Inorg. Chem. **1997,** *36,* 5419−5420 **5419**

An Exploratory Evaluation of the Reactions of Organic Oxidants with Polyhedral Borane Anions

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Received March 11, 1997

The $[B_{20}H_{18}]^{2-}$ anion, which has a structure characterized by two 10-boron atom cages linked by a pair of two-electron three-center bonds, remains a starting point for the synthesis of many important polyhedral borane species.[1] In general, the $[B_{20}H_{18}]^{2-}$ ion is produced by the oxidative coupling of two $[closo\text{-}B_{10}H_{10}]^{2-}$ cages using various metal ions such as ferric and ceric ions[2] as oxidizing agents. Reduction of the $[B_{20}H_{18}]^{2-}$ ion by sodium in liquid ammonia solution produces a kinetically controlled product, $[e^2\text{-}B_{20}H_{18}]^{4-}$, whose structure is characterized by a boron−boron bond between the equatorial sites of two 10-boron atom cages. The $[e^2\text{-}B_{20}H_{18}]^{4-}$ anion can be rearranged via acidification followed by basification to a second more thermodynamically stable isomer $[a^2\text{-}B_{20}H_{18}]^{4-}$, where the two 10-boron atom cages are linked by a bond between two apical boron atoms.[3] The $[e^2\text{-}B_{20}H_{18}]^{4-}$, $[a^2\text{-}B_{20}H_{18}]^{4-}$, and $[closo\text{-}B_{10}H_{10}]^{2-}$ ions may be oxidized to the $[B_{20}H_{18}]^{2-}$ ion with metal ions (Figure 1).

In hopes of discovering milder and/or nonaqueous oxidation reactions which could be developed for use with a variety of polyhedral borane species, we examined the ability of simple organic oxidizing agents to react with $[closo\text{-}B_{10}H_{10}]^{2-}$, $[e^2\text{-}B_{20}H_{18}]^{4-}$, and $[a^2\text{-}B_{20}H_{18}]^{4-}$ ions in model reactions to produce the well-known $[B_{20}H_{18}]^{2-}$ ion. The results of this initial study are described here.

Experimental Section

Materials and General Procedures. All reactions were performed under a nitrogen atmosphere. $K_4[e^2\text{-}B_{20}H_{18}]$ was prepared by published methods.[3] Benzoquinone (Matheson Coleman & Bell) was sublimed prior to use. All other chemicals were reagent grade and used without further purification. ^{11}B NMR spectra were recorded on a Bruker ARX 500 NMR spectrometer and referenced to external $BF_3{\cdot}O(C_2H_5)_2$.

Oxidation of $K_4[e^2\text{-}B_{20}H_{18}]$. Aqueous HCl (1 N, 15 mL) was added to a solution of $K_4[e^2\text{-}B_{20}H_{18}]$ (2.07 g, 4.86 mmol) in 100 mL of water. Benzoquinone (1.05 g, 9.73 mmol) was added, and the solution immediately turned dark yellow. After the solution was stirred for 4 h at room temperature, a saturated solution of tetraethylammonium bromide in water was added to produce a yellow precipitate. The solid was isolated by filtration and recrystallized from hot water to yield 2.10 g of $[(C_2H_5)_4N]_2[B_{20}H_{18}]$ (4.24 mmol, 87%), identified by its ^{11}B NMR spectrum.[2]

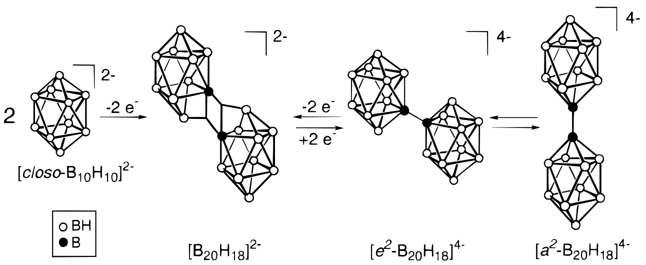

Figure 1. Reduction and oxidation reactions of the $[closo\text{-}B_{10}H_{10}]^{2-}$, $[e^2\text{-}B_{20}H_{18}]^{4-}$, $[a^2\text{-}B_{20}H_{18}]^{4-}$, and $[B_{20}H_{18}]^{2-}$ ions.

Oxidation of $[(CH_3CH_2)_4N]_4[a^2\text{-}B_{20}H_{18}]$. Trifluoroacetic acid (1 mL) was added to a stirred solution of $[(C_2H_5)_4N]_4[a^2\text{-}B_{20}H_{18}]$ (0.56 g, 0.74 mmol) in 100 mL of dichloromethane and 25 mL of acetonitrile. Solid 1,4-benzoquinone (0.20 g, 1.85 mmol) was added, and the solution immediately turned bright yellow. The mixture was heated at reflux overnight. The solvent was removed by evaporation under reduced pressure. The residue was digested in 150 mL of boiling water, and the mixture was filtered. Upon cooling, yellow needles of $[(C_2H_5)_4N]_2[B_{20}H_{18}]$ (0.33 g, 0.67 mmol) crystallized in 90% yield and were characterized by the ^{11}B NMR spectrum.[2]

Oxidation of $[(CH_3CH_2)_3NH]_2[closo\text{-}B_{10}H_{10}]$. Trifluoroacetic acid (1 mL) was added to a stirred solution of $[(C_2H_5)_3NH]_2[closo\text{-}B_{10}H_{10}]$ (1.01 g, 3.13 mmol) in 70 mL of acetonitrile. Solid 1,4-tetrachlorobenzoquinone (1.54 g, 6.25 mmol) was added, and the solution immediately turned bright yellow. The mixture was stirred at room temperature overnight. The solvent was removed by evaporation under reduced pressure. The residue was digested in 80 mL boiling water, and the mixture was filtered. Upon cooling, yellow needles of $[(C_2H_5)_3NH]_2[B_{20}H_{18}]$ (0.49 g, 1.12 mmol) crystallized in 72% yield and were characterized by the ^{11}B NMR spectrum.[2]

Results and Discussion

In aqueous solution, the equatorial−equatorial (e^2) isomer of the polyhedral boron anion $[e^2\text{-}B_{20}H_{18}]^{4-}$ reacted with the organic oxidizing agent *p*-benzoquinone at room temperature to rapidly produce the $[B_{20}H_{18}]^{2-}$ anion. Precipitation and recrystallization produced the salt $[(C_2H_5)_4N]_2[B_{20}H_{18}]$ in 87% yield. In 4:1 dichloromethane/acetonitrile, the apical−apical (a^2) isomer of the polyhedral boron anion $[a^2\text{-}B_{20}H_{18}]^{4-}$ reacted with the organic oxidizing agent *p*-benzoquinone at the reflux temperature to produce the $[B_{20}H_{18}]^{2-}$ anion. Recrystallization produced the salt $[(C_2H_5)_4N]_2[B_{20}H_{18}]$ in 90% yield. In analogous reactions, the mild organic oxidants azobenzene, nitrobenzene, and benzophenone did not react with the $[e^2\text{-}B_{20}H_{18}]^{4-}$ anion, even when the reaction mixture was heated at the reflux temperature for extended periods of time.

The oxidant 1,4-tetrachlorobenzoquinone reacted with the $[closo\text{-}B_{10}H_{10}]^{2-}$ ion in acetonitrile at room temperature to produce the $[B_{20}H_{18}]^{2-}$ ion. Evaporation of the solvent and recrystallization from boiling water produced $[(C_2H_5)_3NH]_2[B_{20}H_{18}]$ in 72% yield. All attempts to oxidize the $[closo\text{-}B_{10}H_{10}]^{2-}$ anion with azobenzene, nitrobenzene, benzophenone, or *p*-benzoquinone were also unsuccessful.

Tetrachlorobenzoquinone has the ability to oxidize the $[closo\text{-}B_{10}H_{10}]^{2-}$ ion to the $[B_{20}H_{18}]^{2-}$ ion under nonaqueous conditions. Benzoquinone did not oxidize the $[closo\text{-}B_{10}H_{10}]^{2-}$ anion, but it did convert both the $[a^2\text{-}B_{20}H_{18}]^{4-}$ and $[e^2\text{-}B_{20}H_{18}]^{4-}$ anions to the $[B_{20}H_{18}]^{2-}$ anion using nonaqueous and aqueous solvents, respectively. The weaker oxidizing agents such as benzophenone, nitrobenzene, and azobenzene did not react with either anion. The $[B_{20}H_{18}]^{2-}$ product synthesized by using either tetrachlorobenzoquinone or benzoquinone was easily isolated and purified.

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S0020-1669(97)00279-6 CCC: $14.00

The advantages of the quinone oxidants over metal-containing oxidizing agents in reactions of polyhedral borane anions is exemplified when aqueous reaction conditions are for some reason unacceptable. In addition, organic oxidants, particularly benzoquinone, have proven useful in other polyhedral borane anion systems where metal-containing oxidizing agents proved to be too harsh or where isolation of the desired product has proven difficult.[4]

Acknowledgment. This research was conducted with funding from the U.S. Department of Energy, Office of Energy, Research Contract No. DE-FG03-95ER61975, and the National Institutes of Health Grant No. NIH GM08496.

IC970279T

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(4) Li, F.; Hawthorne, M. F. Unpublished results.

Additions and Corrections

1997, Volume 36

Philip J. Bailey,* Simon F. Bone, Lindsey A. Mitchell, Simon Parsons, Kenneth J. Taylor, and Lesley J. Yellowlees: A New Bridging Ligand for the $[Mo_2]^{4+}$ Dimer: Syntheses and X-ray Crystal Structures of the Redox Pair $[Mo_2\{\mu\text{-}\eta^2\text{-}(NPh)_2CNHPh\}_4]^{0/+}$.

Pages 867−871. Owing to a transcription error in the cell dimensions made at the start of structure analysis, the *c* cell dimension of compound **2** was given incorrectly as 25.573(7) Å, when the correct value is 23.573(7) Å. All the structural parameters in Table 3 are therefore in error, and correct values are given below. Note that Mo(1)−Mo(2) is now 2.1194(12) Å, which is in the range expected for an Mo−Mo bond of order 3.5.

Table 3. Selected Bond Lengths (Å) for **2**

Mo(1)−Mo(2)	2.1194(12)	C(1A)−N(3A)	1.373(11)
Mo(1)−N(1D)	2.127(7)	C(1B)−N(1B)	1.350(10)
Mo(1)−N(1A)	2.132(7)	C(1B)−N(3B)	1.351(10)
Mo(1)−N(1C)	2.145(7)	C(1B)−N(2B)	1.361(10)
Mo(1)−N(1B)	2.146(7)	C(1C)−N(1C)	1.341(11)
Mo(2)−N(2A)	2.115(7)	C(1C)−N(2C)	1.347(11)
Mo(2)−N(2C)	2.122(7)	C(1C)−N(3C)	1.378(11)
Mo(2)−N(2D)	2.134(7)	C(1D)−N(1D)	1.339(10)
Mo(2)−N(2B)	2.147(7)	C(1D)−N(2D)	1.342(11)
C(1A)−N(2A)	1.324(11)	C(1D)−N(3D)	1.371(11)
C(1A)−N(1A)	1.347(11)		

Received April 14, 1997.

IC970430Z