New Examples of B_9 and B_{11} Polyhedral Borane Derivative Chemistry

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Direct electrophilic substitutions have been carried out on $B_9H_9^{2-}$ in nonaqueous solvents under anaerobic conditions. Isolated products include amino-, trimethylamino-, dimethylsulphido-, and bis-(boranyl)keto-derivatives. Reaction of acetic anhydride/DMSO with $B_{11}H_{11}^{2-}$ yielded its dimethylsulphido-derivative which is fluxional in solution. These compounds represent the first examples of non-halogenated derivatives of the B_9 and B_{11} polyhedral boranes.

Introduction

The ten-vertex $B_{10}H_{10}^{2-}$ and twelve-vertex $B_{12}H_{12}^{2-}$ polyhedral boranes have extensive electrophilic and nucleophilic substitution chemistry that fully justify their classification as inorganic aromatic systems [1, 2]. Other members of this family of boron cluster compounds include $B_nH_n^{2-}$ (n = 6, 7, 8, 9, 11). Together they offer a unique series of polyhedral geometries with continuous variations in vertex coordination number suitable for structure–reactivity studies [1]. Unfortunately the significantly decreased hydrolytic and oxidative stability of the other dianions have frustrated extension of this chemistry beyond B_{10} and B_{12} systems. For example, $B_9H_9^{2-}$ has two distinct sites for electrophilic attack (Fig. 1) of which the three five-coordinate sites are predicted by ground state MO calculations to have much higher electron densities [3]. Similar predictions for the $B_{10}H_{10}^{2-}$ derivatives have been borne out experimentally in many instances although exceptions are also well documented [1, 2]. Development of similar types of substitution derivatives for $B_9H_9^{2-}$ will be invaluable in supporting or refuting these predictions. To date only halogenation reactions have been successfully carried out on this borane. Known derivatives include $B_9Br_6H_3^{2-}$ and recently, the $B_9Cl_9^{2-}$, $B_9Br_9^{2-}$, and $B_9I_9^{2-}$ compounds [4, 5]. A similar situation exists for $B_{11}H_{11}^{2-}$. This boron hydride (Fig. 2) is unique in its high fluxionality yet literature reports of its derivative chemistry are limited to the $B_{11}Br_9H_2^{2-}$ [4], $B_{11}Br_4H_7^{2-}$ [6], and $B_{11}H_9(Se)_3^{2-}$ species [7].

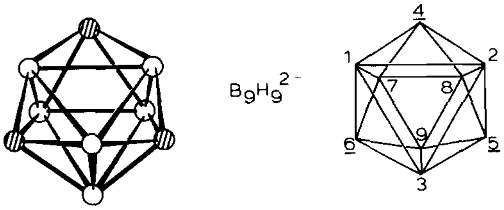

Fig. 1. The $B_9H_9^{2-}$ anion.

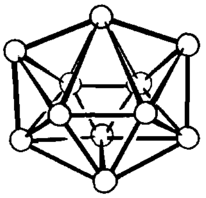

Fig. 2. Possible limiting structure of $B_{11}H_{11}^{2-}$.

We have studied the substitution chemistry of $B_9H_9^{2-}$ using nonaqueous solvents under anaerobic reaction conditions and report here our preliminary findings of its derivative chemistry. We also report here the successful isolation of a substitution compound from $B_{11}H_{11}^{2-}$.

Results and Discussion

Reaction of $B_9H_9^{2-}$ with excess hydroxylamine-O-sulfonic acid in DMSO at room temperature gave moderate yields of the amino-derivative $B_9H_8NH_3^-$ isolated as NMe_4 and PPN (μ-nitrido-bis-triphenylphosphorus) salts. Similar reactions in alkaline aqueous solutions required heating to 80° with extensive degradation of the polyhedral borane [8]. The infra-red spectrum exhibited N–H bands around 3200 cm^{-1} and NH_3^+-band at 1400 cm^{-1}. Its ^{11}B NMR spectrum (Table I) is uninformative with respect to the amination site.

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TABLE I. 28.70 MHz ^{11}B NMR Data.

Compound (Solvent)	Chemical Shift[a]
$NMe_4B_9H_8NH_3$ (d_6-DMSO)	9.0, 2.2, –2.9, –8.0, –12.4, –15.1, –25.5 (^{1}H-decoupled: 6.5, –0.2, –9.9, –15.0, –22.6)
$PPNB_9H_8NMe_3$ ($C_2D_2Cl_4$)	4.2(sh), –3.9, –8.3, –19.2 (^{1}H-decoupled: 2.4, –6.1, –19.2)
$(NMe_4)_2(Me_2SB_{10}H_8COH)_2B_9H_7$ (CD_3CN)	26.0, 20.2, 13.0 to 7.8[b], –11.0, –18.7 (^{1}H-decoupled: 25.8, 20.4, 13.1, 7.3, –9.5(sh), –18.3)
$(NMe_4)_3(Me_2SB_{10}H_8CO)_2HB_9H_7$ (CD_3CN)	27.5, 20.7, 15.6, 11.2 to 7.8[b], –7.5(sh), –10.9(sh), –17.7(sh), –20.2, –23.6(sh), –29.6(sh) (^{1}H-decoupled: 25.8, 20.7, 13.6, 7.6, 9.17(sh), –19.0, –27.3(sh))
$NEt_4B_{11}H_{10}SMe_2$ (d_6-DMSO)	4.8, –9.2, –13.9 (^{1}H-decoupled: 4.8, –11.6)

[a] Chem. shift ref. to external $BF_3 \cdot OEt_2$. [b] Broad, unresolved resonances.

To establish the position of substitution, this compound was permethylated using MeI under basic conditions.

$$B_9H_9^{2-} + NH_2OSO_3H \rightarrow B_9H_8NH_3^- + HSO_4^-$$

$$B_9H_8NH_3^- + MeI \rightarrow B_9H_8NMe_3^-$$

The $B_9H_8NMe_3^-$ derivative as the PPN salt was isolated. Its ^{1}H NMR spectrum consisted of two signals in the methyl region: 2.65 (area 3) and 3.30 (area 1) ppm. By analogy to the $B_{10}H_9NMe_3^-$ isomers [8], we can assign the preferred amination site as the six-coordinate vertices (the 1-isomer). This selectivity is similar to that observed for the B_{10}-system and both results are inconsistent with ground state MO predictions [3].

The stereochemical rigidity of this species was established by variable temperature ^{1}H and ^{11}B NMR in $C_2D_2Cl_4$ solution up to 100 °C when decomposition was observed.

Reaction of the B_{10}-derivative 1,6-$Me_2SB_{10}H_8$-CO with the parent $B_{10}H_{10}^{2-}$ species has produced bisboranylketones containing two B_{10}-cages coupled through a CO-bridge [9].

$$Me_2S\text{-}B_{10}H_8\text{-}CO + B_{10}H_{10}^{2-} \rightarrow Me_2SB_{10}H_8C(OH)\text{-}B_{10}H_9^{2-}$$

Similar reaction of $B_9H_9^{2-}$ with 1,6-$Me_2SB_{10}H_8CO$ in acetonitrile gave a novel disubstitution product formulated as $(Me_2SB_{10}H_8COH)_2B_9H_7^{2-}$:

$$2Me_2SB_{10}H_8CO + B_9H_9^{2-} \rightarrow (Me_2SB_{10}H_8COH)_2B_9H_7^{2-}$$

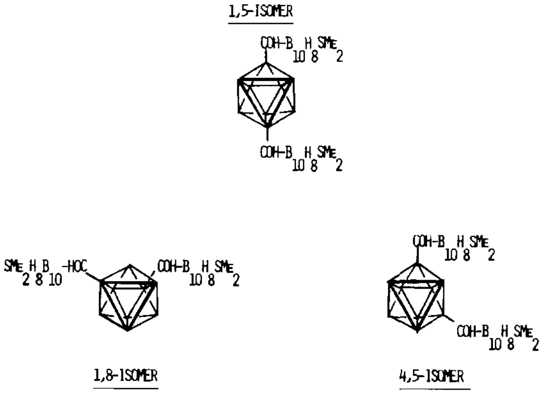

Fig. 3. Possible nonvicinal isomers of $(Me_2SB_{10}H_8COH)_2$-$B_9H_7^{2-}$.

Interestingly, even a deficiency of the B_{10} carbonyl reagent resulted in the same light orange disubstituted product. Its ^{1}H NMR spectrum exhibited a single methyl peak at 2.90 ppm and its ^{11}B NMR spectrum at 28.7 MHz is too poorly resolved to provide structural details (Table I). To confirm that this is a coupled B_9–B_{10} system, the deuterated compound 1,6-$Me_2SB_{10}D_8CO$ was prepared and used to form $(Me_2SB_{10}D_8COH)_2B_9H_7^{2-}$ which showed both B–H (2500 cm^{-1}) and B–D (1870 cm^{-1}) stretches.

Although the actual structure of this tris-boranyldiketone derivative remains to be established, steric considerations should allow only nonvicinal sites on the B_9 cage. Thus only the 1,5-, 1,8(9)-, and 4,5-isomers are reasonable candidates (Fig. 3).

As expected, this dianion can be deprotonated to give the trianionic species:

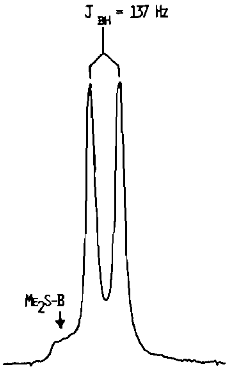

Fig. 4. 28.70 MHz ^{11}B NMR spectrum of $B_{11}H_{10}SMe_2^-$.

$$\underset{\text{(orange)}}{(Me_2SB_{10}H_8COH)_2B_9H_7^{2-}} \rightleftharpoons \underset{\text{(yellow)}}{(Me_2SB_{10}H_8CO)_2H\text{-}B_9H_7^{3-}} + H^+$$

Reaction of acetic anhydride/DMSO has been used to give SMe_2-derivatives of $B_{12}H_{12}^{2-}$ [12]. Similar reaction using $B_9H_9^{2-}$ produced both $B_9H_8SMe_2^-$ and $B_9H_7(SMe_2)_2$ derivatives which have fluxional properties in solution. The detailed studies of their ^{1}H, ^{13}C, and ^{11}B NMR will be published separately [15].

Room temperature reaction of $B_{11}H_{11}^{2-}$ with acetic anhydride/DMSO yielded the $B_{11}H_{10}SMe_2^-$ derivative isolated as its NEt_4 and PPN salts:

$$B_{11}H_{11}^{2-} + (CH_3CO)_2O + (CH_3)_2SO \rightarrow B_{11}H_{10}SMe_2^- + CH_3COO^- + CH_3COOH$$

The ^{1}H NMR of this product contains only a single resonance in the methyl region at 2.4 ppm. This is indicative of either formation of a single isomer of $B_{11}H_{10}SMe_2^-$ or fluxional behavior in solution. That the latter is the case is confirmed by its ^{11}B NMR spectrum (Fig. 4) of a singlet at 4.8 ppm (area 1) and a doublet at −11.6 ppm (J_{BH} = 137 Hz, area 10). Further elucidation of its solution and solid-state structures is under way.

These preliminary results show that substitution chemistry is indeed feasible for the B_9 and B_{11} polyhedral boranes when reaction conditions are adjusted to minimize oxidative and hydrolytic processes. Although the number of isolated derivatives is insufficient to make general comparisons with the established B_{10} and B_{12} substitution chemistry, we already see many similarities as well as distinctive results in these reactions. Future efforts into this area of boron cluster chemistry should prove fruitful.

Experimental

All reactions were performed under prepurified nitrogen atmosphere using Schlenk glassware. DMSO was distilled freshly from NaOH. Methylene chloride was distilled from CaH_2 and treated with NaH before use. Hexane and acetonitrile were distilled from CaH_2. PPN^+F^- was prepared from the anion exchange of PPN^+Cl^- purchased from Alfa Ventron Chemical Co. Acetic anhydride and hydroxylamine-O-sulfonic acid were from Aldrich Chemical Co. Diethylether was distilled from Na-benzophenone ketyl. Tetramethylammonium hydroxide was purchased as a 20% solution in methanol from Aldrich. 1,6-$Me_2SB_{10}H_8$-CO, $K_2B_9H_9$, $(NMe_4)_2B_9H_9$, and $(NBu_4)_2B_9H_9$. $(NEt_4)_2B_{11}H_{11}$ were prepared according to literature methods [13,5,6].

Infra-red spectra were recorded as KBr wafers on a Perkin Elmer 377 spectrometer. The ^{1}H NMR spectra were recorded on a Varian EM 360A spectrometer at 60 M Hz and a JEOL FX-90Q spectrometer at 90 MHz. Chemical shifts are reported relative to internal TMS. ^{11}B NMR spectra at 28.7 MHz were obtained on a JEOL FX-90Q spectrometer with deuterium-lock and chemical shifts are relative to external $BF_3 \cdot OEt_2$.

Reaction progress was monitored with TLC using 1.7 cm X 6.7 cm strips of Baker PEI-F cellulose plates using 6 *M* NH_4NO_3 as eluant. Visualization was by H_2PdCl_4 spraying. C, H and N analyses were performed by the University of New Hampshire Instrumentation Center.

$NMe_4B_9H_8NH_3$

A solution of 455 mg (4.02 mmol) NH_2OSO_3H in 5 ml of DMSO was added dropwise to a chilled solution of 500 mg (1.96 mmol) $(NMe_4)_2B_9H_9$ in 10 ml of DMSO. After warming to room temperature, the suspension was stirred for 3 hours to give a clear, orange-brown solution. This was filtered through Celite into 200 ml of 2-propanol to precipitate 315 mg of crude product. Residual $(NMe_4)_2SO_4$ was removed by washing with 25 ml of ethanol to give 250 mg (65% yield) of $NMe_4B_9H_8NH_3$ as a white, fluffy powder. Analytical samples were further purified by recrystallization from warm water.

Infra-red data: 3300, 3230, 3100, 2510, 2480, 1400, 1280, 1200, 1180, 1060, 1000 cm^{-1} in addition to NMe_4^+ bands at 1480 and 950 cm^{-1}. *Anal.* Calculated for $NMe_4B_9H_8NH_3$: C, 24.44; H, 11.79; N, 14.25. Found: C, 24.22; H, 12.04; N, 13.85.

$PPNB_9H_8NMe_3$

$NMe_4B_9H_8NH_3$ (330 mg, 1.68 mmol) was converted to the Na^+ form by cation exchange and dried in vacuum to give the hydroscopic NaB_9H_8-$NH_3 \cdot xH_2O$ salt. This was dissolved in 10 ml of methanol. A solution of 948 mg (1.7 mmol) of PPN

F in 10 ml of methanol was added with stirring to it. After one hour the suspension was filtered and the filtrate warmed to 60 ℃ and diluted with 100 ml of 60 ℃ water to precipitate 795 mg (1.20 mmol) of PPN $B_9H_8NH_3$. The light green product was dried under vacuum at 40 ℃. Its infra-red spectrum includes absorptions at 3100–3300, 3050, and 2480 cm^{-1}.

Under nitrogen, 250 mg (0.38 mmol) of $PPNB_9H_8NH_3$ was dissolved in 4 ml of CH_2Cl_2 and slowly added to a solution of 14 ml CH_2Cl_2 containing 0.5 ml (7.8 mmol) of CH_3I over 300 mg of 50% NaH dispersion. The solution was stirred for 24 hours and filtered. The filtrate was evaporated to dryness and extracted with CCl_4 to remove the oil. 180 mg of a light yellow powder was obtained after drying. This can be recrystallized from CH_2Cl_2/ether to give 80 mg of a clear, green-tinted crystalline product. Its infra-red spectrum contains bands at 3050, 1950, and 2480 cm^{-1}. The ^1H NMR spectrum in $CDCl_3$ contains resonances at 7.2–8.0 (phenyl), 2.65 and 3.30 ppm (methyls). Integration is in agreement with 75% of the 1-isomer and 25% of the 4-isomer of $B_9H_8NMe_3^-$.

$(NMe_4)_2(Me_2SB_{10}H_8COH)_2B_9H_7$

Five ml of acetonitrile was added to a mixture of 63 mg (0.24 mmol) of $(NMe_4)_2B_9H_9$ and 100 mg (0.47 mmol) of $1,6\text{-}Me_2SB_{10}H_8CO$. After one hour of stirring, the excess $B_9H_9^{2-}$ was filtered off and the orange filtrate concentrated to about 0.5 ml. Five ml of ether was slowly added with stirring and the precipitate was collected and dried to give an orange powder. The yield was 100 mg or 60%. Its infra-red spectrum includes bands at 3600, 3050, 2925, 2500, 1600, 1500, 1450, 1350, 1200, 1100, 1050, 1000, and 950 cm^{-1}. The ^1H NMR in CD_3CN contains singlets at 3.1 (24 H) and 2.9 (12 H) ppm. *Anal.* Calcd. for $(NMe_4)_2(Me_2SB_{10}H_8COH)_2B_9H_7$: C, 25.20; H, 9.21; N, 4.19. Found: C, 24.88; H, 9.20; N, 4.60.

$(NMe_4)_2(Me_2SB_{10}D_8COH)_2B_9H_7$

This was prepared as above using $1,6\text{-}Me_2SB_{10}D_8CO$ which was prepared from a 95% deuterated sample of $Na_2B_{10}H_{10}$ [14]. Infra-red peaks include those at 2500, 1870, 1200, 1040, 1000, 950, and 800 cm^{-1}.

$K_2(Me_2SB_{10}H_8COH)_2B_9H_7$

This was prepared as above from $K_2B_9H_9$. *Anal.* Calcd. for $K_2(Me_2SB_{10}H_8COH)_2B_9H_7 \cdot (CH_3CN)_{0.62}$: C, 13.97; H, 6.29; N, 1.40. Found: C, 13.80; H, 6.29; N, 1.40.

$(NMe_4)_3(Me_2SB_{10}H_8CO)_2HB_9H_7$

A solution of 0.25 mmol of NMe_4OH in CH_3CN was added to 93.6 mg (0.12 mmol) of $(NMe_4)_2(Me_2SB_{10}H_8COH)_2B_9H_7$ to form a yellow precipitate. After evaporation to dryness, the residue was washed with 2% NMe_4OH in methanol followed by ether. ^1H NMR showed two singlets in d_6-DMSO at 2.9 (12 H) and 3.1 (36 H) ppm. *Anal.* Calcd.: C, 29.20; H, 9.80; N, 5.67. Found: C, 28.72 H, 10.00; H, 5.64.

$NEt_4B_{11}H_{10}SMe_2$

An amount of 500 mg (1.27 mmol) of $(NEt_4)_2B_{11}H_{11}$ was stirred with 3.5 ml of acetic anhydride and 3.5 ml of DMSO for 16 hours. The cloudy solution was filtered through Celite into 100 ml of 2-propanol containing a small amount of NEt_4OH. The white precipitate was filtered off, washed with ethanol, ether, and dried at 45 ℃ overnight. The crude product was recrystallized from 15% aqueous acetonitrile at 80 ℃ to give 80–100 mg of crystalline $(NEt_4)B_{11}H_{10}SMe_2$. Its infra-red absorptions include bands at 2480, 1480, 1450–1380, 1360, 1175, 1080, 1050–975, 850, and 750 cm^{-1}. The ^{11}B NMR spectrum in D_6-DMSO is presented in Fig. 4 and Table I. *Anal.* Calcd.: C, 37.37; H, 11.29; N, 4.35. Found: C, 36.98; H, 11.28; N, 4.26.

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