryst	colorless
cryst dimens	0.18 × 0.18 × 0.23 mm
space group	$P2_1/a$
cell dimens (at −160 °C; 44 reflcns)	
a	24.026 (12) Å
b	10.188 (4) Å
c	5.982 (2) Å
β	85.92 (2)°
Z (molecules/cell)	4
vol	1460.42 Å^3
d_{calcd}	1.058 g cm^{-3}
wavelength	0.71069 Å
M_R	232.56
linear abs coeff	0.497 cm^{-1}
detector to sample dist	22.5 cm
sample to source dist	23.5 cm
take-off angle	2.0 deg
av ω scan width at half-height	0.25 deg
scan speed	4.0 deg/min
scan width	2.0° + dispersion
single bkgd time at extremes of scan	10 s
limits of data collcn	
min 2θ	6 deg
max 2θ	45 deg
total no. of reflcns collcd	2694
no. of unique intensities	1912
no. with $F > 0.0$	1717
no. with $F > \sigma(F)$	1601
no. with $F > 2.33\ \sigma(F)$	1441
final residuals	
$R(F)$	0.054
$R_w(F)$ (w based on counting statistics)	0.055
goodness of fit for last cycle	1.156
max Δ/σ for last cycle	0.05

$N(CH_3)_4[B_9H_9N]$. In an "H-shaped" reactor, 2 g of NaH was placed as an oil dispersion. Under a stream of nitrogen, the NaH was washed with several portions of hexane and then with several portions of dry THF to remove the oil. The azaborane B_9H_9NH (0.5 g, 4 mmol) was added to the THF slurry, and vigorous gas evolution was observed. The reaction mixture was stirred at room temperature for 2 h and then filtered through the glass frit of the reactor. The solvent was removed under vacuum and the yellow residue dissolved in a minimum amount of water. Addition of a concentrated solution of tetramethylammonium chloride to the aqueous filtrate gave a precipitate of the crude product, which was crystallized from acetone–water to give 0.71 g (90% yield) of pure $N(CH_3)_4[B_9H_9N]$. The ^{11}B and proton NMR data are presented in Tables III and IV, respectively. The IR spectrum includes absorptions at 3020 (m), 2950 (w), 2900 (w), 2560 (s), 2505 (s), 1480 (s), 1410 (s), 1280 (m), 1260 (m), 1110 (s), 1070 (m), and 1010 (s) cm^{-1}.

$B_9H_9NCH_3$. The azaborane B_9H_9NH was reacted with sodium hydride as described in the previous section. After filtration through the glass frit of the H reactor, CH_3I (0.8 mL, 4 mmol) was added and the reaction left stirring for another hour. The solvent was then removed under vacuum to give an off-white residue of crude product. Pure $B_9H_9NCH_3$ (0.5 g, 80% yield) was obtained by sublimation at 25–40 °C (0.01 Torr); mp 71–72 °C. The ^{11}B and proton NMR data are given in Tables V and VI, respectively. The IR spectrum includes absorptions at 2990 (m), 2975 (m), 2885 (m), 2570 (s), 2520 (s), 1450 (br), 1400 (s), 1350 (br), 1260 (s), 1185 (m), 1160 (s), 1120 (s), 1065 (m), and 1040 (br) cm^{-1}. A mixture of $B_9H_9NCH_3$, 0.5 g (3.8 mmol), and KOH, 0.6 g (10.7 mmol), in 15 mL of dry ethanol was refluxed for 3 h. The ^{11}B NMR spectrum of the crude material indicated that the major product was $K[B_9H_9N]$.

Crystallography of 9-[$(C_6H_{11})NC$]-6-NHB_9H_{11}. A large colorless needlelike single crystal was grown by slow evaporation from a methylene chloride–hexane mixture. The crystal chosen for data collection of dimension 0.18 × 0.18 × 0.23 mm was cleaved from the large crystal and mounted on a previously described goniostat[28] and cooled to −160 °C.

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Lattice parameters were determined from a least-squares fit of angular data from 44 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 VIII.

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Registry No. $B_{10}H_{14}$, 17702-41-9; $B_9H_{12}NH^-$, 66272-83-1; $B_9H_{14}^-$, 12430-28-3; $B_{10}H_{15}^-$, 39448-33-4; $Ph_3P{=}N{=}PPh_3[B_9H_{12}NH]$, 103885-37-6; $B_9H_{11}NH$, 58985-53-8; $B_9H_{11}NH{\cdot}CN(t\text{-}C_4H_9)$, 103904-38-7; $B_9H_{11}NH{\cdot}CN(C_6H_{11})$, 103904-39-8; $B_9H_{11}NH{\cdot}py$, 103904-40-1; B_9H_9NH, 103904-41-2; $N(CH_3)_4[B_9H_9N]$, 103904-43-4; $B_9H_9NCH_3$, 103933-00-2; $K[B_9H_9N]$, 103904-44-5; $NaNO_2$, 7632-00-0.

Supplementary Material Available: Tables of atomic coordinates and isotropic temperature factors (Table Is), anisotropic temperature factors (Table IIs), and selected bond angles (Table IIIs) (6 pages). Ordering information is given on any current masthead page.

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Spectrophotometric and X-ray Absorption Edge Study of Complexation of Carbon Monoxide with Ferric Tetrasulfophthalocyanine in Alkaline Solution

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The square-planar macrocyclic chelate ferric tetrasulfophthalocyanine ($C_{32}H_{12}N_8(SO_3)_4Na_4Fe$) was found to reversibly complex carbon monoxide in anaerobic, alkaline solution. The complex gave an electronic spectrum substantially different from that normally observed in solution for phthalocyanines, suggesting a redox process involving the organic ring. Reexposure to O_2 generated an intermediate species that exhibited a normal electronic spectrum. By comparison of the X-ray absorption edge spectra of the complexed iron in the various stages of reaction to its oxide powders, the changes between ferric and ferrous oxidation states could be monitored. Results suggest that the combined effect of CO and hydroxide on the Fe center is to lower the unfilled d_{xy} orbital below the filled a_{1u} orbital of the phthalocyanine ligand, enabling reduction of ferric ion to the ferrous state by the macrocyclic ring.

Introduction

In a study of C_1 electrochemistry in aqueous solutions of various metal phthalocyanine tetrasulfonates, it was observed that in alkaline solution the ferric phthalocyanine underwent a substantial color change in the presence of carbon monoxide.[1] The normally bright blue aqueous complex became dull purple or brown at millimolar concentrations. Subsequent exposure to air (i.e., oxygen) caused another color change to a greenish hue. The apparent redox chemistry involves some combination of ring- and/or metal-centered charge transfers. The potential catalytic significance of a specific CO/FePc/OH^- interaction warranted further study.

Iron phthalocyanine is a relatively large, aromatic, macrocyclic square-planar N_4 chelate, consisting of four azo-bridged pyrrole units, each with a benzene ring fused to its base. By sulfonation of the benzene moieties, the compound can be made water soluble. The two lowest energy $\pi \rightarrow \pi^*$ electronic transitions, which result in the Q band in the red region of the visible spectrum and the Soret band in the near-ultraviolet spectrum, are quite intense ($\epsilon = 10^4$–10^5 l/(mol cm)), and so electronic structural changes are easily observable. Its catalytic ability is well-known, especially in the electroreduction of oxygen.[2–5]

X-ray absorption spectroscopy, including extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES), has been receiving increased attention among chemists for its use as an analytical tool.[6] The X-ray absorption edge of an element can be analyzed to give the number and type of nearest-neighbor atoms, as well as their bond distances. The edge and pre-edge structure of the absorption band contains bound-state transitions that yield information about coordination geometry, type of ligand, and valence state. In this report we will discuss how observation of the Fe absorption edge enabled us to monitor the charge state of the metal center exclusive of any changes occurring on the macrocyclic ring.

Experimental Section

The tetrasodium salt of tetrasulfophthalocyanine ferric chloride, $[\mathrm{Fe^{III}TsPc}]Cl$, was prepared by the condensation of 4-sulfophthalic acid (Kodak) around an iron salt in a melt of urea, as described by Weber and Busch.[7] While it is possible to prepare either ferric or ferrous phthalocyanine in this manner, unless protected from air the ferrous derivative will be mostly oxidized by the time workup is complete.[8] Thus, either ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$; Allied Chemical) or ferric chloride ($FeCl_3{\cdot}6H_2O$; J. T. Baker) could be used interchangeably to produce the same result. To ensure complete oxidation, however, solutions were heated to 80 °C under a purge of O_2 before use. Conversion to the ferric state was substantiated by observing an absorption maximum at 636 nm, characteristic of $\mathrm{Fe^{III}TsPc}$.[8–10]

UV–visible absorption spectra were taken with a Beckman DU-8 spectrophotometer. The macrocycle concentration was initially 1.0×10^{-5} M. Successive spectra were obtained by purging the same test solution in situ with the appropriate gas.

The X-ray absorption measurements were carried out on beamline X-11A of the National Synchrotron Light Source located at Brookhaven National Laboratory. The electron storage ring had an electron energy of 2.5 GeV and a current between 150 and 30 mA. The details of the beamline design have been published.[11] During this run the monochromator was operated in the two-crystal mode using Si(111) crystals. The incident and transmitted X-rays are measured with gas-filled ion chambers in which the gas mixtures are adjusted depending on the absorption energy of the element of interest. Normally, the initial chamber is adjusted to absorb only 10% of the incident radiation.

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