Inorg. Chem. **1995,** *34,* 4523−4524

The Dianion of *nido*-Decaborane(14), *nido*-Dodecahydrodecaborate(2−), [$B_{10}H_{12}{}^{2-}$], and Its Solution Behavior

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Received December 13, 1994

Our continuing interest in borane cage expansion via insertion of boron and other main-group moieties has led us to investigate the somewhat elusive *nido*-$B_{10}H_{12}{}^{2-}$ anion, the most reactive and least well characterized of the five known decaborane anions: *closo*-$B_{10}H_{10}{}^{2-}$ (22 skeletal electrons, e^-), *nido*-$B_{10}H_{12}{}^{2-}$ (24 e^-), *nido*-$B_{10}H_{13}{}^-$(24 e^-), *arachno*-$B_{10}H_{14}{}^{2-}$ (26 e^-), and *arachno*-$B_{10}H_{15}{}^-$(26 e^-). Our investigations of the $B_{10}H_{12}{}^{2-}$ anion and its chemistry using current high-field NMR analyses led us to believe that the earlier report[1] on the characterization of unsolvated $[Ph_4As]_2B_{10}H_{12}$ and $[Ph_3PMe]_2B_{10}H_{12}$ may have contained characterization errors owing to unsuspected side reactions (*vide infra*).

nido-$B_{10}H_{12}{}^{2-}$ has proved to be difficult to characterize structurally, as it is a very aggressive proton "sponge", forming *nido*-$B_{10}H_{13}{}^-$, and will convert to other decaborane anions in many coordinating solvents. These properties of *nido*-$B_{10}H_{12}{}^{2-}$ do not appear to have been fully appreciated in prior studies.[1,2] Herein we report improved syntheses of *nido*-$B_{10}H_{12}{}^{2-}$, its high-field NMR characterization, its decomposition under various conditions, and some unexpected new reactions.

The original synthesis of $Na_2[B_{10}H_{12}]$ was carried out in a steel reactor over 6 days in diethyl ether.[3] Yields of 75% were reported, based on H_2 evolution. Re-examinations of the reaction, using both NaH and KH, have shown it to be very dependent on both the hydride and the solvent employed. Diglyme and Et_2O are the most satisfactory,[4] presumably because the product is completely insoluble. In the preferred diglyme solvent, the reaction is generally complete in 6 h at room temperature and yields are quantitative, based on H_2 evolution (eq 1).[5] The diethyl ether and diglyme insoluble

$$B_{10}H_{14} + \text{excess MH} \xrightarrow{\text{diglyme}} [M\cdot 0.7\text{diglyme}]_2[B_{10}H_{12}] + 2H_2 \quad (1)$$

$$M = Na, K$$

$[Na\cdot 0.7\text{diglyme}]_2[B_{10}H_{12}]$ is sparingly soluble in glyme (1,2-dimethoxyethane, DME) and moderately soluble in THF and CH_3CN, forming yellow solutions, the color being attributed to solvent complex formation.[6] $[K\cdot 0.7\text{diglyme}]_2[B_{10}H_{12}]$ dissolves only in CH_3CN, also forming a yellow solution.[7]

The white, unsolvated sodium and potassium salts of the $B_{10}H_{12}{}^{2-}$ anion, prepared in Et_2O, and the corresponding $[M\cdot 0.7\text{diglyme}]_2[B_{10}H_{12}]$ solvates, prepared in diglyme, appear to be indefinitely stable in the absence of air and proton sources. ^1H NMR confirms the presence of diglyme in the product, and it appears to be associated with the metal ion. The diglyme has no effect on the ^{11}B NMR spectrum or the reactivity of the dianion in THF compared to the diglyme-free salts prepared in Et_2O. The diglyme molecules remain associated with $Na_2B_{10}H_{12}$ in THF solution and are not removed by precipitation with Et_2O. The diglyme can, however, be removed by vacuum pyrolysis, during which decomposition occurs, giving products similar to those observed by Wilkes and Carter.[8]

An intriguing aspect of $M_2[B_{10}H_{12}]$ solutions in THF, CH_3CN, and DME is their yellow color, which we attribute to loose solvent−$B_{10}H_{12}{}^{2-}$ complex formation. Evaporation of these solutions re-forms the original white, solvent-free $M_2[B_{10}H_{12}]$, (or $[M\cdot 0.7\text{diglyme}]_2[B_{10}H_{12}]$) salts. When isolation from THF solution is followed by dissolution in CD_3CN, the ^1H NMR spectrum of the resulting yellow solution shows no evidence of THF. (Unsolvated $Na_2[B_{10}H_{12}]$ is precipitated from THF and CH_3CN solutions upon addition of Et_2O.)

The 160 MHz ^{11}B NMR spectrum of $Na_2B_{10}H_{12}$ in THF is consistent with a high-symmetry solution structure (and very unlike the spectrum reported[1] for $[Ph_4As]_2B_{10}H_{12}$). In CH_3CN, the essentially identical spectrum is better resolved (Figure 1) and is readily assigned on the basis of $^{11}B-^{11}B$ COSY NMR. The spectrum is remarkably similar to that of $B_{10}H_{13}{}^-$, the most noticeable difference being a single B(1,3) resonance in the $B_{10}H_{12}{}^{2-}$ spectrum. The considerable broadening of the B(6,9) resonance, even in CH_3CN, is tentatively attributed to solvent interaction at those sites. Similar broadening is observed in *arachno*- decaborane systems (i.e. $B_{10}H_{12}\cdot 2L$, $B_{10}H_{13}{}^-\cdot L$) in which ligands are coordinated to the cage B(6,9) positions. Strong cross-coupling observed between the B(6,9) and the B(5,7,8,10) resonances in the $^{11}B-^{11}B$ COSY NMR spectrum

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(1) Youll, B.; Greenwood, N. N. *J. Chem. Soc., Dalton Trans.* **1975,** 158.

(2) Greenwood, N. N.; Sharrocks, D. N. *J. Chem. Soc. A* **1969**, 2334.

(3) Wilkes, P. H.; Carter, J. C. *J. Am. Chem. Soc.* **1966**, *88*, 3441.

(4) Purity of the solvents is critical. Impurities in the solvents may not only reduce yields but also alter the entire course of the reaction. This is particularly true of diglyme (bp 162 °C), which is difficult to dry and must always be distilled under vacuum.

(5) Under nitrogen in a 50 mL Schlenk vessel, equipped with a stir bar, is dissolved 0.709 g (5.80 mmol) of decaborane(14) in about 25 mL of dry diglyme. Then, 0.334 g (13.91 mmol) of oil-free NaH is added *slowly, cautiously* in small amounts to the decaborane solution under N_2. The mixture effervesces copiously and becomes bright yellow. After addition, the mixture is stirred for 12 h or is stirred until all the yellow color has faded. The reaction mixture is filtered, and the solid is washed several times with dry ether until it is gray-white. The heterogeneous solid mixture (NaH and $[Na\cdot 0.7\text{diglyme}]_2[B_{10}H_{12}]$) is then extracted with THF to give a bright yellow filtrate. Immediate vacuum evaporation of the THF extract leaves a free-flowing white solid. The solid is collected using a fine frit and washed several times with dry ether to give 1.919 g of $[Na\cdot 0.7\text{diglyme}]_2[B_{10}H_{12}]$ in a 93% yield. For synthetic applications, the freshly prepared THF extract is used directly.

(6) The amount of diglyme associated with the dianion was determined by heating the solid in a vacuum to 200 °C, driving off the diglyme, and weighing the diglyme retrieved. Although $B_{10}H_{12}{}^{2-}$ decomposes at this temperature, the products are nonvolatile borane anions and H_2, which do not affect the gravimetric measurement.

(7) $[K\cdot 0.7\text{diglyme}]_2[B_{10}H_{12}]$ can be prepared as above using slightly less than 2 molar equiv of KH/mol of decaborane(14) in diglyme. In a typical reaction, 0.965 g (7.90 mmol) of $B_{10}H_{14}$ is dissolved in 15 mL of dry diglyme and 0.606 g (15.15 mmol) of KH is added slowly to the solution under N_2. After much effervescence, the yellow solution is allowed to stir briskly for 4 days, during which time a white precipitate forms. The mixture is then filtered through a fine frit and the solid is washed with diglyme, Et_2O, and then several portions of dry THF to leave 1.888 g of a white, hydride-free product mixture of $[K\cdot 0.7\text{diglyme}]_2[B_{10}H_{12}]$,74% along with 13% of both $B_{10}H_{10}{}^{2-}$ and $B_{10}H_{14}{}^{2-}$ salts (^{11}B NMR analysis of the totally soluble reaction mixture in CH_3CN). The actual yield of $[K\cdot 0.7\text{diglyme}]_2[B_{10}H_{12}]$ is 46%.

(8) Carter, J. C.; Wilkes, P. H. *Inorg. Chem.* **1970**, *9*, 1777.

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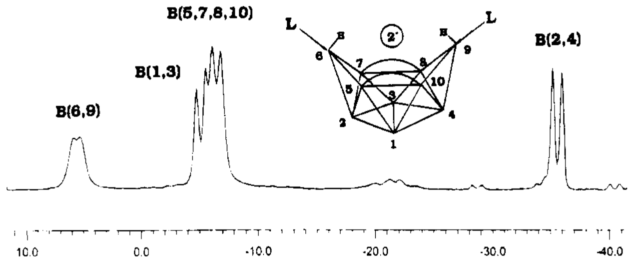
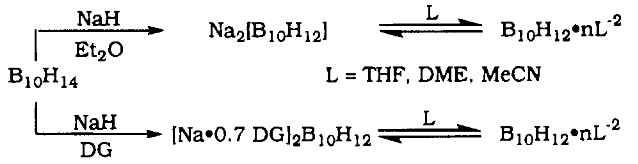


Figure 1. The 160 MHz ^{11}B NMR spectrum of $Na_2[B_{10}H_{12}]$ in CH_3-CN showing resonance assignments with positive downfield shifts referenced to $BF_3{\cdot}Et_2O$.

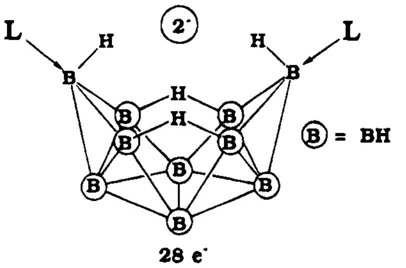
of $B_{10}H_{12}^{2-}$ augurs well for the ***absence*** of bridging hydrogens spanning these positions [B(5−6), B(6−7), B(8−9), B(9−10)].

In the 499 MHz ^{1}H spectrum of $Na_2[B_{10}H_{12}]$ in CD_3CN solution,[9] the unusually high field shift for the bridging hydrogens of intensity 2 at (δ) = −4.2 ppm is similar to that observed for the bridging hydrogens spanning the B(7−8) and B(5−10) vertices in *arachno*-$B_{10}H_{12}{\cdot}2L$, and *arachno*-$B_{10}H_{14}^{2-}$.

These data and the instability (*vide infra*) of the yellow $M_2[B_{10}H_{12}]$ solutions in CH_3CN, THF, and DME lead us to suggest that they contain loose solvent complexes of the $B_{10}H_{12}^{2-}$ anion as shown in the following scheme:



We further suggest that these are most likely $B_{10}H_{12}{\cdot}2L^{2-}$ complexes having an overall structure similar to that of *arachno*-$B_{10}H_{12}{\cdot}2L$ and *arachno*-$B_{10}H_{14}^{2-}$, while having a skeletal electron count (28 e⁻) of a *hypho* dianion cluster fragment, as shown below. The instability of this complex is similar to that observed for the only fully characterized *hypho* dianion, $B_5H_{11}^{2-}$:[10]



Aside from this arrangement, which is the only *static* possibility that preserves the observed symmetry, the hydrogens could be in flux around the cage face, as suggested by Todd[11] to explain the high symmetry of the ^{11}B NMR spectra of $B_{10}H_{13}^-$ solutions, but such a process is not consistent with the ^{11}B NMR and ^{11}B−^{11}B COSY NMR analysis (*vide supra*). Another plausible explanation is that a very labile *arachno*-$B_{10}H_{12}{\cdot}L^{2-}$ solution species exists in which monobase dissociation/association occurs rapidly on the NMR time scale at the B(6,9) positions. Such a species avoids consideration of an unprecedented *hypho*-decaborane dianion[12] but could still provide the driving force for the disproportionation and decomposition of $B_{10}H_{12}^{2-}$ solutions (*vide infra*).

The solution species, $[B_{10}H_{12}^{2-}]{\cdot}n$L (L = DME, THF, CH_3-CN), are not stable. In DME, the sparingly soluble $Na_2B_{10}H_{12}$ converts entirely to $B_{10}H_{10}^{2-}$ over a 24 h period. In contrast, THF solutions of $Na_2[B_{10}H_{12}]$ slowly convert to a 1:1 mixture of *closo*-$B_{10}H_{10}^{2-}$ and *arachno*-$B_{10}H_{14}^{2-}$, as well as *closo*-$B_9H_9^{2-}$. These species have also been observed as decomposition products in the vacuum pyrolysis[8] of $Na_2B_{10}H_{12}$. The CH_3CN solutions of $Na_2[B_{10}H_{12}]$ and $K_2[B_{10}H_{12}]$ decompose to a more complex mixture of products, the most prominent of which are $B_9H_9^{2-}$ and $B_{10}H_{10}^{2-}$.

Attempts to isolate crystalline salts of $B_{10}H_{12}^{2-}$ via metathesis with various large, cationic salts (i.e. $[Ph_3PMe]Br$, $[Ph_4As]Cl$, $[Bu_4N]Br$) in a THF/CH_2Cl_2 solution did not produce the expected $B_{10}H_{12}^{2-}$ species as reported by Greenwood,[1] but rather a mixture of products, including a 1:1 mixture of $B_{10}H_{10}^{2-}$ and $B_{10}H_{14}^{2-}$. While the yield of these dianions varied with the particular cation employed, the 1:1 ratio was always observed, and the introduction of CH_2Cl_2 solutions of the phosphonium and arsonium salts accelerated this conversion process. The observation of simultaneous formation of $B_{10}H_{14}^{2-}$ and $B_{10}H_{10}^{2-}$ leads irresistibly to the suggestion that two hydrogen atoms transfer from one $B_{10}H_{12}^{2-}$ group to another, though the actual transfer mechanism remains unknown. Another unexpected product isolated from these reaction mixtures is the monocarbon carborane anion $B_{10}H_{12}CH^-$. Indeed, reactions with Na_2B_{10}-$H_{12}{\cdot}2THF$ and CH_2X_2 (X = Br, I) in THF produced a 1:1 mixture of $B_{10}H_{12}CH^-$ and $B_{10}H_{13}^-$ exclusively,[13] which leads us to suggest that $B_{10}H_{12}^{2-}$ is acting both as a receptacle for CH_2X_2 insertion and as a proton acceptor. This carbon insertion route to the $B_{10}H_{12}CH^-$ anion may prove to be more convenient than the multistep synthesis currently available for $B_{10}H_{12}CH^-$.[14]

Acknowledgment. We thank the National Science Foundation for support of this research and for major departmental instrumentation grants.

Supporting Information Available: Figures of the ^{11}B−^{11}B COSY NMR and ^{1}H{^{11}B} NMR spectra of $[Na{\cdot}0.7diglyme]_2[B_{10}H_{12}]$ in CD_3-CN solution (3 pages). Ordering information is given on any current masthead page.

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(9) ^{1}H{^{11}B} NMR at 499 MHz in CD_3CN (B−H region only): δ = +2.4 (2H$_t$), +1.9 (6H$_t$), −0.6 (2H$_t$), −4.2 (2H$_b$). The spectrum is available as supporting information.

(10) McGaff, R. W.; Gaines, D. F. *Inorg. Chem.* **1995**, *34*, 1009.

(11) Todd, L. J.; Bodner, G. M.; Siedle, A. R. *J. Inorg. Nucl. Chem.* **1971**, *33*, 3671.

(12) We thank a reviewer for suggesting this alternate explanation.

(13) In a typical reaction, 1.64 mmol of $[Na{\cdot}0.7diglyme]_2[B_{10}H_{12}]$ is prepared from 0.20 g(1.6 mmol) of $B_{10}H_{14}$ and 0.15 g(6.2 mmol) of NaH as described above and dissolved in 35 mL of THF under N_2. Then 1.20 g (6.90 mmol) of CH_2Br_2 is added to the solution. The reaction mixture is stirred at room temperature overnight, during which time a white precipitate forms. Analysis by ^{11}B NMR shows two products: $B_{10}H_{13}^-$ and $B_{10}H_{12}CH^-$. NaH is then added to the reaction mixture and stirring is continued for an additional 12 h. NaH is added in order to regenerate the $B_{10}H_{12}^{2-}$ anion for further insertion of CH_2-Br_2. Subsequent analysis by ^{11}B NMR shows $B_{10}H_{12}CH^-$ as the major product with smaller amounts of $B_{10}H_{13}^-$ and some other impurities. The solution is filtered, and the filtrate is acidified with 1.3 mL of 1 M HCl/Et_2O. The solvent and excess acid are immediately removed under vacuum. The residue is kept under vacuum overnight in order to remove most of the $B_{10}H_{14}$. The residue is then extracted with several portions of hot hexanes and redissolved in THF. Then 0.143 g (1.31 mmol) of Me_4NCl is added to the solution, and the mixture is stirred for several hours. The solution is filtered again to remove NaCl, and most of the THF/Et_2O is removed to yield a bright-yellow liquor. The product is precipitated with Et_2O, filtered off, and recrystallized from THF/Et_2O to yield 0.089 g (0.403 mmol) of $Me_4N[B_{10}H_{12}CH]$ in a 25% yield. ^{11}B NMR shows trace contamination of $B_9H_{14}^-$.

(14) Knoth, W. H.; Little, J. L.; Lawrence, J. R.; Scholer, F. R.; Todd, L. J. *Inorg. Synth.* **1968**, *11*, 33.