The Synthesis and Characterization of Bis-Substituted Derivatives of the $[a^2\text{-}B_{20}H_{18}]^{4-}$ Anion and the Interconversion of Isomers

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The apical−apical (a^2) isomer of $[Et_4N]_4[B_{20}H_{18}]$ reacts with oxalyl chloride in dichloromethane to produce a protonated bis-substituted carbonyl species, $[Et_4N][a^2\text{-}B_{20}H_{17}(CO)_2]$ ($[Et_4N][H\mathbf{1}]$), in 60% yield. Removal of the bridging hydrogen of the $[H\mathbf{1}]^-$ anion in aprotic media results in rearrangement to form the equatorial−equatorial $[e^2\text{-}B_{20}H_{16}(CO)_2]^{2-}$ anion ($[e^2\text{-}\mathbf{1}]^{2-}$). The reaction of $[Et_4N][H\mathbf{1}]$ with sodium azide in acetonitrile produces $[Et_4N]_3[a^2\text{-}B_{20}H_{17}(NCO)_2]$ ($[Et_4N]_3[H\mathbf{2}]$) in 53% yield, which subsequently reacts with isopropylamine in acetonitrile to provide the urea derivative $[a^2\text{-}B_{20}H_{16}(NH_2C(O)NH(i\text{-}Pr))_2]^{2-}$ ($[Et_4N]_2[\mathbf{4}]$) in 89% yield. The $[H\mathbf{1}]^-$ ion is hydrolyzed in aqueous acetonitrile to give a protonated $[a^2\text{-}B_{20}H_{17}(CO_2H)_2]^{3-}$ ion ($[H\mathbf{3}]^{3-}$) in 61% yield. The a^2 isomers of the bis-substituted species $[B_{20}H_{16}(CO_2H)_2]^{4-}$ ($[\mathbf{3}]^{4-}$), $[B_{20}H_{16}(NCO)_2]^{4-}$ ($[\mathbf{2}]^{4-}$), and $[B_{20}H_{16}(NH_2C(O)NH(i\text{-}Pr))_2]^{2-}$ ($[\mathbf{4}]^{2-}$), formed by the removal of the bridging proton from their protonated precursors, rearrange to form a mixture of *ae* isomers in solution.

The search for hydrolytically stable, hydrophilic, boron-rich species for exploitation in boron neutron capture therapy (BNCT) has led to the synthesis and characterization of a variety of novel 20-boron-atom derivatives.[1] The majority of these species were synthesized via the attack of a nucleophile upon the electron-deficient three-center, two-electron bonds of the $[B_{20}H_{18}]^{2-}$ anion.[2−4] The $[B_{20}H_{18}]^{2-}$ anion is also the precursor to a set of electron-rich $[B_{20}H_{18}]^{4-}$ isomers in which the aromatic character of the component $[closo\text{-}B_{10}H_9]^{2-}$ cages is similar to that of the $[closo\text{-}B_{10}H_{10}]^{2-}$ cage itself.[5,6] Whereas the derivative chemistry of the $[closo\text{-}B_{10}H_{10}]^{2-}$ anion has been studied extensively,[7] the potential of the $[B_{20}H_{18}]^{4-}$ isomers to undergo new reactions and to form new derivatives has remained virtually unexplored.

The reduction of $[Et_3NH]_2[B_{20}H_{18}]$ with sodium in liquid ammonia produces the kinetic reaction product, $[e^2\text{-}B_{20}H_{18}]^{4-}$, an anion consisting of two *closo*-decaborate (2−) cages linked through an equatorial−equatorial (e^2) boron−boron bond, usually isolated as its potassium salt.[5,6] Protonation of $K_4[e^2\text{-}B_{20}H_{18}]$ (Scheme 1) produces a mixture of isomeric $[B_{20}H_{19}]^{3-}$ anions in solution.[5] The rapid basification of this mixture results in $K_4[ae\text{-}B_{20}H_{18}]$, whose anion consists of two decaborate cages linked through an apical−equatorial (*ae*) boron−boron bond. Protonation of $K_4[ae\text{-}B_{20}H_{18}]$ produces an isomeric anion mixture that includes the $[a^2\text{-}B_{20}H_{19}]^{3-}$ anion, whose solid state structure has been crystallographically determined to consist of two decaborate cages linked by a bridging hydrogen atom between two apical boron atoms.[8] In most solvents, the $[a^2\text{-}B_{20}H_{19}]^{3-}$ anion (and other protonated $[B_{20}H_{18}]^{4-}$ derivatives) exists as a mixture of tautomers and/or isomers, and exhibits a complex ^{11}B NMR spectrum because of the fluxionality of the bridging proton and the presence of equilibrium concentrations of species such as $[ae\text{-}B_{20}H_{19}]^{3-}$.[5,8] These rearrangements leading to isomerization of the $[B_{20}H_{18}]^{4-}$ ion are not well understood but appear to involve the migration of intact $[closo\text{-}B_{10}H_9]^{2-}$ clusters promoted by acid catalysis and protic solvents. Basification of solutions of the $[a^2\text{-}B_{20}H_{19}]^{3-}$ anion yields the kinetic reaction product, which is also the most thermodynamically stable isomer, the $[a^2\text{-}B_{20}H_{18}]^{4-}$ ion.[5] The latter structure consists of two $[closo\text{-}B_{10}H_9]^{2-}$ cage fragments linked to each other by a bond between an apical boron atom of each cage (Scheme 1).

The carbonyl group is a versatile substituent that has been shown to be a useful precursor to a wide variety of other substituents in polyhedral borane chemistry.[9−12] Acyl derivatives, such as amides and esters, are obtained by the reaction of nucleophiles with such carbonyl groups.[13,14] Substitution of the carbonyl group can lead to the formation of amines, and reaction of the carbonyl group with an azide anion forms an isocyanate through the Curtius rearrangement.[13] Most difficulties arise from the synthesis of the initial polyhedral borane carbonyl

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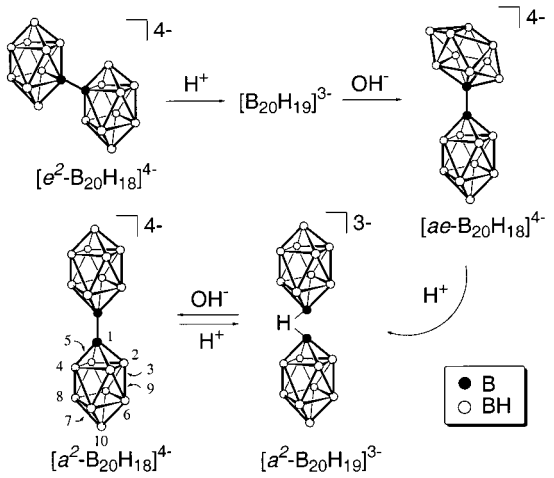
Scheme 1



precursor. However, oxalyl chloride was found to react with several [*closo*-$B_{10}H_{10}]^{2-}$ salts to form a single monosubstituted carbonylated anion product, [*closo*-2-$B_{10}H_9CO]^-$, which was subsequently used to synthesize a variety of other derivatives.[15]

With the promise of the possible use of many of these reactive polyhedral borane species in BNCT chemistry, a compound containing a larger number of boron atoms has a higher probability of therapeutic success than one with fewer boron atoms. Therefore, the derivatization of the 20-boron-atom species [a^2-$B_{20}H_{18}]^{4-}$ was investigated because of the similarity between this compound and the [*closo*-$B_{10}H_{10}]^{2-}$ anion. We report here the reaction of oxalyl chloride with $[Et_4N]_4$[a^2-$B_{20}H_{18}$] to produce a single, kinetically controlled, protonated, bis-substituted derivative, [a^2-$B_{20}H_{17}(CO)_2]^-$, in good yield. The carbonyl substituents present in this species react in a fashion similar to that observed in other previously reported polyhedral borane carbonyls to afford the desired bis-substituted species. However, all of the new derivatives are subject to unprecedented isomerization reactions. The synthesis, characterization, and structural rearrangements of representative derivatives are presented.

Experimental Section

Materials and General Procedures. The potassium salt of [a^2-$B_{20}H_{18}$·xH$_2$O]$^{4-}$ was prepared by published methods.[5,6] Oxalyl chloride was obtained from Aldrich as a 2.0 M solution in dichloromethane and used as received. Dichloromethane and acetonitrile were freshly distilled over calcium hydride. Diethyl ether was dried over sodium metal and distilled before use. All other reagents were obtained from commercial sources and used without further purification unless otherwise noted. Silica gel was activated by oven drying prior to use. Standard glovebox, Schlenk, and vacuum-line techniques were employed for all manipulations of air- and moisture-sensitive compounds.

Physical Measurements. The ^{11}B NMR spectra were recorded at 160 MHz using a Bruker ARX 500 NMR spectrometer and referenced to external BF_3·OEt_2 in $CDCl_3$. Resonances upfield with respect to the reference are designated as negative. The ^{1}H NMR spectra (400 MHz) were recorded on a Bruker ARX 400 NMR spectrometer. Infrared spectra were obtained from solutions dried under nitrogen on sodium chloride plates with a Nicolet 205 FT-IR spectrometer; only anion absorptions are reported. Electrospray ionization mass spectra (ESI-MS) were obtained by injection of dissolved samples into an ion spray source (typical flow, 10 μL/min; orifice voltage, 30 V) connected to a quadrupole mass spectrometer (PE Sciex API III, Perkin-Elmer, Norwalk, CT), which was scanned from *m*/*z* 50 to 500 (step size, 0.1 Da; scan speed, 5 s). The mass spectrometer was operated in the negative-ion mode using signals of the multiply charged ion series from a separate injection of polypropylene glycol.

Assignment of Structures and ^{11}B NMR Spectra. In all reactions, the decaborate cages appeared to remain intact, and the only rearrangements observed involved intercage bonding. Attempts to obtain crystals suitable for X-ray crystallography were unsuccessful (a common difficulty with $[B_{20}H_{18}]^{4-}$ derivatives). However, some of the derivatives reported here produced two-dimensional (2D) COSY ^{11}B{^{1}H} NMR spectra with sufficient resolution to allow their complete assignment. In other cases, insufficient resolution of the equatorial region of the spectrum (>10 ppm) did not permit a unique determination of substitutional isomers, but the intercage bonding could still be determined by analysis of the apical (B1, B10) region of the spectrum (<10 ppm).

The ^{11}B NMR spectra of protonated derivatives were invariably complicated by additional peaks because of the fluxionality of the bridging proton (as in the parent $[B_{20}H_{19}]^{3-}$ ion).[8] These spectra were highly solvent- and moisture-dependent and gave the appearance of a normal spectrum for an [a^2-$B_{20}H_{18}]^{4-}$ derivative, along with some additional low-intensity peaks and shoulders (which disappear upon deprotonation), which are usually associated with the signals for the B1−B5 atoms (see, for example, the NMR of [H**1**] in Figure 1). These signals (doublets) were not resolved well and could not be integrated, lying primarily in the equatorial region of the spectrum. When observed and reported here, these peaks are designated in this section as "tautomeric".

Preparation of $[Et_4N][a^2\text{-}B_{20}H_{17}(CO)_2]$ ($[Et_4N][H1]$). The tetraethylammonium salt of the [a^2-$B_{20}H_{18}]^{4-}$ ion was prepared from a hot, saturated aqueous solution of K_4[a^2-$B_{20}H_{18}$·xH$_2$O][6] by addition of saturated aqueous tetraethylammonium bromide. The precipitated $[Et_4N]_4$[a^2-$B_{20}H_{18}$] was filtered and dried overnight under vacuum.

A slurry of $[Et_4N]_4$[a^2-$B_{20}H_{18}$] (3.42 g, 4.54 mmol) in dichloromethane (150 mL) was cooled in an ice bath. A 2.0 M solution of oxalyl chloride in dichloromethane (5 mL, 10 mmol) was added. Upon addition of the oxalyl chloride, the suspension slowly turned bright yellow. The mixture was stirred overnight while slowly warming to room temperature. The solvent and excess oxalyl chloride were removed under reduced pressure. Dichloromethane (100 mL) was added, and the insoluble, unreacted starting material was removed by filtration. Addition of diethyl ether (300 mL) to the filtrate yielded 1.14 g of $[Et_4N]$[H**1**] (2.72 mmol, 60%). IR (NaCl plate): 2536 (BH), 1859 (BHB), 2157 cm^{-1} (CO). ^{11}B NMR in CH_2Cl_2 (ppm; relative area, multiplicity, and assignment, if determined, in parentheses): 14.0 (2, d, B10), −1.9 (2, s, B1), −18.2 (2, d, B8), −20.8 (4, d, B2/B3), −23.1 (4, d, B4/B5), −27.1 (4, d, B7/B9), −41.5 (2, s, B6) (tautomeric peaks at 5.0, −21.9, −24.2, −25.2). ESI-MS (CH_3CN/H_2O, *m*/*z*): 144.0 {[**1**]}$^{2-}$, 161.5 {$(H_2O)_2$[**1**]}$^{2-}$, 289.1 {[H**1**]}$^-$, 307.1 {(H_2O)[H**1**]}$^-$, 419.3 {(Et_4N)[**1**]}$^-$.

Preparation of $[(C_6H_5)_3PCH_3]_2[e^2\text{-}B_{20}H_{16}(CO)_2]$ ($[(C_6H_5)_3PCH_3]_2$-$[e^2$-1**$]$).** The methyltriphenylphosphonium salt of the [a^2-$B_{20}H_{18}]^{4-}$ anion was prepared in a fashion analogous to that of the tetraethylammonium salt. The same synthetic procedure was employed with $[(C_6H_5)_3PCH_3]_4$-[a^2-$B_{20}H_{18}$] (0.57 g, 0.42 mmol) in 80 mL of dichloromethane and 5 mL (10 mmol) of 2.0 M oxalyl chloride solution. Addition of diethyl ether (300 mL) to the filtrate yielded 0.32 g of yellow $[(C_6H_5)_3PCH_3]_2$-[e^2-**1**] (0.39 mmol, 89%). IR (NaCl plate): 2510 (BH), 2111 cm^{-1} (CO). ^{11}B NMR in CH_2Cl_2 (ppm; relative area and multiplicity in parentheses): 10.0 (2, d), 5.8 (2, d), −16.5 (2, d), −17.2 (2, d), −20.0 (2, s), −23.4 (2, d), −24.8 (2, d), −26.9 (4, d), −40.1 (2, s).

The synthesis of the [e^2-**1**]$^{2-}$ anion can also be accomplished by the deprotonation of the [H**1**]$^-$ anion. The addition of dry sodium bicarbonate or calcium carbonate to a solution of $[Et_4N]$[H**1**] in CH_3-CN, after being stirred overnight, produced the [e^2-**1**]$^{2-}$ anion exclusively. Other dry, nonnucleophilic bases such as diazobicycloundecene (DBU) may also be used to perform this deprotonation.

Preparation of $[Et_4N]_3[a^2\text{-}B_{20}H_{17}(NCO)_2]$ ($[Et_4N]_3[H2]$) and $[Et_4N]_4$-$[a^2\text{-}B_{20}H_{16}(NCO)_2]$ ($[Et_4N]_4[2]$). A slurry of $[Et_4N]_4$[a^2-$B_{20}H_{18}$] (2.10 g, 2.78 mmol) in dichloromethane (150 mL) was allowed to react with 14 mL (28 mmol) of a 2.0 M oxalyl chloride solution as described above. Dichloromethane (100 mL) was then added, and the insoluble,

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unreacted starting material was removed by filtration. The solvent was evaporated under reduced pressure. The residue was redissolved in 75 mL of CH_3CN, and sodium azide (0.24 g, 3.69 mmol) was added. The mixture was stirred overnight and then filtered. Diethyl ether (300 mL) was added, and the mixture was cooled in an ice bath. A yellow precipitate, $[Et_4N]_3$[H**2**] (1.04 g, 1.47 mmol), was isolated in 53% yield. IR (NaCl plate): 2503 (BH), 2326 (CN), 1838 (BHB), 1616 cm^{-1} (CO). ^{11}B NMR in CH_3CN (ppm; relative area, multiplicity, and assignment, if determined, in parentheses): 6.3 (2, d, B10), −6.1 (2, s, B1), −14.9 (2, s, B6), −18.2 (4, d), −21.9 (4, d), −22.9 (4, d), −28.9 (2, d, B8) (tautomeric peaks at 1.0, −19.3, −25.7). ESI-MS (CH_3CN/H_2O, *m*/*z*): 577.6 $\{(Et_4N)_2$[H**2**]$\}^-$, 223.4 $\{(Et_4N)$[H**2**]$\}^{2-}$, 240.9 $\{(H_2O)_2(Et_4N)$-[H**2**]$\}^{2-}$.

$[Et_4N]_3$[H**2**] (1.52 g, 2.15 mmol) was prepared as described above and dissolved in 75 mL of CH_3CN. Diazobicycloundecene (DBU, 10 mL) was added, and the mixture was stirred for 15 min. Diethyl ether (300 mL) was added, and the mixture was cooled in an ice bath. A yellow precipitate, $[Et_4N]_4$[**2**] (1.42 g, 1.72 mmol), was isolated in 79% yield. IR (NaCl plate): 2455 (BH), 2309 (CN), 1644 (CO), 1611 cm^{-1} (CO). ^{11}B NMR in CH_3CN (ppm; relative area, multiplicity, and assignment, if determined, in parentheses): 7.3 (2, s, B1), −3.8 (2, d, B10), −15.3 (2, s, B6), −23.5 (4, d, B4/B5), −24.1 (4, d, B7/B9), −26.0 (4, d, B2/B3), −29.2 (2, d, B8).

An aqueous solution of Na_4[**2**], upon standing for 1 week, resulted in a mixture of $[ae\text{-}\mathbf{2}]^{4-}$ isomers. ^{11}B NMR in H_2O (ppm; multiplicity in parentheses): 12.1 (s), 3.8 (d), 2.3 (d), −6.0 (d), −9.7 (d), −14.2 (s), −24.5 (d), −30.8 (d). Relative areas of the resonances were variable and dependent upon the quantity of each isomer present.

Preparation of $[Bu_4N]_3[a^2\text{-}B_{20}H_{17}(CO_2H)_2]$ ($[Bu_4N]_3$[H3**]) and $[Bu_4N]_4[a^2\text{-}B_{20}H_{16}(CO_2H)_2]$ ($[Bu_4N]_4$[**3**]).** A slurry of $[Et_4N]_4[a^2\text{-}B_{20}H_{18}]$ (2.38 g, 3.15 mmol) in dichloromethane (150 mL) was allowed to react with 16 mL (32 mmol) of a 2.0 M oxalyl chloride solution in CH_2Cl_2 as described above. Dichloromethane (100 mL) was then added, and the insoluble, unreacted starting material was removed by filtration. The solvent was evaporated under reduced pressure. The residue was redissolved in 75 mL of CH_3CN, and 25 mL of H_2O was added. The mixture was stirred for 30 min, and the pH of the solution was adjusted to 10 by addition of 1.0 M NaOH(aq). The solvent was then removed by evaporation under reduced pressure. The residue was dissolved in 50 mL of H_2O. A saturated solution of tetrabutylammonium bromide in H_2O (5 mL) was added. Aqueous HCl (1.0 M, 10 mL) was added, and a pale yellow solid precipitated from solution. The solid was extracted from the aqueous solution with dichloromethane (5 × 20 mL). The dichloromethane was removed by evaporation under reduced pressure to yield 2.02 g of the yellow solid $[Bu_4N]_3$[H**3**] (1.93 mmol, 61%). IR (NaCl plate): 3422 (br, OH), 2501 (BH), 1868 (BHB), 1704 (C═O), 1636 (C═O), 1382 cm^{-1} (C−O). ^{11}B NMR in CH_3CN (ppm; relative area, multiplicity, and assignment, if determined, in parentheses): 7.4 (2, d, B10), −4.9 (2, s, B1), −21.9 (6, d), −23.2 (4, d), −26.9 (6, d) (tautomeric peak at 0.3). ESI-MS (CH_3CN/H_2O, *m*/*z*): 282.6 $\{(Bu_4N)$[H**3**]$\}^{2-}$, 549.3 $\{(Bu_4N)[B_{20}H_{17}(CO)(CO_2H)]\}^{2-}$, 808.6 $\{(Bu_4N)_2$-[H**3**]$\}$.

The complex $[Bu_4N]_3$[H**3**] (1.84 g, 1.75 mmol) was prepared as described above and added to 3.5 mL of 0.5 M NaOH(aq). The mixture was warmed slightly until all of the solid dissolved. The solvent was removed under reduced pressure to yield 1.63 g of the yellow solid $[Bu_4N]_3$Na[**3**] (1.52 mmol, 87%). IR (NaCl plate): 3285 (br, OH), 2453 (BH), 1646 (C═O), 1323 cm^{-1} (C−O). ^{11}B NMR in CH_3CN (ppm; relative area, multiplicity, and assignment, if determined, in parentheses): 13.2 (2, s, B1), −4.0 (2, d, B10), −21.4 (2, s, B6), −25.2 (14, d).

A solution of $[Bu_4N]_4$[**3**] in CH_3CN will isomerize to a mixture of $[Bu_4N]_4[ae\text{-}\mathbf{3}]$ isomers with the addition of heat or upon standing for 8 h. ^{11}B NMR in CH_3CN (ppm; multiplicity in parentheses): 13.4 (s), 5.0 (d), 3.5 (d), −1.5 (d), −5.3 (s), −23.9 (d), −26.4 (d), −27.6 (d). The relative areas of the resonances were variable and dependent upon the quantity of each isomer present.

Preparation of $[Et_4N]_2[a^2\text{-}B_{20}H_{16}(NH_2C(O)NH(i\text{-}Pr))_2]$ ($[Et_4N]_2$-[4]) and $[Et_4N][a^2\text{-}B_{20}H_{17}(NH_2C(O)NH(i\text{-}Pr))_2]$ ($[Et_4N]$[H4]). The complex $[Et_4N]_3$[H**2**] (1.97 g, 2.79 mmol) was prepared as described above and dissolved in 75 mL of CH_3CN. Isopropylamine (15 mL) was added, and the mixture was stirred overnight. A tan precipitate, $[Et_4N]_2$[**4**] (1.73 g, 2.48 mmol), was isolated in 89% yield. IR (NaCl plate): 3557 (NH), 3333 (NH), 2450 (BH), 1608 (C═O), 1536 (NH), 1438 (CN), 1116 cm^{-1} (CN). ^{11}B NMR in H_2O (ppm; relative area, multiplicity, and assignment in parentheses): 11.9 (2, s, B1), −11.0 (2, d, B10), −15.2 (2, s, B6), −25.2 (8, d, B4/B5/B7/B9), −27.4 (4, d, B2/B3), −31.5 (2, d, B8). ESI-MS (CH_3CN/H_2O, *m*/*z*): 217.8 $\{$[**4**]$\}^{2-}$, 566.6 $\{[Et_4N]$[**4**]$\}^-$. ^1H NMR in D_2O (ppm; relative area and multiplicity in parentheses): 3.54 (2H, heptet, J = 6.5 Hz), 1.08 (12H, d, J = 6.5 Hz), $[Et_4N]$ 1.12 (24H, triplet (J = 6.4 Hz) of doublets, J = 1.8 Hz), $[Et_4N]$ 3.11 (16H, q, J = 6.4 Hz).

The complex $[Et_4N]_2$[**4**] (0.51 g, 0.73 mmol) was prepared as described above and dissolved in 5 mL of H_2O. A dilute solution of 1.0 M aqueous HCl (2 mL) was added to produce a yellow precipitate, $[Et_4N]$[H**4**] (0.30 g, 0.53 mmol), which was isolated by filtration in 53% yield. IR (NaCl plate): 2499 (BH), 1849 (BHB), 1666 cm^{-1} (C−O). ^{11}B NMR in H_2O (ppm; relative area, multiplicity, and assignment, if determined, in parentheses): 3.1 (2, d, B10), −4.7 (2, s, B1), −14.8 (2, s, B6), −18.8 (4, d), −23.0 (8, d), −28.5 (2, d, B8) (tautomeric peaks at −4.9, −17.0, −20.1). ESI-MS (CH_3CN/H_2O, *m*/*z*): 217.8 $\{$[**4**]$\}^{2-}$, 437.4 $\{$[H**4**]$\}^-$.

A CH_3CN/H_2O solution of $[Et_4N]_2$[**4**], upon standing for 4 h, resulted in a mixture of $[ae\text{-}\mathbf{4}]^{2-}$ isomers. ^{11}B NMR in CH_3CN (ppm; multiplicity in parentheses): 11.7 (s), 3.2 (d), 1.7 (d), −6.9 (d), −10.9 (d), −14.7 (s), −26.0 (d), −31.6 (d). The relative areas of the resonances were variable and dependent upon the quantity of each isomer present.

Results and Discussion

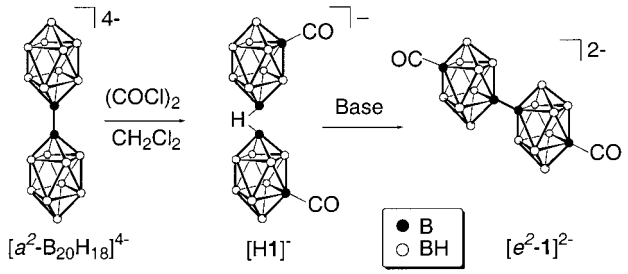
Synthesis and Characterization of the $[a^2\text{-}B_{20}H_{17}(CO)_2]^-$ ($[H1]^-$) and $[e^2\text{-}B_{20}H_{16}(CO)_2]^{2-}$ ($[e^2\text{-}1]^{2-}$) Anions. Oxalyl chloride reacts with $[Et_4N]_4[a^2\text{-}B_{20}H_{18}]$ at 0 °C to produce carbon monoxide and the protonated, disubstituted $[H\mathbf{1}]^-$ anion in good yield. This reaction has been observed previously with the $[closo\text{-}B_{10}H_{10}]^{2-}$ anion[15] and proceeds according to the equation below.

$$[B_{20}H_{18}]^{4-} + 2(COCl)_2 \rightarrow [B_{20}H_{17}(CO)_2]^- + HCl + 3Cl^- + 2CO$$

The use of excess oxalyl chloride did not lead to additional substitution. Although the reaction was also observed in CH_3CN, the cleanest product mixtures were obtained with CH_2Cl_2 as the solvent. Heating the reaction mixture did not improve the yield but, instead, produced a mixture of the $[H\mathbf{1}]^-$, $[e^2\text{-}\mathbf{1}]^{2-}$, and $[closo\text{-}2\text{-}B_{10}H_9CO]^-$ anions, which could be partially separated by liquid chromatography in 1:3 CH_3CN/CH_2Cl_2 using freshly dried silica gel. The isolation of $[Et_4N]$[H**1**] is often unnecessary if it is merely to be used as a precursor in subsequent reactions (e.g., the synthesis of $[H\mathbf{2}]^{3-}$). The use of the methyltriphenylphosphonium counterion led to the rapid and exclusive formation of the $[e^2\text{-}\mathbf{1}]^{2-}$ anion. The role of the cation in such isomerization reactions is not yet understood.

Deprotonation of $[Et_4N]$[H**1**] with nonaqueous, nonnucleophilic bases did not lead to the $[a^2\text{-}B_{20}H_{16}(CO)_2]^{2-}$ anion, but instead resulted in deprotonation and rearrangement to form the $[e^2\text{-}\mathbf{1}]^{2-}$ anion exclusively (Scheme 2). This result contrasts with the behavior of the unsubstituted[5,6] and monosubstituted[2−4] $[B_{20}H_{18}]^{4-}$ ions, wherein the thermodynamically most stable isomer was shown to be the a^2 isomer. However, in the case of the unprotonated bis-carbonyl species, the e^2 isomer is the more stable species. Heat, deprotonation, and changes in the associated cation consistently led to an increase in the relative amount of the e^2 isomer of the bis-carbonyl species compared to the amount of the a^2 isomer. This is the first reported example demonstrating changes in the apparent thermodynamic stability of the different cage-link isomers brought about by cage substitution. In this

Scheme 2



case, the strongly electron-withdrawing carbonyl substituents appear to stabilize the e^2 linkage of the component cages.

The ^{11}B NMR spectrum of [Et_4N][H**1**] was well resolved, and the two-dimensional ^{11}B{^{1}H} COSY NMR spectrum allowed the assignment of all of the principal resonances (Figure 1). The singlet at −41.5 ppm, assigned to (B6, B6′), was indicative of the carbonyl-substituted boron atoms, and this chemical shift is similar to that observed for the [*closo*-2-$B_{10}H_9$-CO]$^-$ anion in which an equatorial boron bearing a carbonyl substituent was assigned to a singlet at −43.8 ppm.[15] In the apical region of the spectrum, the occurrence of one doublet (14.0 ppm, B−H) and one broad singlet (−1.9 ppm, B−B) clearly established the apical−apical nature of the intercage bonding.

As was the case for the spectrum of the [a^2-$B_{20}H_{19}$]$^{3-}$ anion,[8] the ^{11}B NMR spectrum of the [H**1**]$^-$ anion also contained resonances that are unassignable. These low-intensity signals have been observed in the spectra of all protonated [$B_{20}H_{18}$]$^{4-}$ derivatives and do not change in proportion to the other resonances. This finding has been interpreted as arising from the fluxionality in solution of the proton bridging the two cages as it floats between the intercage B−B bond and adjacent intracage B−B bonds. As seen in Figure 1, the most prominent of these signals appear in the apical region of the spectrum (5.0 ppm) and in the vicinity of the resonances attributed to B2−B5 (i.e., the equatorial belt adjacent to the intercage bonding). These fluxional resonances disappear upon deprotonation of the anion.

The electrospray mass spectrum of a solution [Et_4N][H**1**] in aqueous acetonitrile contained several boron envelopes, each of which could be attributed to the desired product. The FT-IR spectrum of the [H**1**]$^-$ anion exhibited a strong absorption at 2157 cm^{-1}, indicative of the CO substituent and similar to that found with the [*closo*-2-$B_{10}H_9CO$]$^-$ anion at 2129 cm^{-1}.[15] A second strong absorption at 2536 cm^{-1} was assigned to the terminal boron−hydrogen bonds found in the anion. Finally, the medium-intensity absorption at 1859 cm^{-1} was assigned to the bridging hydrogen found in the [H**1**]$^-$ anion and is comparable to that found in the [a^2-$B_{20}H_{19}$]$^{3-}$ anion at 1851 cm^{-1}.[5,8]

In the ^{11}B NMR spectrum of [$(C_6H_5)_3PCH_3$]$_2$[e^2-**1**], the appearance of two doublets coupled to hydrogen (each of relative area 2) in the apical region of the spectrum (10.0 and 5.8 ppm) confirms that the intercage bonding involves equatorial boron atoms. A singlet at −40.1 ppm with relative integration of 2 was indicative of the carbonyl-substituted equatorial boron atoms, and a second singlet at −20.0 ppm was assigned to the two equatorial boron atoms linking the two decaborate cages. Although the 2D ^{11}B{^{1}H} COSY NMR spectrum was not sufficiently resolved to completely assign the remaining resonances, it indicated that the carbonyl-substituted boron atoms were in an equatorial belt different from that containing the intercage B−B bond. The structure depicted in Scheme 2 represents only one of the possible isomers consistent with the ^{11}B NMR (two enantiomeric pairs and two *meso* structures).

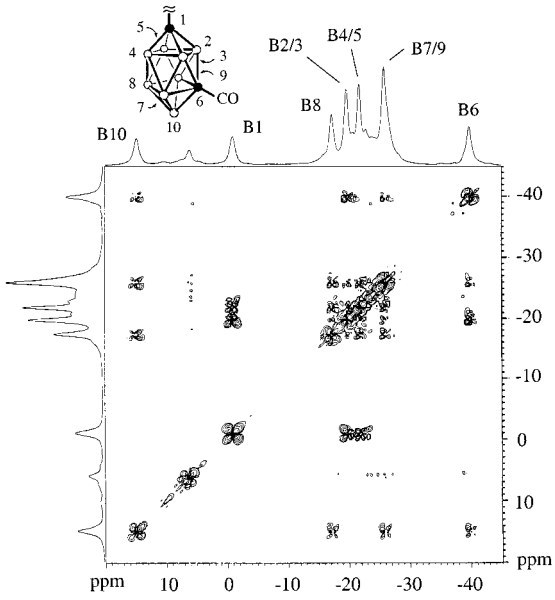


Figure 1. 2D COSY ^{11}B{^{1}H}NMR spectrum of the [H**1**]$^-$ anion in CH_2Cl_2.

The FT-IR spectrum of the unprotonated species, the [e^2-**1**]$^{2-}$ anion, was similar to that of the protonated species and exhibited strong absorptions at 2111 and 2510 cm^{-1} that are attributable to the CO substituent and terminal B−H stretch, respectively. However, no absorption in the 1800−1900 cm^{-1} range that could be attributed to a bridging (B−H−B) proton was observed.

Synthesis and Characterization of the [a^2-$B_{20}H_{17}(NCO)_2$]$^{3-}$ ([H2]$^{3-}$) and [a^2-$B_{20}H_{16}(NCO)_2$]$^{4-}$ ([2]$^{4-}$) Anions. The reaction of [Et_4N][H**1**] with sodium azide in acetonitrile slowly evolves nitrogen gas. The reaction proceeds by the initial formation of an acyl azide followed by a Curtius rearrangement leading to an isocyanate. The FT-IR spectrum of the [H**2**]$^{3-}$ anion exhibited the usual strong absorption at 2503 cm^{-1} that is characteristic of terminal B−H. Strong absorptions were also observed at 2326 and 1616 cm^{-1} and assigned to C−N and C═O stretching modes, respectively. In addition, a weak absorption at 1838 cm^{-1} was attributed to the bridging hydrogen.

As was the case with the [H**1**]$^-$ ion, the ^{11}B NMR spectrum of [Et_4N]$_3$[H**2**] established the apical−apical intercage bonding, exhibiting a singlet (−6.1 ppm, B1) and a hydrogen-coupled doublet (6.3 ppm, B10) in the apical region of the spectrum. It was not possible to unambiguously assign the three doublets arising from the B2/B3, B4/B5, and B7/B9 boron atom pairs. The spectrum also contained several low-intensity resonances due to tautomerization of the bridging hydrogen, as is typical for [$B_{20}H_{19}$]$^{3-}$ derivatives.

Deprotonation of [Et_4N]$_3$[H**2**] was readily achieved using nonnucleophilic, nonaqueous bases such as DBU. The ^{11}B NMR spectrum of the anion changed considerably upon deprotonation, losing the tautomeric resonances, and a simple, easily assignable spectrum was produced. The 2D COSY ^{11}B{^{1}H} NMR spectrum and peak assignments for the [**2**]$^{4-}$ ion are shown in Figure 2. In a manner analogous to that of the [H**1**]$^-$ anion, the spectrum is consistent with a species that is substituted on the two equatorial belts farthest removed from the boron−boron bond linking the two cages. Finally, whereas the FT-IR spectrum of the [**2**]$^{4-}$ anion contained strong C−N and terminal B−H absorptions and two peaks due to symmetric and asymmetric

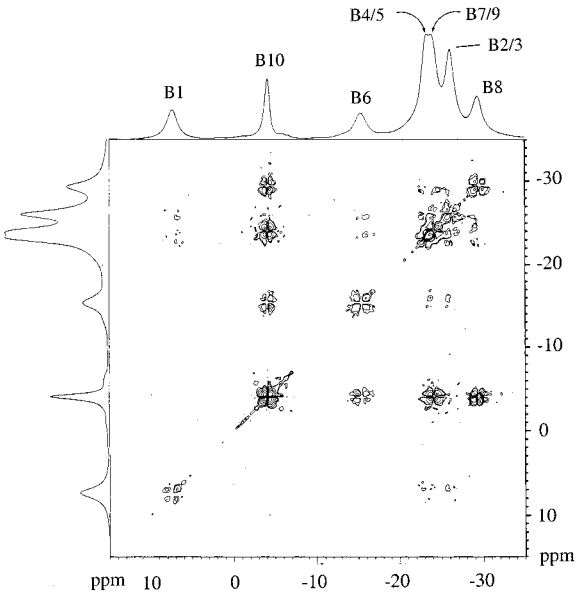


Figure 2. 2D COSY $^{11}B\{^1H\}$NMR spectrum of the $[\mathbf{2}]^{4-}$ anion in CH_3CN.

C═O stretching modes, it no longer exhibited an absorption that could be attributed to a bridging (B−H−B) proton, as was seen for the $[H\mathbf{2}]^{3-}$ ion.

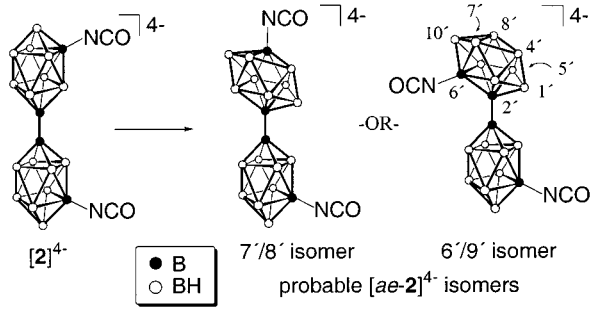
Synthesis and Characterization of the $[a^2\text{-}B_{20}H_{17}(CO_2H)_2]^{3-}$ ($[H\mathbf{3}]^{3-}$) and $[a^2\text{-}B_{20}H_{16}(CO_2H)_2]^{4-}$ ($[\mathbf{3}]^{4-}$) Anions. In aqueous solvent mixtures, the hygroscopic $[Et_4N][H\mathbf{1}]$ salt was readily transformed to the $[H\mathbf{3}]^{3-}$ anion. Both the $[H\mathbf{1}]^-$ and $[e^2\text{-}\mathbf{1}]^{2-}$ anions produced the same $[H\mathbf{3}]^{3-}$ product upon exposure to water, as demonstrated by the ^{11}B NMR spectra. A mixture of the $[H\mathbf{1}]^-$ and $[e^2\text{-}\mathbf{1}]^{2-}$ anions can be regenerated from the $[H\mathbf{3}]^{3-}$ anion upon removal of the solvent and drying under nitrogen.

The FT-IR spectrum of $[Bu_4N]_3[H\mathbf{3}]$ exhibited all of the absorptions expected for a carboxylic acid (C═O, C−O, and OH), and an absorption resulting from the bridging (B−H−B) proton was observed at 1868 cm^{-1}. The ^{11}B NMR spectrum of the $[H\mathbf{3}]^{3-}$ anion was much less informative than the spectra of the anions described above. Although the apical region of the spectrum was indicative of an a^2 isomer, the equatorial resonances were poorly resolved because of overlap or coincidence of the signals. However, by analogy, the $[H\mathbf{3}]^{3-}$ anion was presumed to have the same structure as the $[H\mathbf{1}]^-$ anion and the $[H\mathbf{2}]^{3-}$ anions. As with all of the anions that contain the bridging proton, the spectrum contains resonances consistent with the dynamic fluxionality of the proton as it produces a mixture of tautomers in solution.

Deprotonation of $[Bu_4N]_3[H\mathbf{3}]$ by aqueous NaOH produced the $[\mathbf{3}]^{4-}$ anion. The ^{11}B NMR spectrum of $[Bu_4N]_3Na[H\mathbf{3}]$ exhibited the usual apical resonances for an a^2 isomer and a singlet (−21.4 ppm) attributed to the substituted B6 atoms. The remaining equatorial resonances were unresolved.

Synthesis and Characterization of the $[a^2\text{-}B_{20}H_{16}(NH_2C(O)NH(i\text{-}Pr))_2]^{2-}$ ($[\mathbf{4}]^{2-}$) and the $[a^2\text{-}B_{20}H_{17}(NH_2C(O)NH(i\text{-}Pr))_2]^-$ ($[H\mathbf{4}]^-$) Anions. An acetonitrile solution of $[Et_4N]_3[H\mathbf{2}]$ reacted with isopropylamine to form the unprotonated $[\mathbf{4}]^{2-}$ anion in high yield. The ^{11}B NMR spectrum of the $[\mathbf{4}]^{2-}$ anion was relatively simple, very similar to that of the $[\mathbf{2}]^{4-}$ anion, and was consistent with an analogous structure. Protonation of $[Et_4N]_2[\mathbf{4}]$ was readily achieved using aqueous hydrochloric acid. The ^{11}B NMR spectrum of the $[\mathbf{4}]^{2-}$ anion changed considerably to give a spectrum of $[H\mathbf{4}]^-$ similar to that of the

Scheme 3



$[H\mathbf{2}]^{3-}$ anion. As with the other protonated species, additional low-intensity resonances were observed, indicative of the presence of tautomers resulting from the fluxionality of the bridging proton.

The FT-IR and mass spectra of the two anions were also consistent with the assigned structure. The IR spectra of the two anions were very similar with the exception of an additional absorption at 1849 cm^{-1} in the spectrum of $[H\mathbf{4}]^{2-}$, attributed to the bridging (B−H−B) hydrogen.

Interconversion of Isomers. Whereas deprotonation of the $[H\mathbf{1}]^-$ anion produced the $[e^2\text{-}\mathbf{1}]^{2-}$ ion exclusively, deprotonation of the other bis-substituted derivatives eventually resulted in mixtures of *ae* isomers upon rearrangement. The ease of rearrangement was dependent upon the solvent and the particular substituent. Relative isomer populations of the products varied with the reaction conditions, but it was impossible to induce the production of a single *ae* isomer, and no isomer separation was attempted.

Although the *ae* isomer mixtures could not be unambiguously assigned by ^{11}B NMR spectroscopy, structures could be deduced with the assumption that no polyhedral rearrangements or substituent migrations occurred and that the only rearrangements observed involved localized migrations of the intercage B−B bonding. This assumption is reasonable considering the mild conditions under which rearrangement occurs and the relatively predictable paths previously observed for such rearrangements.[2,4,5]

Beginning with a species substituted on the equatorial belts farthest from the bond linking the two cages, four *ae* isomers (two *dl* pairs) are possible, and each enantiomeric pair can be distinguished by ^{11}B NMR spectroscopy. As illustrated in Scheme 3, substitution at the 6′ or 9′ position produces one of the *dl* pairs (the 6′/9′ isomer), whereas a separate enantiomeric pair is produced by substitution at the 7′ or 8′ position.

In a typical sequence, the $[\mathbf{4}]^{2-}$ anion rearranged to a mixture of *ae* isomers, slowly in water (2−3 days) and quickly in aqueous acetonitrile (4−8 h). The 2D COSY $^{11}B\{^1H\}$ NMR spectrum of the resultant mixture of $[ae\text{-}\mathbf{4}]^{2-}$ isomers is shown in Figure 3. In this spectrum, the broad signals attributed to the B−N and apical B−B bonds (at −15.2 and 11.9 ppm, respectively) were relatively insensitive to chemical shift changes. The unresolved mass of overlapping equatorial signals was uninformative, but some information could be gleaned from the number and coupling of the apical signals. As the rearrangement progressed, the intensity of the resonance due to the apical B−B bond decreased (as the B−B bond became apical−equatorial), as did the intensity of the signal from the apical B−H bonds (as one of the B−H vertexes becomes nonequivalent). At the same time, a new signal attributed to B10′ for both *ae* isomers grew in at −6.9 ppm (identified by its cross-coupling to the B−N resonance), and two resonances appeared at 1.7 and 3.2 ppm because of the B1′ atoms (one for each *ae* isomer).

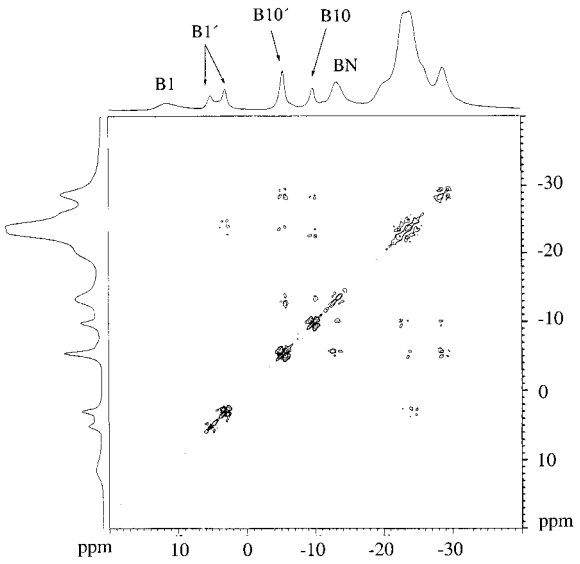


Figure 3. 2D COSY $^{11}B\{^1H\}$NMR spectrum of the [*ae*-**4**]$^{2-}$ isomer mixture in CH_3CN/H_2O.

Reactions of $[Et_4N]_3$[H**2**] with other amines, such as diisopropylamine, aniline, and benzylamine, were also attempted, and all reactions produced the corresponding urea derivatives analogous to [**4**]$^{2-}$. However, the specific isomer formed depended upon the identity of the amine employed. Isolation of the a^2 isomer of the urea formed with diisopropylamine was possible, but it rearranged to a mixture of *ae* isomers more rapidly than the isopropylamine derivative. When aniline and benzylamine were employed, it was not possible to isolate an a^2 isomer, and only *ae* isomer mixtures were obtained.

The a^2 isomers of the [**2**]$^{4-}$ and [**3**]$^{4-}$ anions also rearranged to produce *ae* isomer mixtures, but at different rates. The [**2**]$^{4-}$ anion was the most stable anion toward rearrangement investigated in this study. A solution of the [**2**]$^{4-}$ anion in aqueous acetonitrile produced a mixture of the [*ae*-**2**]$^{4-}$ isomers upon standing 2−3 weeks at room temperature, and the ^{11}B NMR spectrum changed accordingly. The a^2 isomer of the [**3**]$^{4-}$ anion was quite unstable in solution and quickly isomerized to a mixture of [*ae*-**3**]$^{4-}$ isomers. Changes in the spectrum continued until all of the resonances associated with the a^2 isomer of the [**3**]$^{4-}$ anion were no longer present and a mixture exclusively of *ae* isomers was obtained.

Again, the a^2 isomer of the unsubstituted $[B_{20}H_{18}]^{4-}$ ion was found to be the thermodynamically most stable isomer.[5] The unprotonated bis-substituted species exhibited a more varied behavior. The e^2 isomer of the bis-carbonyl substituted anion was the more stable species, whereas the *ae* isomers were found to be the more thermodynamically stable products for the isocyanate, carboxylic acid, and urea-substituted anions.

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