Exploring the Redox Reactivity of the $[B_{20}H_{18}]^{2-}$ Ion with Carbon-Based Nucleophiles and Electrophiles

Sedriel J. Montalvo, Todd W. Hudnall, and Debra A. Feakes*

Department of Chemistry and Biochemistry, Texas State University, San Marcos, TX 78666

*Corresponding Author, email: df10@txstate.edu

Dedicated to Professor Russell N. Grimes on the occasion of his 80 birthday.

Abstract

The $[B_{20}H_{18}]^{2-}$ ion is characterized by the presence of electron-deficient, three-center, two-electron bonds which are susceptible to nucleophilic attack. Since the first synthesis of the ion in 1962, products of the nucleophilic attack have been reported for oxygen, nitrogen, and sulfur nucleophiles; however, no ions have been reported which result from nucleophilic attack of the $[B_{20}H_{18}]^{2-}$ ion by carbon nucleophiles. Herein we report the preparation and single crystal X-ray analysis of the $[B_{20}H_{17}CH_3]^{2-}$ ion, prepared by the oxidation of the $[B_{20}H_{17}CH_3]^{4-}$ ion *in situ*. Oxidation of the $[B_{20}H_{18}]^{4-}$ ion and its derivatives, $[B_{20}H_{17}X]^{4-}$ where X is the nucleophile, have been reported using both ferric chloride and organic oxidants; however, the oxidations only proceed in acidic solution. The $[B_{20}H_{17}OH]^{4-}$ and $[B_{20}H_{17}OH]^{2-}$, both reported previously, were prepared in order to investigate the oxidation reaction. Single crystals of the $[B_{20}H_{17}OH]^{2-}$ ion were obtained and characterized by X-ray diffraction. Oxidation of the $[B_{20}H_{17}OH]^{4-}$ was achieved in the absence of acid, but in the presence of iodomethane; however, the anticipated methylation was not observed and instead, the $[\mu-B_{20}H_{17}OCH_3]^{2-}$ was isolated and characterized

by single crystal X-ray diffraction. The role of the acid, or the iodomethane, in the oxidation process appears to be as an electrophile in the initiation of the oxidation process.

Introduction

The $[\text{B}_{20}\text{H}_{18}]^{2-}$ ion, first reported by Kaczmarczyk,¹ in 1962 is susceptible to nucleophilic attack at the two electron-deficient, three-center, two-electron bonds, producing a reduced substituted ion of the form $[\text{B}_{20}\text{H}_{17}\text{X}]^{4-}$ where X is $-\text{OH}$,^{2,3} $-\text{OR}$,^{2,3} $-\text{NH}_3$,⁴ $-\text{NHRR}'$,⁵ and $-\text{SH}$ (**Scheme 1**, conversion of **1** to **2**).⁶ The proposed mechanism of nucleophilic attack was reported by Hawthorne in 1965 using the hydroxide ion as the nucleophile.³ The reaction was initiated by the attack of the equatorial boron in one of the electron-deficient, three-center, two-electron bonds by the hydroxide ion followed by a migration of one of the cages. A second equivalent of the nucleophile is required to remove the bridging hydrogen and convert the $[\text{B}_{20}\text{H}_{18}\text{X}]^{3-}$ ion into the $[\text{B}_{20}\text{H}_{17}\text{X}]^{4-}$ ion. The kinetic isomer of the product, $[\text{B}_{20}\text{H}_{17}\text{X}]^{4-}$, is characterized by an apical-equatorial connection between the two boron cages and is designated $[ae\text{-B}_{20}\text{H}_{17}\text{X}]^{4-}$. Conversion of the kinetic isomer to the thermodynamic isomer is accomplished by heating an aqueous solution of the former or can be catalyzed by the addition of acid (**Scheme 1**, conversion of **2** to **3**). The thermodynamic isomer of the product is characterized by an apical-apical connection between the two boron cages and is designated $[a^2\text{-B}_{20}\text{H}_{17}\text{X}]^{4-}$. Single crystals of the $[\text{B}_{20}\text{H}_{17}\text{X}]^{4-}$ isomers suitable for characterization by X-ray crystallography have been challenging to obtain and, as a result, very few crystal structures have been reported. Aqueous oxidation of the $[\text{B}_{20}\text{H}_{17}\text{OH}]^{4-}$ ion using ferric chloride was reported by Hawthorne in 1965 (**Scheme 1**, conversion of **2** or **3** to **4**).³

Scheme 1: **1 to 2** – Nucleophilic attack of the $[\text{B}_{20}\text{H}_{18}]^{2-}$ ion; **2 to 3** – Conversion of *ae* isomer to *a*² isomer; **2 or 3 to 4** – Oxidation of $[\text{B}_{20}\text{H}_{17}\text{X}]^{4-}$. X = nucleophile; ○ = BH; ● = B.

The ferric chloride oxidation takes place under harsh reaction conditions and subsequently, a milder oxidation process using benzoquinone was reported using the unsubstituted $[\text{B}_{20}\text{H}_{18}]^{4-}$ ion⁷ and the $[\text{B}_{20}\text{H}_{17}\text{NH}_3]^{3-}$ ion.⁸ Single crystals of the oxidized species, with an appropriate cation, have been easier to obtain. To date, no reactions of the $[\text{B}_{20}\text{H}_{18}]^{2-}$ ion with a carbon nucleophile have been reported. Herein we report the preparation and characterization of the $[\text{B}_{20}\text{H}_{17}\text{CH}_3]^{2-}$ ion, resulting from nucleophilic attack of the $[\text{B}_{20}\text{H}_{18}]^{2-}$ ion by a methyllide anion. Additionally, as part of the effort to investigate the reactivity of the $[\text{B}_{20}\text{H}_{18}]^{2-}$ ions with carbon nucleophiles, the oxidation of the $[\text{B}_{20}\text{H}_{17}\text{OH}]^{4-}$ ion has been reinvestigated and the single crystal X-ray structures of the $[\text{B}_{20}\text{H}_{17}\text{OH}]^{2-}$ (**4**, X = OH in **Scheme 1**) ion and the $[\mu\text{-B}_{20}\text{H}_{17}\text{OCH}_3]^{2-}$ ion are reported.

Results and Discussion

Reaction of $[\text{Et}_3\text{NH}]_2[\text{B}_{20}\text{H}_{18}]$ and methylmagnesium bromide in diethylether at room temperature produced, *in situ*, an apical-equatorial isomer of the $[\text{B}_{20}\text{H}_{17}\text{CH}_3]^{4-}$ ion (**Scheme 2**).

Although the product was not isolated, the proton-decoupled ^{11}B NMR spectrum of the reaction mixture was obtained and exhibited quantitative conversion to the $[\text{B}_{20}\text{H}_{17}\text{CH}_3]^{4-}$ ion.

Additionally, the isomeric assignment was confirmed by the presence of three apical boron atom signals, at 2.2, -1.6 , and -7.6 ppm, which exhibited doublets in the proton-coupled ^{11}B NMR spectrum. The broad signal at 13.8 ppm is assigned to the two boron atoms of the inter cage connection. The signal for the substituted boron is observed at -9.0 ppm and is broader than the signals for the apical boron atoms in the proton-decoupled spectrum. The remaining equatorial boron atom signals are located between approximately -20 and -35 ppm, consistent with the ^{11}B NMR spectrum of similar polyhedral borane anions.³⁻⁶ The methyl group was not observed in either the ^1H NMR spectrum or the ^{13}C NMR spectrum, presumably due to coupling to the adjacent and neighboring boron atoms which have large quadrupolar moments and nuclear spins $I = 3/2$.

Scheme 2: Reaction of the $[\text{B}_{20}\text{H}_{18}]^{2-}$ ion with methylmagnesium bromide followed by oxidation of the *in situ* $[\text{B}_{20}\text{H}_{17}\text{CH}_3]^{4-}$ ion to the $[\text{B}_{20}\text{H}_{17}\text{CH}_3]^{2-}$ ion.

○ = BH; ● = B.

Oxidation of the $[ae\text{-B}_{20}\text{H}_{17}\text{CH}_3]^{4-}$ ion was achieved using *p*-benzoquinone in an aqueous acidic solution at room temperature (**Scheme 2**). The ^{11}B NMR spectrum of the oxidized product was consistent with the spectrum observed for the $[\text{B}_{20}\text{H}_{18}]^{2-}$ ion.⁹ Specifically, the spectrum is characterized by the expanded spectroscopic window of the oxidized products, +35 ppm to –35 ppm, and the characteristic singlets at 18.2 and 16.1 ppm which is assigned to the equatorial boron atoms in the electron deficient bonding region. The substituted boron atom is not evident in the ^{11}B NMR spectrum, but may be buried under the other signals.

Single crystals of the methyltriphenylphosphonium salt of the $[\text{B}_{20}\text{H}_{17}\text{CH}_3]^{2-}$ ion were obtained and the crystal was characterized by X-ray crystallography (**Figure 1**). Although no significant structural differences were observed between the crystal structure of the $[\text{B}_{20}\text{H}_{18}]^{2-}$ ion¹⁰ and the crystal structure of the $[\text{B}_{20}\text{H}_{17}\text{CH}_3]^{2-}$ ion regarding the polyhedral borane framework, it is noteworthy that the methyl substituent was located on the equatorial belt adjacent to the terminal boron apex rather than the equatorial belt adjacent to the electron-deficient bonding region. The location of the substituent is the subject of another study to be reported at a later date. The B5–C1 distance is 1.497(7) Å, and is similar to reported B–C(*sp*³) bond lengths in polyhedral boron clusters (ca. 1.53–1.59 Å).^{11,12} In the absence of the acid, no oxidation was observed.

Figure 1: ORTEP drawing (ellipsoids set at 50% probability) of the crystal structure of the $[\text{B}_{20}\text{H}_{17}\text{CH}_3]^{2-}$ ion. Relevant bond lengths include: B5–C1 1.497(7) Å, B9'–B10 1.916(5) Å, and B9–B10' 1.916(5) Å.

The potassium salt of the $[\text{ae-B}_{20}\text{H}_{17}\text{OH}]^{4-}$ ion was prepared as described previously.³ Oxidation of the $[\text{ae-B}_{20}\text{H}_{17}\text{OH}]^{4-}$ to form the $[\text{B}_{20}\text{H}_{17}\text{OH}]^{2-}$ was accomplished using *p*-benzoquinone in an aqueous acid solution (**Scheme 1**, conversion of **2** to **4** where X is OH). Formation of this product is consistent with the observations that the normal isomer of the $[\text{B}_{20}\text{H}_{18}]^{2-}$ ion is formed in aqueous solutions. The ^{11}B NMR spectrum of the oxidized product was consistent with the spectrum observed for the substituted $[\text{B}_{20}\text{H}_{17}\text{X}]^{2-}$ ions.³ Specifically, the spectrum is characterized by the expanded spectroscopic window of the oxidized products, +35 ppm to –35 ppm, and the presence in this case of two singlets at 15.0 and 13.8 ppm which are assigned to the equatorial boron atoms in the electron deficient bonding region. The substituted boron atom is not evident in the ^{11}B NMR spectrum, but may be buried under the other signals. The product was isolated as the methyltriphenylphosphonium salt and single crystals were obtained by slow vapor diffusion of diethylether into a solution of the salt in acetonitrile. No

significant structural differences are observed between the crystal structure of the $[\text{B}_{20}\text{H}_{18}]^{2-}$ ion¹⁰ and the crystal structure of the $[\text{B}_{20}\text{H}_{17}\text{OH}]^{2-}$ ion (**Figure 2**). The hydroxide substituent was located in the anticipated position on the equatorial belt adjacent to the electron-deficient bonding region. The B7–O1 distance of 1.400(6) Å is shorter than what Hawthorne observed in the bridging hydroxy-substituted ion $[\mu\text{-B}_{20}\text{H}_{17}\text{OH}]^{2-}$ (avg. B–O bonds lengths = 1.483 Å)¹³ as can be expected for a terminal versus bridging substituent. In the absence of the acid, no oxidation was observed.

Figure 2: ORTEP drawing (ellipsoids set at 50% probability) of the crystal structure of the $[\text{B}_{20}\text{H}_{17}\text{OH}]^{2-}$ ion. Relevant bond lengths include: B7–O1 1.400(6) Å, B9'–B10 1.916(5) Å, and B9–B10' 1.916(5) Å.

Based on the mechanism of nucleophilic attack proposed by Hawthorne³ and the required presence of the acid, one would expect the oxidation process to be initiated by the protonation of the $[\text{B}_{20}\text{H}_{17}\text{OH}]^{4-}$ ion to form the $[\text{B}_{20}\text{H}_{18}\text{OH}]^{3-}$ ion. The hydrogen resulting from the protonation process would ultimately reside on one of the apical boron vertices which constitute the three-center, two-electron bonds characteristic of the $[\text{B}_{20}\text{H}_{18}]^{2-}$ ion and its derivatives. As a result, in

the absence of the acidic solution, the oxidation process cannot proceed; however, in the presence of a suitable electrophile, the oxidation process should proceed and result in the addition of a substituent at one of the apical boron vertices which constitute the three-center, two-electron bond. Based on this hypothesis, the methyltriphenylphosphonium salt of the $[\text{B}_{20}\text{H}_{17}\text{OH}]^{4-}$ ion was oxidized using *p*-benzoquinone in the presence of excess (greater than two equivalents) iodomethane. The first equivalent of iodomethane was anticipated to alkylate the hydroxyl group and the second equivalent of iodomethane was anticipated to complete the oxidation reaction. The product was isolated by recrystallization and single crystals were obtained by slow vapor diffusion of diethylether into a solution of the salt in acetonitrile. Rather than obtaining the anticipated doubly-substituted $[\text{B}_{20}\text{H}_{16}(\text{CH}_3)(\text{OCH}_3)]^{2-}$ product, the $[\mu\text{-B}_{20}\text{H}_{17}\text{OCH}_3]^{2-}$ product, containing both oxygen and hydrogen-bridge bonds, was obtained (**Figure 3**). Formation of the bridging product is consistent with earlier observations that the bridging isomer is formed when the reactions are completed in non-aqueous solutions.¹⁴ The $[\mu\text{-B}_{20}\text{H}_{17}\text{OCH}_3]^{2-}$ product has been reported earlier from the ferric chloride oxidation of the $[\text{B}_{20}\text{H}_{17}\text{OR}]^{4-}$ ion in anhydrous ethanol; however, only the single crystal structure of the $[\mu\text{-B}_{20}\text{H}_{17}\text{OH}]^{2-}$ ion was reported. The apical intercage B10–B20 separation in the $[\mu\text{-B}_{20}\text{H}_{17}\text{OCH}_3]^{2-}$ ion is 1.916(5) Å, and is consistent to that in the reported structure of the $[\mu\text{-B}_{20}\text{H}_{17}\text{OH}]^{2-}$ ion (1.907(9) Å).¹³ Additionally, the B9–O1 and B19–O1 distances of 1.481(4) and 1.488(4) Å, respectively, are both longer than what we observed with the terminal hydroxyl-derivative, $[\text{B}_{20}\text{H}_{17}\text{OH}]^{2-}$, and similar to what Hawthorne reported in the bridging hydroxyl derivative (avg. B–O bonds lengths = 1.483 Å).¹³

Scheme 3: Oxidation of $[ae-B_{20}H_{17}OH]^{4-}$ in the presence of iodomethane to form the $[\mu-B_{20}H_{17}OCH_3]^{2-}$ ion. $\bigcirc = BH$; $\bullet = B$.

Figure 3: ORTEP drawing (ellipsoids set at 50% probability) of the crystal structure of the $[\mu-B_{20}H_{17}OCH_3]^{2-}$ ion. Relevant bond lengths include: O1–C1 1.440(3) Å, B9–O 1.481(4) Å, and B19–O1 1.488(4) Å.

Based on the observed reactivity, it appears that both the hydrogen ion in the acidic solution and the iodomethane in the non-aqueous solution are functioning as electrophiles and initiate the oxidation reaction.

Experimental Section

General

Reactions. Synthetic reactions were performed under an argon atmosphere using Schlenk techniques when necessary. The polyhedral borane starting materials, $(\text{Et}_3\text{NH})_2[\text{B}_{10}\text{H}_{10}]$ and $(\text{Et}_3\text{NH})_2[\text{B}_{20}\text{H}_{18}]$, were prepared using published methods.^{16,1,17} Acetonitrile and dichloromethane were dried, degassed, and collected from an Innovative Technology solvent purification system. All other reagents were obtained either from Sigma-Aldrich Chemical Company (St. Louis, MO) or VWR and used without further purification.

NMR Spectroscopy. The ^{11}B Fourier transform NMR spectra were obtained with a Varian INOVA instrument operating 128 MHz. Boron chemical shifts were externally referenced to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in C_6D_6 ; peaks up-field of the reference are designated as negative.

X-Ray Crystallography. All crystallographic measurements were carried out on a Rigaku Mini CCD area detector diffractometer using graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 223 K using an Oxford Cryostream low-temperature device. A sample of suitable size and quality was selected and mounted onto a nylon loop. Data reductions were performed using Crystal Clear Expert 2.0. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinements on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms. Colorless, single crystals of $[\text{C}_{19}\text{H}_{18}\text{P}]_2[\text{B}_{20}\text{H}_{17}\text{CH}_3]$, $[\text{C}_{19}\text{H}_{18}\text{P}]_2[\text{B}_{20}\text{H}_{17}\text{OH}]$, and $[\text{C}_{19}\text{H}_{18}\text{P}]_2[\mu\text{-B}_{20}\text{H}_{17}\text{OCH}_3]$ were obtained by slow vapor diffusion of dry diethylether into a dry acetonitrile solution saturated with the compound. $[\text{C}_{19}\text{H}_{18}\text{P}]_2[\text{B}_{20}\text{H}_{17}\text{CH}_3]$ and $[\text{C}_{19}\text{H}_{18}\text{P}]_2[\mu\text{-B}_{20}\text{H}_{17}\text{OCH}_3]$ crystallized in the monoclinic space group $P2_1/c$. The $[\text{C}_{19}\text{H}_{18}\text{P}]_2[\mu\text{-B}_{20}\text{H}_{17}\text{OCH}_3]$ crystal contained one interstitial

molecule of acetonitrile in the asymmetric unit. Colorless crystals of $[\text{C}_{19}\text{H}_{18}\text{P}]_2[\text{B}_{20}\text{H}_{17}\text{OH}]$ crystallized in the triclinic space group $P\bar{1}$. Key details of the crystal and structure refinement data are summarized in Table S1. Further crystallographic details may be found in the respective CIF files which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The CCDC reference numbers for $[\text{C}_{19}\text{H}_{18}\text{P}]_2[\text{B}_{20}\text{H}_{17}\text{CH}_3]$, $[\text{C}_{19}\text{H}_{18}\text{P}]_2[\text{B}_{20}\text{H}_{17}\text{OH}]$, and $[\text{C}_{19}\text{H}_{18}\text{P}]_2[\mu\text{-B}_{20}\text{H}_{17}\text{OCH}_3]$ were assigned as 1057240, 1057241, and 1057242, respectively.

Synthesis

$[\text{B}_{20}\text{H}_{17}\text{CH}_3]^{2-}$: A clean, dry 100.0 mL Schlenk flask was equipped with a stir bar, stoppered, and flushed with argon gas. Diethylether (15.0 mL) was syringed into the reaction flask. A solution of methylmagnesium bromide (3.0 M, 1.4 mL, 4.2 mmol) was syringed into the reaction mixture while the solution was stirred. After stirring for five minutes, the septum was removed under an increased flow of argon and $(\text{Et}_3\text{NH})_2[\text{B}_{20}\text{H}_{18}]$ (0.258 g, 0.588 mmol) was added to the flask and the septum was replaced. The reaction was allowed to stir at room temperature for 12 h. Reaction completion was confirmed by ^{11}B NMR spectroscopy. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum in D_2O exhibited the following peaks: 13.8, 2.2, -1.6 , -7.6 , -9.0 , -27.1 , -30.2 . The reaction solvent was removed. Distilled water was added to the residue and the solids were removed by filtration. The solution was used, without further purification, for the oxidation reaction in the formation of the $[\text{B}_{20}\text{H}_{17}\text{CH}_3]^{2-}$ ion. The solution of the $[\text{B}_{20}\text{H}_{17}\text{CH}_3]^{4-}$ ion was transferred to a clean, dry 50 mL round bottom flask. While stirring, HCl (1.0 M, 1.0 mL) was added to the reaction mixture. Once dissolved, *p*-benzoquinone (0.185 g, 1.71 mmol) was added, and the reaction was allowed to stir at room temperature for 4 h. Reaction completion was confirmed by ^{11}B NMR spectroscopy. Excess *p*-benzoquinone was filtered and

the $[\text{B}_{20}\text{H}_{17}\text{CH}_3]^{2-}$ anion was precipitated as the methyltriphenylphosphonium, $\text{C}_{19}\text{H}_{18}\text{P}^+$, salt by addition of a solution of $\text{C}_{19}\text{H}_{18}\text{PBr}$ (0.5 M) in distilled water to the filtered reaction mixture. The precipitate was filtered, dried, and recrystallized from acetonitrile:ether, resulting in 0.362 g, 76.5% yield of $(\text{C}_{19}\text{H}_{18}\text{P})_2[\text{B}_{20}\text{H}_{17}\text{CH}_3]$. $^{11}\text{B}\{^1\text{H}\}$ NMR (δ , CD_3CN) 32.0, 30.6, 18.2, 16.1, -6.8, -12.4, -16.0, -19.4, -25.6, -28.3.

$[\text{B}_{20}\text{H}_{17}\text{OH}]^{2-}$: $\text{K}_4[\text{ae-B}_{20}\text{H}_{17}\text{OH}]$ (0.105 g, 0.258 mmol) was dissolved in 10.0 ml of distilled water in a 50 mL round bottom flask. HCl (1.0 M, 1 ml) was added to the stirred reaction mixture. After dissolution, *p*-benzoquinone (0.084 g, 0.78 mmol) was added and the reaction was allowed to stir at room temperature for approximately 4 h. Reaction completion was confirmed by ^{11}B NMR spectroscopy. Excess *p*-benzoquinone was removed by filtration and the $[\text{B}_{20}\text{H}_{17}\text{CH}_3]^{2-}$ anion was precipitated as a methyltriphenylphosphoniumsalt by the addition of a solution of $\text{C}_{19}\text{H}_{18}\text{PBr}$ (0.5 M) in distilled water. The precipitate was filtered, dried, and recrystallized from acetonitrile:ether, resulting in 0.125 g, 57.8% yield of $(\text{C}_{19}\text{H}_{18}\text{P})_2[\text{B}_{20}\text{H}_{17}\text{CH}_3]$. $^{11}\text{B}\{^1\text{H}\}$ NMR (δ , CD_3CN) 30.1, 29.0, 15.0, 13.8, -7.5, -10.8, -13.5, -14.8, -16.7, -20.2, -22.7, -24.7, -29.5.

$[\mu\text{-B}_{20}\text{H}_{17}\text{OCH}_3]^{2-}$: A clean, dry 100 mL Schlenk flask was equipped with $(\text{C}_{19}\text{H}_{18}\text{P})_4[\text{ae-B}_{20}\text{H}_{17}\text{OH}]$ (0.163 g, 0.120 mmol) and a stir bar and was stoppered and flushed with argon gas. Dry dichloromethane (80 mL) and dry acetonitrile (20 ml) was syringed into the reaction flask. Once dissolved, iodomethane (1.00 ml, 16.1 mmol) was syringed into the reaction flask and allowed to stir for five minutes. The septum was removed under an increase flow of argon and freshly sublimed *p*-benzoquinone (0.069g, 0.638 mmol) was added to the mixture and the mixture was refluxed for approximately 12 h. Reaction completion was confirmed by ^{11}B NMR spectroscopy. Once cooled, the reaction mixture was dried *in vacuo*, washed with distill

water to remove excess methyl iodide, dried, and recrystallized from acetonitrile:ether, resulting in 0.075 g, 76% yield of $(C_{19}H_{18}P)_2[\mu-B_{20}H_{17}OCH_3]$. $^{11}B\{^1H\}$ NMR (δ , CD_3CN) 29.9, 28.6, 15.7, 13.6, 12.0, 6.5, 3.7, -5.0, -7.8, -10.4, -13.9, -15.1, -16.8, -21.3, -22.7, -24.8, -27.3, -29.1, -30.5.

Conclusion

The reaction of the $[B_{20}H_{18}]^{2-}$ ion and methylmagnesium bromide formed the $[B_{20}H_{17}CH_3]^{4-}$ ion *in situ* which was then oxidized using *p*-benzoquinone to form the $[B_{20}H_{17}CH_3]^{2-}$ ion. To our knowledge, the $[B_{20}H_{17}CH_3]^{4-}$ ion is the first polyhedral borane anion to result from reaction of the $[B_{20}H_{18}]^{2-}$ ion with a carbon nucleophile and the $[B_{20}H_{17}CH_3]^{2-}$ ion is the first to be crystallographically characterized. Establishing that the $[B_{20}H_{18}]^{2-}$ ion reacts with carbon nucleophiles provides an opportunity to investigate a wide variety of compounds with potential applications in BNCT, a binary cancer therapy based on the propensity of the boron-10 isotope to capture thermal neutrons.¹⁷ The reported oxidations of the $[B_{20}H_{17}X]^{4-}$ derivatives do not occur in the absence of acid. In an effort to study the oxidation mechanism, the $[B_{20}H_{17}OH]^{4-}$ and $[B_{20}H_{17}OH]^{2-}$ ions, both of which had been reported earlier, were prepared and the $[B_{20}H_{17}OH]^{2-}$ ion was crystallographically characterized. Oxidation of the $[B_{20}H_{17}OH]^{4-}$ in the presence of iodomethane resulted in the oxidation of the polyhedral borane anion; however, the anticipated methylation was not observed. The methyl, and presumably the hydrogen ion in the acidic solutions, served instead as an electrophile to initiate the oxidation reaction. Oxidation of the $[B_{20}H_{17}OH]^{4-}$ ion in the presence of iodomethane yielded the $[\mu-B_{20}H_{17}OCH_3]^{2-}$ ion, containing both oxygen and hydrogen-bridge bonds, which was crystallographically characterized.

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Graphical Abstract