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Reaction of $B_{11}H_{14}NR_4$ (R = Et, Bu) with M_2O_3 (M = As, Sb, Bi) in biphasic systems

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Abstract

The reaction of $B_{11}H_{14}NR_4$ (R = Et, Bu) with M_2O_3 (M = As, Sb Bi) in biphasic systems H_2O/CH_2Cl_2 or $NaOH/CH_2Cl_2$, with $C_6H_5NEt_3Cl$ as phase transfer catalyst, was investigated as a new route to the already described icosahedral $B_{11}H_{11}MNR_4$ (M = As, Sb, Bi; R = Et, Bu). When the above reaction was performed in basic medium, besides the expected heteroboranes, a new anionic species could be isolated and characterized by its 1D ^{11}B, $^1H\{^{11}B\}$ and 2D ^{11}B–^{11}B NMR spectra. Consistently with these data the formula $B_{11}H_{13}OB_{11}H_{13}{}^{2-}$,$2NEt_4{}^+$ is proposed, the anionic part consisting of two icosahedral fragments $B_{11}H_{13}$ (eleven normal B–H bonds and two bridge hydrogens in the open face) linked via a B–O–B bond; on both sides, the oxygen atom is attached, in *endo* position, to the unbridged boron atom of the open face. The same compound could be prepared by reaction of $B_{11}H_{14}{}^-$ with PO_4HNa_2, in $NaOH/CH_2Cl_2$ mixtures. A possible path involving a mild oxidation of $B_{11}H_{13}{}^{2-}$ by M_2O_3 (M = As, Sb, Bi) is suggested.

Introduction

The current resurgence in the tetrahydroundecaborate(−1) ion chemistry stems from the ready availability of $B_{11}H_{14}{}^-$, either from the reaction of pentaborane(9), B_5H_9, with MH (M = Na, K) [1] or from the well established reaction of $NaBH_4$ with $BF_3 \cdot Et_2O$ in diglyme [2]. Several icosahedral heteroboranes have been prepared by addition of a twelfth atom such as Al [3], P [4, 5], As [6], Sb [7], Se and Te [8] to the framework of $B_{11}H_{14}{}^-$ or the closely related $B_{11}H_{13}{}^{2-}$ dianion. Unfortunately, low yields and tedious workup have usually hampered further investigation of these compounds. The recent publication of a paper related to icosahedral boranes containing bismuth [9] prompted us to publish our own results concerning new synthetic routes to the derivatives $B_{11}H_{11}M^-$ (M = As, Sb, Bi) by use of biphasic systems under phase transfer catalysis conditions. During the course of this study, we were led to investigate the chemistry of $B_{11}H_{14}{}^-$ under basic conditions and in the presence of mild oxidants such as As_2O_3 and Sb_2O_3. Evidence for the new anionic species $(B_{11}H_{13})_2O^{2-}$ was derived from 1-D ^{11}B, $^1H\{^{11}B\}$ and 2-D ^{11}B–^{11}B NMR spectroscopy.

Experimental

Physical measurements

Boron (^{11}B) NMR spectra were obtained at 96.28 MHz with a Brüker AM 300 spectrometer and were externally referenced to $BF_3 \cdot Et_2O$ (positive values downfield). Two-dimensional NMR (^{11}B–^{11}B) spectra were obtained on the same instrument. Broad-band ^1H decoupling was continuously used. A general description for the two-dimensional (^{11}B–^{11}B) NMR technique has been previously reported [10]. Typically, 144 FIDs of 1K data points were collected. Acquisition times of 0.063 s were used with a relaxation delay of 0.01 s. Prior to 2-D Fourier transformation, the signal was apodized with a $\pi/2$ shifted sine bell. Longitudinal relaxation times T_1 (^{11}B) were measured by an inversion recovery sequence and values range between 6.6 and 10.3 ms. ^1H NMR spectra were obtained at 300.13 MHz on the same instrument. In the $^1H\{^{11}B\}$ experiments, use was made of the procedure in which a $^1H\{^{11}B(\text{off-resonance})\}$ spectrum is substracted from a $^1H\{^{11}B(\text{on-resonance})\}$

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spectrum in order to remove lines arising from ^{1}H resonances not coupled to the ^{11}B nucleus of interest [11].

Materials

All reactions were performed under an atmosphere of dry argon. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone; triethylamine was distilled from sodium hydroxide. Schlenk techniques were used with air-sensitive compounds. $NaB_{11}H_{14}$ was prepared from $NaBH_4$ and Et_2OBF_3 [2]. It was dissolved in water and converted to $Me_3NHB_{11}H_{14}$ by addition of Me_3NHCl to the solution. Further, the anionic species $B_9H_{14}^-$ was readily obtained (up to 40%) by degradation of $Me_3NHB_{11}H_{14}$ in aqueous solutions as soon as 30 °C (δ ^{11}B = −8.3, −22.6 and −24.6 ppm, J_{BH} = 139, 136 and 135 Hz with a ratio 1/1/1; lit. −8.2, −20.4 and −23.7 ppm, J_{BH} = 140, 132 and 140 Hz [12]). Similar behaviour was noticed with the 'acidic' salt $Et_3NHB_{11}H_{14}$, but not with the neutral ones $R_4NB_{11}H_{14}$ (R = Et, Bu).

$(NEt_4)_2(B_{11}H_{13})_2O$ (I)

To a solution of 0.57 g (2 mmol) of $Et_4NB_{11}H_{14}$ in 30 ml of methylene chloride were added 0.53 g (2.6 mmol) of arsenic(III) oxide in 20 ml water containing 4.0 g NaOH and 0.01 g (0.05 mmol) benzyltriethylammonium chloride as phase transfer catalyst. The resulting mixture was stirred for 5 days at room temperature (25 °C). The organic layer was recovered and washed with several portions of water. The organic solution was evaporated to dryness and after crystallization from methylene chloride/hexane, 0.08 g of **I** was obtained as a white material (14.3%), contaminated by a small amount of $NEt_4B_{11}H_{11}As$ (Fig. 1). The remaining solution was evaporated to dryness, stirred with hot water and filtered. A solution of Et_3NHCl was then added leading to a precipitate of 0.30 g of $NEt_3HB_{11}H_{11}As$ (50%).

$NEt_4B_{11}H_{11}Bi$

To a solution of 0.55 g (2 mmol) of $Et_4NB_{11}H_{14}$ in 50 ml THF and 1.2 ml (8.6 mmol) of triethylamine was added 0.7 g (2 mmol) of $BiCl_3$ in 20 ml of THF. The solution was stirred for 30 h at room temperature and the THF was removed under vacuum. The solid residues were extracted with acetone and precipitated with an aqueous solution of tetraethylammonium bromide. The crude precipitate was collected by filtration and crystallized from acetone/water to give 0.25 g (27%) of $NEt_4B_{11}H_{11}Bi$.

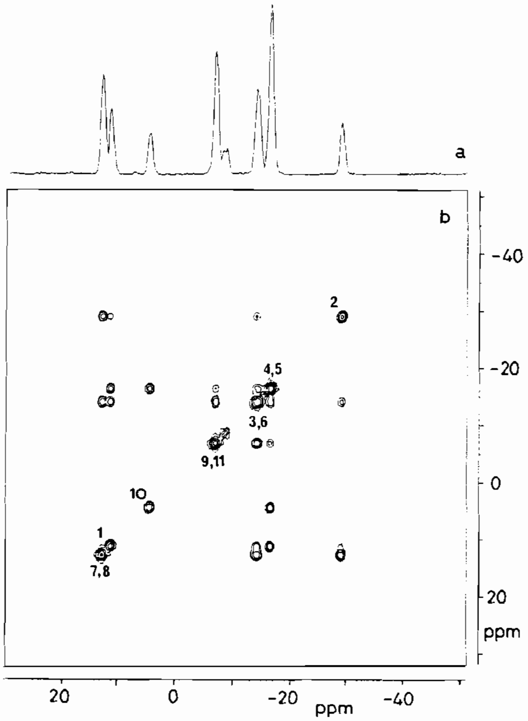

Fig. 1. a: Normal ^{11}B NMR spectrum of **I**, ^{1}H broad band decoupled; solvent $CDCl_3$; reference BF_3Et_2O; circles at 7.1, −8.2 and −8.8 ppm denote the presence of $B_{11}H_{11}As^-$ as an impurity. b: ^{11}B–^{11}B COSY spectrum of **I** with ^{1}H broad band decoupling.

$Na_2B_{11}H_{13}$

The $B_{11}H_{13}^{2-}$ anion can be obtained from $B_{11}H_{14}^-$ by proton abstraction with a strong base such as NaOH [13] or NaH [14]. To a solution of 1.51 g (7.8 mmol) of $Me_3NHB_{11}H_{14}$ in 50 ml of THF was added 0.50 g (20.8 mmol) of NaH under argon using Schlenk techniques. The slurry was stirred for 3 h at room temperature. Sodium hydride in excess was filtered and the solution evaporated to dryness under argon giving 1.32 g (7.4 mmol, 95%) of $Na_2B_{11}H_{13}$ (δ ^{11}B = −21.2 and −32.2 ppm, J_{BH} = 118 and 140 Hz; lit. −20.1 and −31.3 ppm, J_{BH} = 125 Hz [15]).

$(NEt_4)_2B_{11}H_{11}$

The $B_{11}H_{11}^{2-}$ anion was first prepared by pyrolysis of $Cs_2B_{11}H_{13}$ [15]. Using a slightly modified procedure, 0.8 g of $Na_2B_{11}H_{13}$ was heated for 3 h at 270 °C under an atmosphere of argon. The resulting solid was dissolved in water and precipitated with an aqueous solution of tetraethylammonium bromide. After crystallization from acetone/water, 0.78 g of $(NEt_4)_2B_{11}H_{11}$ (44%) was recovered (δ ^{11}B = −14.9 ppm, J_{BH} = 124 Hz; lit. −16.7 ppm, J_{BH} = 125 Hz [16]). The sample was contaminated by very small amounts of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ salts easily detected by ^{11}B NMR spectroscopy (δ ^{11}B = 0 and −28.4 ppm for the former; −16.1 ppm for the second).

Results and discussion

We have been investigating the reaction of M_2O_3 (M = As, Sb) with $B_{11}H_{14}NR_4$ (R = Et, Bu) at room temperature in biphasic systems CH_2Cl_2/NaOH 5 N, using $C_6H_5NEt_3^+,Cl^-$ as a phase transfer catalyst; no catalyst was needed when the tetrabutylammonium salt was used. In both cases, the yields of $B_{11}H_{11}M^-,NR_4^+$ (M = As, Sb; R = Et, Bu) were at least as good as those previously reported [6, 7]. When the same kind of reaction was applied to Bi_2O_3, the expected compound could not be obtained because of the known insolubility of Bi_2O_3 in alkaline medium. If the reaction was performed in CH_2Cl_2/H_2O, with or without catalyst added, $B_{11}H_{11}Bi^-$ (45% according to ^{11}B NMR data) was readily obtained together with unreacted $B_{11}H_{14}^-$. The same derivative could be prepared by reaction of $B_{11}H_{14}^-$ with $BiCl_3$ and Et_3N, in THF, although with smaller yield. Several attempts to obtain the related phosphorus insertion compound $B_{11}H_{11}P^-$ from $B_{11}H_{14}^-$ with $PI_3 + Et_3N$ in THF have been unsuccessful so far. The reaction of $B_{11}H_{14}^-$ with Na_2HPO_4, in the CH_2Cl_2/NaOH biphasic medium, failed as well. The ^{11}B NMR data for $B_{11}H_{11}M^-$ salts (M = As, Sb, Bi) are reported in Table 1, our figures being consistent with the literature values [9]. However, the main advantage of the method is a much cleaner reaction, the organic layer providing the expected anionic species $B_{11}H_{11}M^-$ with a small amount of side-products. Thus, when As_2O_3 was reacted with $B_{11}H_{14}^-,NEt_4^+$ in basic medium, besides the expected $B_{11}H_{11}As^-,NEt_4^+$ a secondary product I was obtained in smaller yield and could be isolated in pure form by recrystallization from CH_2Cl_2/hexane. The same compound I was obtained in still greater yield, together with $B_{11}H_{11}Sb^-$ and a small amount of $B_3H_8^-$, when Sb_2O_3 was used instead of As_2O_3 always in basic medium. Further, I becomes the major product when $B_{11}H_{14}^-$ is reacted with Na_2HPO_4. In any case, the presence of a base appears as a prerequisite to the formation of I. The ^1H decoupled ^{11}B NMR spectrum of I displays seven peaks with intensities 2/1/1/2/2/2/1 (Fig. 1), consistent with a boron framework based upon an icosahedron with one vertex removed (C_s symmetry). The only known neutral borane containing eleven boron atoms, the recently reported *nido*-undecaborane(15) $B_{11}H_{15}$ [17], is a very elusive compound readily decomposed above 0 °C. Among the three well-established anionic undecaborates, two of them, *nido*-$B_{11}H_{14}^-$ and *nido*-$B_{11}H_{13}^{2-}$, despite their pseudo C_s symmetry display very simple ^{11}B NMR spectra. Thus, the ^1B NMR spectrum of $B_{11}H_{14}^-$ was only recently described [1] by three doublets (instead of the broad, so-far reported doublet) in a ratio 1/5/5 corresponding to boron atoms 1, 2–6 and 7–11 [1] (Fig. 2 for the numbering). However, the chemical shifts of this anion being quite sensitive to the solvent used and the associated cation, the ^{11}B chemical shifts and coupling constants of $B_{11}H_{14}^-$ were measured for different cations and solvents (Table 2). The ^{11}B NMR spectrum of $B_{11}H_{13}^{2-}$ has been reported to consist of two doublets in a ratio 10/1 [15]; no better resolution of the signals could be achieved at 96 MHz. The ^{11}B NMR spectrum of $B_{11}H_{11}^{2-}$ is even simpler containing a single line (−14.8 ppm, J_{BH} = 124 Hz; −16.9 ppm, 125 Hz according to ref. 16) as deduced from 2-D ^{11}B–^{11}B NMR spectroscopy: the small cross peak observed for the two signals at 0 and −28.4 ppm was thus attributed to $B_{10}H_{10}^{2-}$ whereas the lack of correlation between the peaks at −14.8 and −16.1 ppm unambiguously supports

TABLE 1. ^{11}B NMR data of $B_{11}H_{11}M^-,NR_4^+$

M R_4N	Solvent	δ ^{11}B[a]	J_{BH}[a]
As Et_3NH	CH_2Cl_2	6.3 (1B)	143
		−8.6 (10B)	142
	THF[b]	7.9 (1B)	138
		−7.8 (5B)	117
		−8.9 (5B)	129
Sb[c] Bu_4N	CH_2Cl_2	10.3 (1B)	133
		−7.4 (5B)	146
		−8.9 (5B)	146
Bi[d] Et_4N	CH_3COCH_3	11.9 (1B)	134
		−5.9 (5B)	126
		−7.0 (5B)	128

[a] Chemical shifts in ppm with $BF_3 \cdot Et_2O$ as external reference, J_{BH} in Herz. [b] From ref. 6: 7.9, −7.9 and −9.0 ppm; J_{BH} = 134, 127 and 138 Hz. [c] From ref. 7: NMe_4^+ salt, DMF; 9.4, −6.9 and −9.3 ppm; J_{BH} = 135, 110 and 120 Hz. [d] From ref. 9: NMe_4^+ salt, same solvent; 12.3, −5.6 and −6.7 ppm; J_{BH} = 140, 134 and 134 Hz.

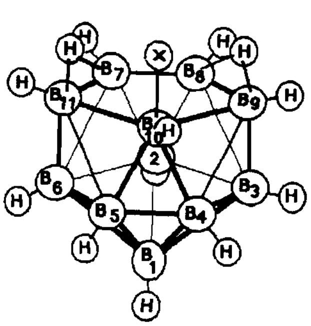

Fig. 2. Numbering used for $B_{11}H_{14}^-$ ($X = H^-$). The $B_{11}H_{13}OB_{11}H_{13}^{2-}$ anion can be viewed as resulting of two such units linked by the oxygen atom in *endo* position (X = O), the plane containing boron atoms (1), (2), (10), (X), (10′), (2′) and (1′) being a symmetry plane.

TABLE 2. ^{11}B NMR data of $B_{11}H_{14}M$

M	Solvent	δ ^{11}B (ppm)	J_{BH} (Hz)
NBu_4	CH_2Cl_2	−14.5, −16.3, −17.0	200(?), 156, 139
	CH_3CN	−14.0, −15.8, −16.5	148, 153, 141
NEt_4	CH_2Cl_2	−14.6, −16.2, −17.1	138, 159, 145
	CH_3COCH_3	−13.4, −15.3, −15.8	142, 146, 150
	DME[a]	−13.8, −15.8	
NEt_3H	CH_2Cl_2	−16.0, −17.4	
	CH_3COCH_3	−13.5, −15.5, −16.0	129, 152, 133
NMe_3H	CH_2Cl_2	−15.1, −16.1, −17.2	
Na	CH_2Cl_2	−14.5, −16.2, −17.0	
	CH_3CN	−13.8, −15.6	
	CH_3COCH_3	−13.3, −14.4, −15.3	
	THF	−14.1, −16.1, −16.5	135, 127, 117
K[b]	DME	−12.5, −14.1, −14.9	146, 156, 138

[a]DME= dimethoxyethane. [b]From ref. 1.

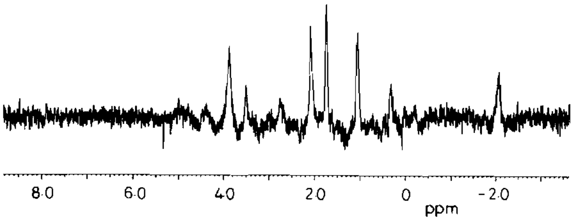

Fig. 3. ^1H NMR difference spectrum of I obtained with a $^1H\{^{11}B$(off resonance)$\}$ spectrum substracted from a $^1H\{^{11}B$(on resonance)$\}$ spectrum. Solvent $CDCl_3$. Reference TMS. Boron bonded protons at 3.9, 3.5, 2.75, 2.05, 1.7, 1.05 and 0.3 ppm (ratio 2/1/1/2/2/2/1); two bridge hydrogen atoms at −2.1 ppm.

the presence of $B_{12}H_{12}^{2-}$ as an impurity with $B_{11}H_{11}^-$. Thus, I appears as a new compound. The ^1H coupled ^{11}B NMR spectrum of I consists of seven doublets, indicative of the presence of eleven protons directly bonded to boron atoms. The $^1H\{^{11}B\}$ spectrum of I is difficult to interpret because of overlap with the strong signals of the NEt_4^+ group; however the difference spectrum (see 'Experimental') is very interesting strongly paralleling the ^{11}B NMR spectrum: thus, seven lines are indeed observed with approximative intensities 2/1/1/2/2/2/1 (Fig. 3), whereas a broad signal upfield corresponds approximatively to two bridge hydrogen atoms. The ratio of the chemical shifts $\delta^{11}B/\delta^1H$ leads to a straight line $y = -31.54 + 11.93x$ ($R = 0.99$). Furthermore, complete assignment for the ^{11}B NMR spectrum of I follows from results of its 2-D ^{11}B–^{11}B COSY (Fig. 1). The argument is as follows: B(2) and B(1) or B(10) and B(1) are the only area 1 boron atoms able to have a common cross-peak; hence the most shielded boron atom can be B(2) or B(10), the only suitable solution being B(2) because of the three cross peaks observed (B(10) should give rise to two cross-peaks only). Thus B(1) is readily attributed and B(3,6) differentiates from B(7, 8) as having a maximum of connectivities, five cross peaks, because of its central position in the boron framework. Thus, the other atoms are readily deduced. Several points are noteworthy: (i) the lack of cross-peaks between B(9, 11) and B(7, 8) is strongly indicative of bridge hydrogens between the corresponding atoms resulting in small electron density between the relevant boron atoms [18]; (ii) a related small electronic density between B(10) and B(9, 11), as a result of an electronegative substituent on B(10), can explain the lack of cross-peak for these atoms although a cross-peak was indeed observed between B(10) and B(4, 5) [10]. All these data, together with the fact that I is only obtained in basic medium, are consistent with a formula such as $B_{11}H_{13}OH^-$, NEt_4^+ with the ligand OH^- attached to B(10). However, the oxygen bonded proton could be detected neither by ^1H NMR spectroscopy (a signal at 3.89 ppm was observed in the related compound $SB_9H_{11}OH^-$ [11]) nor by infrared spectrometry (the stretching vibration ν(B–OH) is usually observed in the range 3400–3500 cm^{-1}). Instead, the IR spectrum of I displays a small peak near 3200 cm^{-1} that could be attributed to a B–O–B bond. Thus, the most likely formulation for I appears to be $B_{11}H_{13}OB_{11}H_{13}^{2-}$,$2NEt_4^+$, with the two eleven boron units being linked by an oxygen atom to B(10) and B(10′), respectively (C_s symmetry). Anyhow, additional proofs of the existence of such a B–O bond may be obtained by comparison of the ^{11}B NMR spectra of $B_{11}H_{14}^-$ and I, the relevant NMR data being reported in Table 3. Thus, a deshielding of about 20 ppm is observed for B(10) which could be accounted for by a boron atom bonded to oxygen; the deshielding is still larger for neighbouring B(9, 11) and also for apical B(1) whereas a shielding is observed for the antipodal B(2). Further, the high values observed for the coupling constants of the boron atoms in the open

TABLE 3. ^{11}B NMR data of $(NEt_4)_2(B_{11}H_{13})_2O$ (I) and $NEt_4B_{11}H_{14}$

I[a]	Atoms	$B_{11}H_{14}^{-b}$	D^c	T_1^d
12.8 (151)	9, 11	−17.1	+29.9	8.4
11.3 (141)	1	−14.6	+25.9	10.8
4.35 (163)	10	−17.1	+21.45	6.6
−7.0 (156)	7, 8	−17.1	+10.1	8.2
−14.15 (134)	4, 5	−16.2	+2.05	11.5
−16.4 (139)	3.6	−16.2	−0.2	9.0
−29.1 (139)	2	−16.2	−12.9	10.2

[a]Chemical shifts in ppm with BF_3Et_2O as external reference, coupling constants in Hz in brackets. [b]NEt_4 salt, solvent CH_2Cl_2. [c]$D = \delta\ ^{11}B\ (I) - \delta\ ^{11}B\ (B_{11}H_{14}^-)$. [d]In ms.

face of the icosahedron B(7, 8), B(9, 11) and B(10) as well as the short T_1 measured for B(10) are in line with the above formulation. Compounds such as $B_{11}H_{13}OH^-$ and $B_{22}H_{26}^{2-}$, prepared by mild oxidation of $B_{11}H_{14}^-$, have been claimed for in earlier literature [19] but no characterization was provided. Let us add that the related neutral compound $B_{11}H_{13}Me_2S$ has also been reported [20]. Our attempts to duplicate this work by reaction of $B_{11}H_{14}^-$ with HBF_4 and Et_2S have been unsuccessful so far, the reaction leading to a destruction of the cage. It is of interest to note that $B_{11}H_{14}^-$ itself can be, formally, considered as a $B_{11}H_{13}L$ species with $L=H^-$.

The formation of such a compound under our conditions is of interest, the only species reported so far concerning the acid–base systems $B_{11}H_{15}$/$B_{11}H_{14}^-$ and $B_{11}H_{14}^-$/$B_{11}H_{13}^{2-}$. The direct oxidation of $B_{11}H_{14}^-$ to $B_{11}H_{13}OH^-$ with air seems unlikely although small amounts of **I** were detected by ^{11}B NMR spectroscopy with $B_{11}H_{13}^{2-}$ as the main product when $B_{11}H_{14}^-$ samples were stirred in CH_2Cl_2/NaOH mixtures in the presence of air. The following path is proposed

$$B_{11}H_{14}^- + OH^- \longrightarrow B_{11}H_{13}^{2-} + H_2O$$

$$3B_{11}H_{13}^{2-} + As_2O_3 + 3H_2O \longrightarrow 3B_{11}H_{13}OH^- + 2As + 3OH^-$$

$$2B_{11}H_{13}OH^- \longrightarrow B_{11}H_{13}OB_{11}H_{13}^{2-}$$

the arsenic trioxide (Sb_2O_3, Bi_2O_3 or PO_4HNa_2) behaving as a mild oxidant. Compound **I** is a very stable compound that could be kept indefinitely in air without apparent modification. When treated by acids **I** leads to $B_{11}H_{14}^-$ with other species corresponding to a degradation of the cage. **Caution**: the so-obtained mixture spontaneously ignites in the presence of air. We are currently investigating the reaction of this compound and related species in connection with the so-far unknown chemistry of $B_{11}H_{14}^-$.

References

1 N. S. Hosmane, J. R. Wermer, Z. Hong, T. D. Getman and S. G. Shore, *Inorg. Chem., 26* (1987) 3638.
2 G. B. Dunks and K. P. Ordonez, *Inorg. Chem., 17* (1978) 1514.
3 T. D. Getman and S. G. Shore, *Inorg. Chem., 27* (1988) 3439.
4 J. L. Little, J. T. Moran and L. J. Todd, *J. Am. Chem. Soc., 89* (1967) 5495.
5 T. D. Getman, H. B. Deng, L. Y. Hsu and S. G. Shore, *Inorg. Chem., 28* (1989) 3612.
6 T. P. Hanusa, N. R. de Parisi, J. G. Kester, A. Arafat and L. J. Todd, *Inorg. Chem., 26* (1987) 4100.
7 J. L. Little, *Inorg. Chem., 18* (1979) 1598.
8 G. D. Friesen and L. J. Todd, *J. Chem. Soc., Chem. Commun.*, (1978) 349.
9 J. L. Little, M. A. Whitesell, J. G. Kester, K. Folting and L. J. Todd, *Inorg. Chem., 29* (1990) 804.
10 T. L. Venable, W. C. Hutton and R. N. Grimes, *J. Am. Chem. Soc., 106* (1984) 29.
11 X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, (1987) 1573.
12 N. N. Greenwood, H. J. Gysling, J. A. Mc Ginnety and J. D. Owen, *J. Chem. Soc., Chem. Commun.*, (1970) 505.
13 F. Klanberg and E. L. Muetterties, *Inorg. Synth., 11* (1968) 24.
14 H. Mongeot, A. Tangi and B. Bonnetot, *Inorg. Chim. Acta, 161* (1989) 143.
15 F. Klanberg and E. L. Muetterties, *Inorg. Chem., 5* (1966) 1955.
16 R. L. Middaugh and R. J. Wiersema, *Inorg. Chem., 10* (1971) 423.
17 T. D. Getman, J. A. Krause and S. G. Shore, *Inorg. Chem., 27* (1988) 2399.
18 D. F. Gaines, G. M. Edvenson, T. G. Hill and B. R. Adams, *Inorg. Chem. 26* (1987) 1813.
19 N. N. Greenwood, in A. F. Trotman-Dickenson (ed.), *Comprehensive Inorganic Chemistry,* Vol. 1, Pergamon, New York, 1st edn., 1973, p. 845.
20 L. J. Edwards and J. M. Makhlouf, *J. Am. Chem. Soc., 88* (1966) 4728.