Inorg. Chem. **1994,** *33,* 1243–1244

Synthesis of *nido*-$B_{11}H_{14}^-$ and Alkyl Derivatives via Systematic Cage Enlargement of the Decaborane(14) System: Crystal Structure of 7-Thx-$B_{11}H_{13}^-$

Donald F. Gaines,* Adam N. Bridges, and Randy K. Hayashi

Department of Chemistry, University of Wisconsin—Madison, 1101 University Avenue, Madison, Wisconsin 53706

Received October 19, 1993

The first synthesis of the tetradecahydroundecaborate(−1) anion, $B_{11}H_{14}^-$, from decaborane(14), $B_{10}H_{14}$, and Na- or $LiBH_4$ in specific ether solvents at elevated temperatures was postulated (and indirectly verified) to proceed via reaction of the $B_{10}H_{13}^-$ anion with borane, BH_3.[1] The mechanism of this formal insertion of "BH", from borane into $B_{10}H_{13}^-$ has not been seriously examined, in part because more convenient routes to $B_{11}H_{14}^-$ from lower boranes have been developed.[2–4] Our interests in the detailed mechanisms of borane cluster growth and substitution have recently led to the development of new, low-energy, regiospecific routes from $B_{10}H_{14}$ to $B_{11}H_{14}^-$ and to the first examples of alkyl derivatives, the 7-alkyl-$B_{11}H_{13}^-$ anions, as reported below.

The reaction of $Na[B_{10}H_{13}]$ with excess $ClBH_2{\cdot}SMe_2$ in Et_2O yields two boron products, $B_{10}H_{14}$ and $B_{11}H_{14}^-$, in a ratio of approximately 1:1. The formation of $B_{10}H_{14}$ led to the postulate that $B_{10}H_{13}^-$ plays the role of a proton acceptor in this reaction and that the reaction likely proceeds via an intermediate, tentatively formulated as $[B_{11}H_{15}(L)]$. Use of an alternate proton acceptor, stronger than $B_{10}H_{13}^-$, to eliminate $B_{10}H_{14}$ production and thereby improve the $B_{11}H_{14}^-$ yield, was subsequently explored. "Proton sponge", 1,8-bis(dimethylamino)napthalene, PS (protonated form = PSH), was first chosen because of its high pK_a (12.34), its ability to deprotonate $B_{10}H_{14}$, and its weak Lewis base donor character. The addition of excess $ClBH_2{\cdot}SMe_2$ to a 1:1 mixture of $B_{10}H_{13}^-$ and proton sponge produced $B_{11}H_{14}^-$ as the sole boron hydride product (eq 1).[5] Less basic amines (i.e.

$$Na[B_{10}H_{13}] + ClBH_2{\cdot}SMe_2 + PS \xrightarrow{Et_2O} [PSH][B_{11}H_{14}] + NaCl \quad (1)$$

Et_3N: $pK_a = 11.01$[6]) were unable to effectively compete with $B_{10}H_{13}^-$, which has been estimated to have a pK_a of ca. 10.5.[7]

Sodium hydride was also found to effect quantitative conversion to $B_{11}H_{14}^-$, albeit more slowly, provided the solvent is THF. The $B_{11}H_{14}^-$ anion can also be obtained directly from $B_{10}H_{14}$, $ClBH_2{\cdot}SMe_2$, and 2 molar equiv of NaH (eq 2).

$$B_{10}H_{14} + ClBH_2{\cdot}SMe_2 + 2NaH \xrightarrow{THF} Na[B_{11}H_{14}] + NaCl + 2H_2 \quad (2)$$

Preliminary observations suggest that PS and NaH may serve different functions in the above reactions. While PS and NaH deprotonate $B_{10}H_{14}$, it is doubtful that NaH can compete with $B_{10}H_{13}^-$ in the deprotonation of the $[B_{11}H_{15}(L)]$ intermediate, owing to its low solubility. The speed with which the proton sponge containing reaction occurs coupled with the absence of PSHCl in the precipitate suggests that PS competes successfully with $B_{10}H_{13}^-$ in the deprotonation of the $[B_{11}H_{15}(L)]$ intermediate. On the other hand, the sluggishness of the sodium hydride reaction and its dependence on the presence of the more basic THF lead us to suggest that the NaH does not compete with $B_{10}H_{13}^-$, but rather regenerates it from the $B_{10}H_{14}$ produced.

Application of the above reactions using 6-alkyldecaboranes[9] has provided the first syntheses of monoalkylundecaborane anions via regiospecific boron insertion chemistry as shown in eq 3. Preparation of the thexyl (2,3-dimethyl-2-butyl) derivative is a typical example.[10] The ^{11}B NMR spectrum of Ph_3PMe[7-Thx-$B_{11}H_{13}$] in CD_2Cl_2 exhibits six resonances (see supplemental data) and contains one coincidental overlap. An ^{11}B–^{11}B COSY analysis allowed unambiguous assignment of all resonances and is consistent with a 7-substituted undecaborane. Conspicuously absent, however, is the cross-coupling between the substituted boron, B(7), and borons B(8,11), suggesting that bridging hydrogens may be disturbing the magnetization vectors. The ^1H and ^{13}C NMR spectra of the thexyl group confirm its identity.[11] Similarly, 6-Me-$B_{10}H_{13}$ and 6-Sia-$B_{10}H_{13}$ react to produce the

$$6\text{-}R\text{-}B_{10}H_{13} + ClBH_2{\cdot}SMe_2 + 2NaH \xrightarrow{THF} 7\text{-}R\text{-}B_{11}H_{13}^- + NaCl + 2H_2 \quad (3)$$

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(2) Palmer-Ordonez, K.; Dunks, G. B. *Inorg. Chem.* **1978,** *17,* 1514.

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(4) Hosmane, N. S.; Wermer, J. R.; Hong, Z.; Getman, T. D.; Shore S. G. *Inorg. Chem.* **1987,** *26,* 3638.

(5) In a typical reaction 1.807 g (12.54 mmol) of $Na[B_{10}H_{13}]$ was prepared in 150 mL of dry Et_2O under N_2. Then 4.965 g (15.81 mmol) of "proton sponge" was added, followed by injection of 4.09 g (28.5 mmol) of 77% $ClBH_2{\cdot}SMe_2$,[8] with stirring. The yellow solution became red-orange and then light yellow, and a precipitate formed. After 20 min, the solution contained a light yellow precipitate. The solid was collected on a fine frit and washed several times with dry Et_2O to remove excess $ClBH_2{\cdot}SMe_2$ and proton sponge. The solids were extracted with four 30-mL portions of THF. The white solid that remained readily dissolves in D_2O and exhibits no ^1H NMR signals. ^{11}B NMR analysis of the yellow THF filtrate shows only $B_{11}H_{14}^-$ resonances at $\delta = -13.8$ d (1B), −15.6 d (5B), and −16.3 d (5B).[13] The filtrate was reduced in volume followed by addition of Et_2O to precipitate 5.297 g (11.82 mmol) of $PSH[B_{11}H_{14}]$ in a 94.3% yield. A ^1H NMR spectrum of the product in CD_3CN shows resonances characteristic of the proton sponge cation.

(6) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; John Wiley & Sons: New York, 1972; p 60.

(7) Atteberry, R. W. *J. Phys. Chem.* **1958,** *62,* 1458.

(8) Neat monochloroborane–dimethyl sulfide complex, $ClBH_2{\cdot}SMe_2$, is available from Aldrich Chemical Co. and is relatively stable. However, the complex undergoes redistribution with time to form equal amounts of $Cl_2BH{\cdot}SMe_2$ and $BH_3{\cdot}SMe_2$, which is monitored by ^{11}B NMR. Whether the redistribution products re-form monochloroborane during the reaction process is still uncertain, and it is possible that the actual amount of $ClBH_2{\cdot}SMe_2$ may be slightly higher than expected.

(9) Bridges, A. N.; Gaines, D. F. *Organometallics* **1993,** *12,* 2015.

(10) In a typical reaction under N_2, a 100-mL vacuum reactor containing 0.480 g (20.0 mmol) of oil-free NaH is cooled to −196 °C and a THF solution of 1.075 g (5.21 mmol) of Thx-$B_{10}H_{13}$ is injected slowly into the flask, followed by 2.373 g (16.54 mmol) of 77% $ClBH_2{\cdot}SMe_2$. The system is resealed, evacuated, warmed to room temperature, and stirred briskly overnight. Upon warming, the mixture evolves gas and becomes light yellow. A total of 11.5 mmol of hydrogen (expected 10.42 mmol) is collected, indicating complete reaction. The ^{11}B NMR spectrum of the reaction mixture shows the Na[Thx-$B_{11}H_{13}$] product along with a small amount of $B_{11}H_{14}^-$. The product is then metathesized to the triphenylmethylphosphonium salt via $[Ph_3PMe]Br$ in THF. Repeated precipitation from THF using hexanes gives 2.315 g of Ph_3PMe[7-Thx-$B_{11}H_{13}$] in an 89.8% yield.

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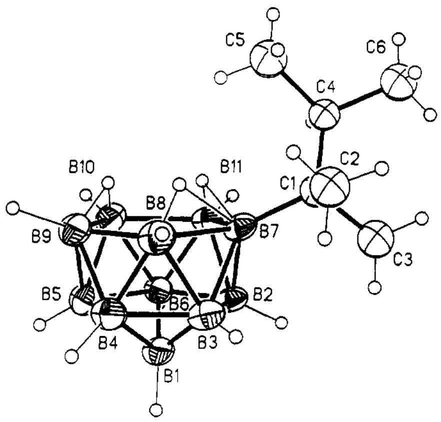

Figure 1. Structure of 7-Thx-$B_{11}H_{13}^-$.

corresponding 7-Me- and 7-Sia-$B_{11}H_{13}^-$ derivatives (Sia = 3-methyl-2-butyl).

An X-ray structural study of 7-Thx-$B_{11}H_{13}^-$, as the triphenylmethylphosphonium salt, was undertaken in order to access the perturbation of the B_{11} cluster by the alkyl substituent (Figure 1). In both 7-Thx-$B_{11}H_{13}^-$ and $B_{11}H_{14}^-$ the average B–B distance in the open face, 1.913 Å, is greater than in the internal tier ring, 1.770 Å.[12,13] In addition, the B–B distances between the alkyl substituted boron B(7) in 7-Thx-$B_{11}H_{13}^-$ and its nearest neighbors are on average 0.045 Å longer than the open face average in the parent, suggesting the alkyl group imparts some cage distortion. In the solid state the exoskeletal hydrogens in 7-Thx-$B_{11}H_{13}^-$ occupy three bridging sites around the cage face in contrast to the parent, $B_{11}H_{14}^-$, which contains two bridging and one endo exoskeletal hydrogen. Two of the bridging hydrogens in the thexyl derivative flank the alkyl site (the B(7)–B(8) and B(7)–B(11) edges), which is consistent with the absence of cross-coupling between these resonances in the 2D COSY array.

Acknowledgment. We would like to thank the National Science Foundation for support of this work.

Supplementary Material Available: ^{11}B NMR spectra and a ^{11}B-^{11}B COSY 2-D NMR spectrum for 7-Thx-$B_{11}H_{13}^-$ and, for the X-ray structure, tables of crystallographic data, atomic positional parameters, interatomic distances and angles, thermal parameters, crystal data, and data collection and refinement parameters (13 pages). Ordering information is given on any current masthead page.

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(11) ^1H NMR (δ, 500 MHz in CD_2Cl_2): +1.65 (sept) J_{H-H} = 6.5 Hz (1H); +0.86 (s) (6H); +0.84 (d) J_{H-H} = 6.5 Hz (6H). ^{13}C NMR (δ, CD_2Cl_2): +37.6 s (1C); +27.7 s (2C); +18.7 s (2C). The carbon atom adjacent to the boron cage is very broad, but appears to be centered at ca. +25 ppm. The ^{13}C shifts correspond well to those observed in 6-Thx-$B_{10}H_{13}$.

(12) Crystals of $Ph_3PMe[7\text{-}Thx\text{-}B_{11}H_{13}]$ were grown from a concentrated CH_2Cl_2 solution into a layer of hexanes. Crystallographic data are as follows: $C_{25}H_{44}B_{11}P$, MW = 494.5; triclinic $P\bar{1}$ (No. 2); a = 9.044(1) Å, b = 11.621(1) Å, c = 14.683(2) Å; α = 88.000(1)°, β = 86.332(9)°, γ = 72.668(8)°; V = 1470.0(3) Å^3; Z = 2; ρ_{calcd} = 1.12 g/cm^3. The structure was solved by direct methods and refined using Siemens SHELXTL Plus. Full-matrix least-squares refinement yielded R = 0.0758, and R_w = 0.0918 for 3011 independent reflections with $|F| > 4\sigma(F)$ measured on a Siemens P4 diffractometer up to 2θ = 114° (Cu Kα radiation λ = 1.541 78 Å, T = −160 °C). All H atoms were located in a difference electron density map. The terminal H atoms were treated as fixed groups, each riding on the B atom to which it is bonded. The positional parameters of the bridging H atoms were refined; the thermal parameters were refined to a single common value. As a check, the thermal parameters of the bridging H atoms were fixed at the final common value and the occupancies allowed to refine. All three of the bridging H atom occupancies refined to 1.0 ± 0.1 in the positions indicated.

(13) Getman, T. D.; Krause, J. A.; Shore, S. G. *Inorg. Chem.* **1988**, *27*, 2398.