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Synthesis and Investigation of $[B_{20}H_{17}O(CH_2)_5]^{3-}$, a Novel Solvent Complex of the $[B_{20}H_{18}]^{4-}$ Ion

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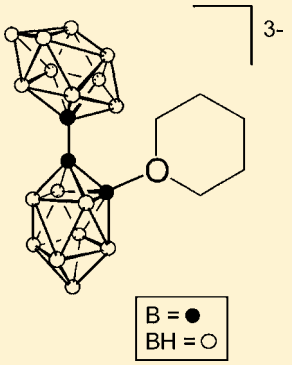
ABSTRACT: Reaction of the [*trans*-$B_{20}H_{18}$]$^{2-}$ ion with the *n*-butoxide ion, formed in situ from reaction of *n*-butanol and NaH, in tetrahydropyran (THP) produces in good yield an unexpected and isolable solvent-coordinated polyhedral borane anion, [*ae*-$B_{20}H_{17}O(CH_2)_5$]$^{3-}$. The anticipated product of nucleophilic attack, [*ae*-$B_{20}H_{17}O$*n*-Bu]$^{4-}$, is not observed under the reaction conditions. The solvent-coordinated product is also formed in the presence of either ethoxide or carbamate ion but is not observed if the ethoxide or carbamate ion is not present in stoichiometric amounts. In the presence of the *n*-butanethiol anion, the coordinated THP ring undergoes a ring-opening reaction, yielding the [*ae*-$B_{20}H_{17}O(CH_2)_5S$*n*-Bu]$^{4-}$ anion. Ring opening is also observed in the presence of the ethoxide ion in refluxing THP. Isolation of the previously proposed analogous solvent-coordinated tetrahydrofuran (THF) product, [*ae*-$B_{20}H_{17}O(CH_2)_4$]$^{3-}$, was unsuccessful; however, the product resulting from ring opening of THF by the *n*-butanethiol anion is reported.



INTRODUCTION

The ability of the electron-deficient, three-center two-electron bonds in the [*trans*-$B_{20}H_{18}$]$^{2-}$ ion to undergo nucleophilic attack was first investigated by Hawthorne and co-workers in 1963.[1] A detailed investigation of the reaction of the [*trans*-$B_{20}H_{18}$]$^{2-}$ ion and the hydroxide ion resulted in the proposed mechanism for the process.[2] The first step of the hypothesized mechanism was attack of the electron-deficient bonds by the nucleophile. The attack was followed by migration of the 10-boron atom cage with concerted migration of the displaced apical proton. The residual proton was then removed by a second equivalent of the nucleophile to produce the apical−equatorial (*ae*) isomer, the kinetic isomer, of the $[B_{20}H_{17}OH]^{4-}$ ion, with the hydroxide substituent located on the equatorial belt adjacent to the intercage linkage (Figure 1). Acid-catalyzed

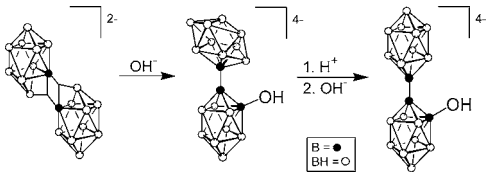


Figure 1. Reaction scheme for preparation of [*ae*-$B_{20}H_{17}OH$]$^{4-}$ and [a^2-$B_{20}H_{17}OH$]$^{4-}$.

rearrangement of the *ae* isomer produced the apical−apical (a^2) isomer, the thermodynamic isomer, with no change in the location of the hydroxide substituent (Figure 1). Analogous reactions have also been reported for synthesis of alkoxy and ammonio derivatives.[2−5]

Renewed interest in the derivative chemistry of the isomers of the $[B_{20}H_{18}]^{2-}$ ion has resulted from their potential application in boron neutron capture therapy (BNCT), a binary cancer therapy which is dependent on the site-selective delivery of large quantities of the boron-containing compound to the interior of tumor cells.[6,7] Synthesis of the $[B_{20}H_{17}SC(O)OC(CH_3)_3]^{4-}$ ion as an intermediate to the desired sulfur derivative, $[B_{20}H_{17}SH]^{4-}$, was reported in 1999.[8] Nucleophilic attack of the protected sulfur anion, $[SC(O)OC(CH_3)_3]^{-}$,[9] on the electron-deficient bonding region in the [*trans*-$B_{20}H_{18}$]$^{2-}$ anion formed, directly and in good yield, an unexpected isomer of $[B_{20}H_{17}SC(O)OC(CH_3)_3]^{4-}$ under mild conditions.[8] The isomer produced in the reaction was characterized by an a^2 boron atom intercage connection as well as the protected sulfur substituent location on the equatorial belt adjacent to the terminal boron apex (Figure 2).[8] No evidence of the *ae* isomer

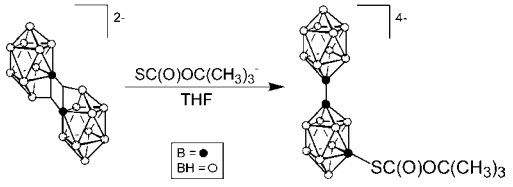


Figure 2. Reaction scheme for preparation of [a^2-$B_{20}H_{17}SC(O)OC(CH_3)_3$]$^{4-}$.

or the expected substitution pattern on the equatorial belt adjacent to the intercage connection was observed while monitoring the reaction. No other reports of the a^2 isomer being formed directly by nucleophilic attack on the [*trans*-$B_{20}H_{18}$]$^{2-}$ have been made; however, no reactions have been reported between the [*trans*-$B_{20}H_{18}$]$^{2-}$ ion and a sterically demanding nucleophile. In 2002, Hawthorne and co-workers summarized the reductive substitution reactions of the $[B_{20}H_{18}]^{2-}$ isomers investigated in their laboratories and

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proposed a revised mechanism which incorporated three distinct types of reactions, dependent on the identity of both the nucleophilic species and the reaction solvent.[10] The first step in the mechanism of Type 3 reactions is reversible coordination of a nucleophilic solvent molecule, such as tetrahydrofuran, to the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion (Figure 3).

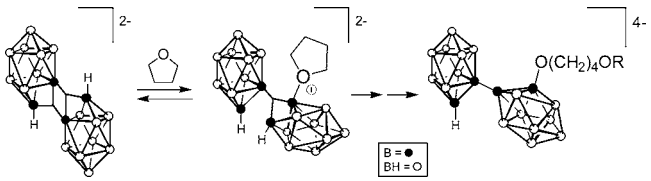

Figure 3. Partial proposed mechanism for formation of the *ae* isomer of the ring-opened product (R = methyl, isopentyl).

Coordination of the solvent molecule to the polyhedral borane anion makes the solvent molecule susceptible to nucleophilic attack by an anionic nucleophile present in solution, ultimately leading, in the case of THF, to ring opening of the THF molecule and production of the $[ae\text{-}B_{20}H_{17}O(CH_2)_4OR]^{4-}$ ions (R = methyl, isopentyl).[11] Formation of the unusual isomer of $[B_{20}H_{17}SC(O)OC(CH_3)_3]^{4-}$ cannot be explained by either mechanism currently in the literature.

The unexpected isomer of $[B_{20}H_{17}SC(O)OC(CH_3)_3]^{4-}$ formed in the reaction may be the result of the increased steric requirements of the protected sulfur anion. Therefore, an investigation of the reaction between the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion and a group of sterically demanding nucleophiles was initiated in an attempt to discern the factors which formed the unusual isomer. Tetrahydropyran (THP) was used as the solvent in each reaction in order to avoid the ring-opening reaction observed with THF.[11] Regardless of the identity of the nucleophile, the reaction yielded an identical product, the solvent complex of the $[B_{20}H_{18}]^{4-}$ ion. We report here the synthesis and chemical investigation of the $[B_{20}H_{17}O(CH_2)_5]^{3-}$ ion (Figure 4).

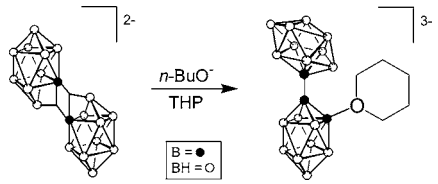

Figure 4. Reaction scheme for preparation of $[ae\text{-}B_{20}H_{17}O(CH_2)_5]^{3-}$.

EXPERIMENTAL SECTION

Materials. Synthetic reactions were performed under an argon atmosphere using Schlenk techniques when necessary. Sublimed decaborane, $B_{10}H_{14}$, was obtained from Professor Lee J. Todd at Gosport Scientific LLC (Gosport, IN). ***Caution: decaborane is a highly toxic, impact-sensitive compound that forms explosive mixtures especially when in contact with halogenated materials. Careful examination of the MSDS is recommended.*** The polyhedral borane starting materials, $(Et_3NH)_2[B_{10}H_{10}]$ and $(Et_3NH)_2[trans\text{-}B_{20}H_{18}]$, were prepared using published methods.[12−14] Tetrahydrofuran and tetrahydropyran were dried over sodium metal and distilled before use. Ethanol, *n*-butanol, and *n*-butanethiol were dried over 3A molecular sieves for a minimum of 24 h. All other reagents were obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO) and used without further purification.

Physical Measurements. ^{1}H, ^{13}C, and ^{11}B Fourier transform NMR spectra were obtained with a Varian INOVA instrument operating at 400, 100, and 128 MHz, respectively. Proton chemical shifts were referenced to residual solvent protons. Carbon chemical shifts were referenced to d_6-DMSO added as an internal standard to aqueous samples. Boron chemical shifts were externally referenced to $BF_3{\cdot}Et_2O$ in C_6D_6; peaks upfield of the reference are designated as negative. FT-IR spectra were obtained as Nujol mulls using a Perkin-Elmer 1300 Instrument. HR-FAB-MS (M + 1) were obtained at the University of Tennessee—Knoxville in a glycerol matrix.

Preparation of $Rb_3[B_{20}H_{17}O(CH_2)_5]$. Freshly distilled THP (20 mL), *n*-butanol (0.60 mL, 6.6 mmol), and a 60% dispersion of NaH in mineral oil (0.24 g, 5.8 mmol) were transferred to a reaction vessel, and the mixture was stirred at room temperature. Once gas evolution was no longer evident, $(Et_3NH)_2[trans\text{-}B_{20}H_{18}]$ (0.50 g, mmol) was added to the flask and allowed to react overnight at room temperature. Solvent was removed under reduced pressure, and the residue was dissolved in a minimum amount of methanol. A saturated solution of rubidium acetate was added to the solution, resulting in precipitation of a white solid. The crude product was isolated by filtration and recrystallized from water:methanol to yield 0.41 g (62% yield) of the desired product. ^{1}H NMR (400 MHz, D_2O, ppm): δ 3.97 (t, 4H, J = 5.4 Hz, O−CH_2), 1.49 (m, 4H, −CH_2−), 1.34 (m, 2H, −CH_2−). ^{13}C (100 MHz, D_2O:d_6-DMSO, ppm): 82.1, 25.2, 20.2. ^{11}B NMR (128 MHz, D_2O, ppm): 2.6, −3.2, −9.7, −25.4, −26.6, −28.4, −29.8, −31.9. IR (cm^{-1}, Nujol): 2426 (BH). HRMS (FAB$^+$) m/z: calcd for $B_{20}H_{27}C_5O$ 319.5019; found 319.4072.

Preparation of $Rb_4[B_{20}H_{17}O(CH_2)_5OEt]$. Freshly distilled THP (25 mL), ethanol (0.40 mL, 6.8×10^{-3} mol), and a 60% dispersion of NaH in mineral oil (0.30 g, 7.3×10^{-3} mol) were transferred to a reaction vessel, and the mixture was stirred at room temperature. Once gas evolution was no longer evident, $(Et_3NH)_2[trans\text{-}B_{20}H_{18}]$ (0.50 g, 1.1×10^{-3} mol) was added to the flask and the reaction mixture was allowed to reflux for 72 h. The reaction was monitored for completion using ^{11}B NMR spectroscopy. Solvent was removed under reduced pressure, and the residue was dissolved in a minimum amount of methanol. A saturated solution of rubidium acetate was added to the solution, resulting in precipitation of a white solid. The crude product was isolated by filtration and recrystallized from water:methanol to yield 0.59 g (60% yield) of the desired product. ^{1}H NMR (400 MHz, D_2O, ppm): 3.51 (q, 2H, J = 6.4 Hz, −OCH_2CH$_3$), 3.44 (t, 2H, J = 7.6 Hz, B−OCH_2CH$_2$), 3.13 (t, 2H, J = 8.0 Hz −OCH_2CH$_2$), 1.49 (m, 4H, J = 8.0 Hz, B−OCH$_2$CH_2), 1.30 (m, 2H, J = 8.0 Hz, C−OCH$_2$CH$_2$CH_2), 1.14 (t, 3H, J = 8.0 Hz, −OCH$_2$CH_3). ^{11}B NMR (128 MHz, D_2O, ppm): ∼7, 2.6, −3.2, −9.7, −25.7, −26.8, −30.0, −32.0, −33.7. IR (cm^{-1}, Nujol) 2423 (BH).

Preparation of $K_4[B_{20}H_{17}O(CH_2)_4Sn\text{-}Bu]$. Freshly distilled THF (20 mL), *n*-butanethiol (0.70 mL, 6.5 mmol), and a 60% dispersion of NaH in mineral oil (0.31 g, 7.4 mmol) were transferred to a reaction vessel, and the mixture was stirred at room temperature. Once gas evolution was no longer evident, $(Et_3NH)_2[trans\text{-}B_{20}H_{18}]$ (0.50 g, 1.1 mmol) was added to the flask and allowed to react overnight at room temperature. Solvent was removed under reduced pressure, and the residue was dissolved in a minimum amount of methanol. A saturated solution of potassium acetate was added to the solution, resulting in precipitation of a white solid. The crude product was isolated by filtration and recrystallized from water:methanol to yield 0.27 g (44% yield) of the desired product. ^{1}H NMR (400 MHz, D_2O, ppm): 3.32 (t, 2H, J = 7.6 Hz, B−OCH_2CH$_2$), 2.36 (m, 4H, CH_2−S−CH_2), 1.0−1.5 (8H, overlapping multiplets), 0.69 (t, 3H, J = 8.0 Hz, −CH$_2$CH_3). ^{13}C (100 MHz, D_2O:d_6-DMSO, ppm): 73.4, 39.8, 39.5, 39.2, 34.3, 32.1 30.0, 21.8. ^{11}B NMR (128 MHz, D_2O, ppm): 6.9, 2.5, −3.5, −6.1, −10.2, −25.3, −30.0, −34.1. IR (cm^{-1}, Nujol): 2430 (BH). High-resolution MS (m/z, [M − H]$^-$): calcd 393.6474; found 393.4264.

Preparation of $K_4[B_{20}H_{17}O(CH_2)_5Sn\text{-}Bu]$. Freshly distilled THP (20 mL), *n*-butanethiol (0.70 mL, 6.5×10^{-3} mol), and a 60% dispersion of NaH in mineral oil (0.30 g, 7.3×10^{-3} mol) were transferred to a reaction vessel, and the mixture was stirred at room temperature. Once gas evolution was no longer evident, $(Et_3NH)_2[trans\text{-}B_{20}H_{18}]$ (0.50 g, 1.1×10^{-3} mol) was added to the

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flask and allowed to react overnight at room temperature. Solvent was removed under reduced pressure, and the residue was dissolved in a minimum amount of methanol. A saturated solution of potassium acetate was added to the solution, resulting in precipitation of a white solid. The crude product was isolated by filtration and recrystallized from water:methanol to yield 0.23 g (26% yield) of the desired product. ^{1}H NMR (400 MHz, D_2O, ppm): 3.36 (t, 2H, J = 7.6 Hz, B−OCH_2CH$_2$), 2.39 (m, 4H, CH_2−S−CH_2), 1.0−1.5 (10H, overlapping multiplets), 0.72 (t, 3H, J = 8.0 Hz, −CH$_2$CH_3). ^{13}C (100 MHz, D_2O:d_6-DMSO, ppm): 72.8, 32.6, 32.5, 32.4, 32.3, 30.2, 26.2, 25.0, 14.5. ^{11}B NMR (128 MHz, D_2O, ppm): 6.2, 2.4, −3.6, −8.6, −10.3, −25.3, −30.1, −34.3. IR (cm^{-1}, Nujol): 2458 (BH). High-resolution MS (m/z, M$^-$): calcd 408.6820; found 408.4500.

RESULTS

Reaction of $(Et_3NH)_2[trans\text{-}B_{20}H_{18}]$ and the n-butoxide ion, formed in situ from reaction of n-butanol and NaH, in tetrahydropyran produces a stable solvent-complexed derivative of the $[B_{20}H_{18}]^{4-}$ anion, $[ae\text{-}B_{20}H_{17}O(CH_2)_5]^{4-}$ (Figure 4). ^{11}B, ^{1}H, and ^{13}C NMR spectra of the resulting compound are consistent with the assignment. In the ^{11}B NMR spectrum, the three terminal apical boron atom signals are present at 2.6, −3.2, and −9.7 ppm. The broad signal, at approximately 7 ppm, is assigned to the two boron atoms involved in the intercage connection. The signal associated with the substituted boron atom is not evident in the spectrum; however, it may be overlapping one of the terminal apical boron atom signals or broadened sufficiently to coincide with the baseline. The remaining equatorial boron atom signals are located between approximately −24 and −35 ppm in the ^{11}B NMR spectrum, consistent with the ^{11}B NMR spectrum of similar polyhedral borane anions.[3−5,8] In the ^{1}H NMR spectrum, the triplet centered at 3.97 ppm is assigned to the four α-hydrogens. Two multiplets, one centered at 1.49 ppm which integrated to four hydrogen atoms and the other centered at 1.34 ppm which integrated to two hydrogen atoms, are assigned to the β and γ hydrogen atoms, respectively, in the complexed solvent. Three signals, at 82.1, 25.2, and 20.2 ppm, were observed in the ^{13}C NMR spectrum and assigned to the α, β, and γ carbon atoms, respectively. The presence of the polyhedral borane was confirmed in the IR spectrum, with a B−H absorption at 2426 cm^{-1}. High-resolution mass spectrometry is consistent with the expected mass of the product.

Reaction of $(Et_3NH)_2[trans\text{-}B_{20}H_{18}]$ and the ethoxide ion in refluxing THP yields an ion which contains a 5-ethoxypentylether substituent on the polyhedral borane anion, $[ae\text{-}B_{20}H_{17}O(CH_2)_5OEt]^{4-}$, resulting from ethoxide-induced ring opening of the THP solvent (Figure 5). ^{11}B, ^{1}H, and ^{13}C NMR spectra of the resulting compound are consistent with the assignment. The product of the reaction is an apical−equatorial isomer, confirmed by the presence of three apical boron atom signals at 2.6, −3.2, and −9.7 ppm. The broad signal, at approximately 7 ppm, is assigned to the two boron atoms of the intercage connection. No signal is observed for the substituted boron atom; however, the signal may coincide with one of the apical boron atom signals or be sufficiently broadened to coincide with the baseline. The remaining signals, below −25 ppm, correspond to the equatorial boron atoms in the two cages. Although elemental analysis and/or high-resolution mass spectral analysis is lacking for this compound, the spectral data for this compound is consistent with that of the ring-opened products previously reported by Hawthorne and co-workers.[11] B−H absorption in the IR spectrum is observed at 2423 cm^{-1}, confirming the presence of the polyhedral borane anion.

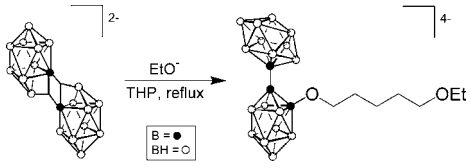

Figure 5. Reaction scheme for preparation of $[ae\text{-}B_{20}H_{17}O(CH_2)_5OEt]^{4-}$.

Reaction of $(Et_3NH)_2[trans\text{-}B_{20}H_{18}]$ and the n-butanethiol ion in THF at room temperature yields the ring-opened product, $[ae\text{-}B_{20}H_{17}O(CH_2)_4Sn\text{-}Bu]^{4-}$. ^{11}B, ^{1}H, and ^{13}C NMR spectra of the resulting compound are consistent with the assignment. The product of the reaction is an apical−equatorial isomer, confirmed by the presence of three apical boron atom signals at 2.5, −3.5, and −10.2 ppm. The broad signal, at approximately 7 ppm, is assigned to the two boron atoms of the intercage connection. The signal for the substituted boron is observed at −6.1 ppm and is broader than the signals for the apical boron atoms in the decoupled spectrum. In the proton-coupled spectrum this signal remains a singlet. The remaining signals, below −25 ppm, correspond to the equatorial boron atoms in the two cages. ^{1}H and ^{13}C NMR are consistent with the saturated aliphatic chain structure of both the ring-opened THF and the n-butyl group. B−H absorption in the IR spectrum is observed at 2430 cm^{-1}, confirming the presence of the polyhedral borane anion. High-resolution mass spectrometry is consistent with the expected mass of the product.

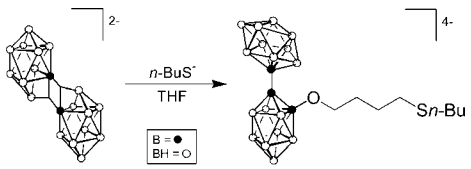

Figure 6. Reaction scheme for preparation of $[ae\text{-}B_{20}H_{17}O(CH_2)_4Sn\text{-}Bu]^{4-}$.

Reaction of $(Et_3NH)_2[trans\text{-}B_{20}H_{18}]$ and the n-butanethiol ion in tetrahydropyran (THP) at room temperature yields the ring-opened product, $[ae\text{-}B_{20}H_{17}O(CH_2)_5Sn\text{-}Bu]^{4-}$. ^{11}B, ^{1}H, and ^{13}C NMR spectra of the resulting compound are consistent with the assignment. The product of the reaction is an apical−equatorial isomer, confirmed by the presence of three apical boron atom signals at 2.4, −3.6, and −10.3 ppm. The broad signal, at approximately 6 ppm, is assigned to the two boron atoms of the intercage connection. The signal for the substituted boron is observed at −8.6 ppm and is broader than the signals for the apical boron atoms in the decoupled spectrum. In the coupled spectrum, this signal remains a singlet. The remaining signals, below −25 ppm, correspond to the equatorial boron atoms in the two cages. ^{1}H and ^{13}C NMR are consistent with the saturated aliphatic chain structure of both the ring-opened THP and the n-butyl group. The presence of the polyhedral borane anion is confirmed by the B−H absorption in the IR spectrum at 2458 cm^{-1}. High-resolution mass spectrometry is consistent with the expected mass of the product.

DISCUSSION

Reaction of $(Et_3NH)_2[trans\text{-}B_{20}H_{18}]$ with the n-butoxide ion, formed in situ from n-butanol and NaH, in THP as the solvent

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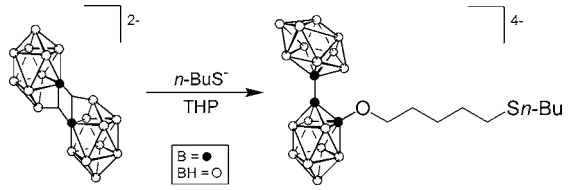

Figure 7. Reaction scheme for preparation of $[ae\text{-}B_{20}H_{17}O(CH_2)_5Sn\text{-}Bu]^{4-}$.

yields an unexpected solvent-complexed ion, $[B_{20}H_{17}O(CH_2)_5]^{3-}$, rather than the expected product, the $[B_{20}H_{17}On\text{-}Bu]^{4-}$ ion, resulting from nucleophilic attack at the electron-deficient bonding region of the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion. The solvent-complexed ion is analogous to that proposed but never isolated by Hawthorne and co-workers for THF in the Type 3 mechanism proposed in 2002.[10] A variety of nucleophiles have been investigated, including the *n*-butoxide, *tert*-butoxide ion, *n*-butylcarbamate ion, and *tert*-butylcarbamate ion. Regardless of the identity of the nucleophile, the solvent-complexed ion is formed. Significantly, no solvent-complexed ion is observed in the ^{11}B NMR spectrum when the $(Et_3NH)_2[trans\text{-}B_{20}H_{18}]$ is dissolved in THP and monitored over a period of 2 months. Hawthorne and co-workers noted the same result, no solvent-complex formation, when the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion was dissolved in THF or CH_3CN and monitored by ^{11}B NMR spectroscopy.[11] As a result, the nucleophile is required for the reaction to occur. Use of a catalytic amount (0.5% or 5% of the nucleophile) resulted in formation of a stoichiometric amount, based on the amount of nucleophile present, of product. Therefore, a stoichiometric amount of the nucleophile is required for complete reaction. When the reaction is completed using stoichiometric amounts of the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion, *n*-butanol, NaH, and THP, in CH_3CN as the solvent, no THP-complexed ion is formed at room temperature. THP must be present in large excess and is presumably forming a solvation shell around the $[trans\text{-}B_{20}H_{18}]^{2-}$ ion, preventing attack by the *n*-butoxide ion. Use of a strong base, such as NaH, in place of the nucleophile results in no reaction. Therefore, the anionic species is not acting as a base in the reactions. Unlike THF, the stability of the THP ring structure enables formation of the solvent complex, rather than the ring-opened product at room temperature. Attempts to isolate the THF-complexed product using (1) a low-temperature (0 °C) synthesis, (2) enhanced amounts of butylated hydroxytoluene (BHT) as the stabilizing agent for THF, and (3) nucleophiles with a larger steric demand, such as the *tert*-butoxide anion, were unsuccessful. All reactions yielded a majority of the THF ring-opened product. A THP-substituted derivative of the $[B_{12}H_{12}]^{2-}$ ion has been reported in the literature;[15] however, the product was formed by alkylation of the $[B_{12}H_{11}OH]^{2-}$ ion with 1,5-dibromopropane. Tetrahydrofuran (THF) and 1,4-dioxane derivatives of the $[B_{12}H_{12}]^{2-}$ ion have also been formed from $[B_{12}H_{12}]^{2-}$ in the presence of boron trifluoride etherate and the appropriate solvent molecule, THF or 1,4-dioxane.[16]

Reaction of $(Et_3NH)_2[trans\text{-}B_{20}H_{18}]$ with the ethoxide ion in refluxing THP yields the ring-opened product, $[B_{20}H_{17}O(CH_2)_5OEt]^{4-}$, in a single reaction, analogous to that observed by Hawthorne and co-workers for the hypothesized THF-complexed intermediate.[11] The ring-opened product can also be obtained from the isolated THP complex, $[B_{20}H_{17}O(CH_2)_5]^{3-}$, by allowing the complex to react with the ethoxide ion in refluxing THP. In the absence of refluxing temperatures, no ring opening will occur. As noted earlier, the THF complex hypothesized by Hawthorne could not be isolated and ring opening occurs at all easily attainable temperatures.[11] Likewise, the THF complex of $[B_{12}H_{12}]^{2-}$ will undergo ring opening in the presence of a variety of strong nucleophilic agents at room temperature.[16] The THP complex of the $[B_{12}H_{12}]^{2-}$ ion was less stable than the THP complex of the $[B_{20}H_{18}]^{4-}$ ion and ring opening occurred in the reaction of $[B_{12}H_{11}O(CH_2)_5]^-$ and either F^- or $[OH]^-$ at room temperature.[15] The stability of the THP complexes to ring opening may be predicted from the ^1H NMR spectrum of each of the complexes. The triplet assigned to the α protons in uncomplexed THP is centered at 3.5 ppm, while the triplets assigned to the α protons in THP complexed to the $[B_{12}H_{12}]^{2-}$ ion and the triplet assigned to the α protons in THP complexed to the $[B_{20}H_{18}]^{4-}$ ion are centered at 4.0 and 4.4 ppm, respectively. The larger downfield shift is consistent with a smaller electron localization at the oxonium ion and a higher susceptibility to nucleophilic ring opening.

Use of sulfur-based nucleophiles provides a route to investigate the substituted sulfur derivatives of the form $[B_{20}H_{17}SR]^{4-}$, a class of compounds under investigation for potential application in boron neutron capture therapy (BNCT). Therefore, in an attempt to isolate the desired $[B_{20}H_{17}X]^{4-}$ derivatives, the *n*-butanethiol anion was selected for investigation in the hopes that the stronger nucleophile, the S*n*-Bu anion, would enhance the reactivity of the nucleophile with the polyhedral borane cage as opposed to the solvent. Room-temperature reaction of $(Et_3NH)_2[trans\text{-}B_{20}H_{18}]$ and the *n*-butanethiol anion in THF as the solvent resulted in ring opening of THF by the nucleophilic sulfur anion and formation of the $[B_{20}H_{17}O(CH_2)_4Sn\text{-}Bu]^{4-}$ ion. In the case of THF, both the oxygen and the sulfur nucleophiles are capable of the nucleophilic ring-opening reaction at room temperature. When THP was used as the solvent, the sulfur anion also induced the nucleophilic ring-opening reaction at room temperature, forming the $[B_{20}H_{17}O(CH_2)_5Sn\text{-}Bu]^{4-}$ ion. In the case of THP, the oxygen-based nucleophile was not sufficiently strong to induce the nucleophilic ring-opening reactions at room temperature whereas the use of the stronger sulfur-based nucleophile produced the ring-opened product without the necessity of refluxing temperatures. Only the oxygen-based nucleophiles have been investigated in prior reports.[15,16]

■ CONCLUSIONS

A novel solvent-coordinated derivative of the $[B_{20}H_{18}]^{4-}$ anion, $[ae\text{-}B_{20}H_{17}O(CH_2)_5]^{3-}$, was synthesized from reaction of the triethylammonium salt of the $[trans\text{-}B_{20}H_{18}]^{2-}$ anion and the *n*-butoxide ion in THP as the solvent. The reaction conditions required for formation of the anion have been determined. A wide variety of nucleophiles, including alkoxides and alkylcarbamate anions, yield the same THP-coordinated product. Although the absolute role of the nucleophile remains unknown, stoichiometric amounts of the nucleophile are required for formation of the THP-coordinated compound. The nucleophile does not act as a catalyst in the reaction nor is the reaction base mediated. The reaction does not occur unless THP is the solvent for the reaction. Therefore, the results suggest that formation of the solvent-coordinated anion is the result of mass action. The ability of the solvent-coordinated anion to ring open was investigated. In refluxing THP, the ethoxide ion opens the THP ring that is coordinated to the polyhedral borane cage, yielding the $[B_{20}H_{17}O(CH_2)_5OEt]^{4-}$

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anion. At room temperature, the anion of *n*-butanethiol opens the THP ring that is coordinated to the polyhedral borane cage, yielding the $[B_{20}H_{17}O(CH_2)_5Sn\text{-}Bu]^{4-}$ anion. Several unsuccessful attempts were made to isolate the THF-coordinated anion $[B_{20}H_{17}O(CH_2)_4]^{3-}$ that was proposed by Hawthorne and co-workers;[10] however, reaction of the triethylammonium salt of the $[trans\text{-}B_{20}H_{18}]^{2-}$ anion and the anion of *n*-butanethiol in THF yields the $[B_{20}H_{17}O(CH_2)_4Sn\text{-}Bu]^{4-}$ anion, which presumably results from the THF-coordinated intermediate.

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Notes

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