Inorganic Chemistry

An Electrochemical Strategy for Chalcogenation of *closo*-Dodecaborate $(B_{12}H_{12})^{2-}$ Anion

Tyler A. Kerr,[‡] Yessica A. Nelson,[‡] Nicholas A. Bernier, and Alexander M. Spokoyny*

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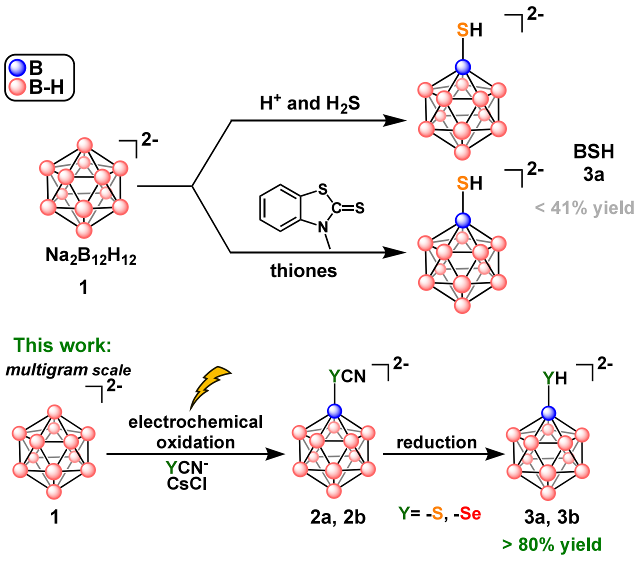
ABSTRACT: Advancements in thermal neutron generation technologies within clinical environments have led to a renewed interest in developing boron-containing compounds for boron neutron capture therapy (BNCT). Previous syntheses of several key boron cluster-based therapeutics with clinical relevance are low-yielding and have complicated workup procedures. Using electrolytic methods, we report the *in situ* oxidation of pseudohalides, $[SCN]^-$ and $[SeCN]^-$, to synthesize pseudohalogenated products, $B_{12}H_{11}YCN^{2-}$ (Y = S or Se). Further, these compounds can be reduced to their respective thiol or selenol, $[B_{12}H_{11}SH]^{2-}$ (BSH) or $[B_{12}H_{11}SeH]^{2-}$ (BSeH), which are exceedingly nucleophilic and able to form zwitterionic sulfonium and selenonium compounds using alkyl-based electrophiles. The newly reported preparation of BSH and BSeH provides an efficient and convenient route to the preparation of key chalcogenated boron cluster building blocks for the biomedical and materials science communities.

Boron-containing compounds are one of two classes of molecular Trojan horses that have been studied *in vivo* for neutron-capture therapy and are the only candidates that have been tested in humans.[1,2] Of these boron-containing compounds, boron clusters make up a significant area of research due to their synthetic versatility, stability, and high boron density.[3,4] $[B_{12}H_{11}SH]^{2-}$ (BSH) emerged early as a candidate for BNCT[5,6] and has been used in pilot clinical studies in humans as recently as 2011.[7] Until recently, the need for a nuclear reactor drastically limited the production of neutrons for therapeutic purposes.[8] Developments in the production of thermal and epithermal neutrons in the clinical setting have garnered renewed interest in BNCT applications and relevant boron-based compounds.[9]

BSH has been previously synthesized in relatively low yields, requiring tedious workups, as summarized in Scheme 1. With the increasing demand for BSH and few viable synthetic options, an improved synthesis for this valuable target is warranted. *Closo*-Dodecaborate has been shown to react with halogens and mixed halogens, forming anywhere from mono- to persubstituted species depending on reaction conditions.[10,11] Pseudohalogens like $(SCN)_2$ and $(SeCN)_2$ were also shown to react with *closo*-dodecaborate, forming the corresponding chalcogenated boron clusters.[12−14] Unlike molecular halogens, $(SeCN)_2$ and $(SCN)_2$ are not commercially available and are unstable under ambient conditions, making wide adoption of these synthetic approaches difficult.

Recently, electrochemical techniques have emerged as scalable, tunable, and versatile tools in synthesis.[20−24] With increasing access to user-friendly electrolytic methods, we sought to develop an electrosynthetic methodology to complement the current mild chemical reactions for boron cluster thiocyanation under aqueous conditions. In the process, we discovered that these electrochemical strategies are also competent for selenocyanation even in aqueous media, and the reduction of $[B_{12}H_{11}SCN]^{2-}$ to BSH can be achieved using mild conditions. A mention of nonaqueous electrochemical thio- and selenocyanation currently exists in a conference proceeding from 1997[25] and is cited in several subsequent review articles.[26−28] Counter to Morris et al.,[25] we show successful cleavage of the Se−C bond in $[B_{12}H_{11}SeCN]^{2-}$

Scheme 1. Top: Current Synthetic Routes for BSH from 1 $(Na_2B_{12}H_{12})$;[15−19] Bottom: Electrochemical Synthesis of 2a and 2b, and Subsequent Reduction to BSH and BSeH



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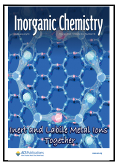

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under Birch reduction conditions and further report the nucleophilic addition of the fully reduced selenide and sulfide into alkyl bromides, forming sulfonium and selenonium compounds underpinning the highly nucleophilic nature of trianionic boron clusters containing exopolyhedral $B-Y^-$ (Y= S or Se) moieties.

Previous reports of boron cluster thiocyanation use a freshly prepared solution of the pseudohalogen[13] or *in situ* chemical oxidation of $[SCN]^-$ in an aqueous solution.[12] We elected to pursue electrochemical techniques, using an electrode rather than a chemical oxidant, according to Figure 1A. Initial cyclic voltammetric studies were performed on individual solutions of 5 mM NaSCN, KSeCN, and $Na_2B_{12}H_{12}$ (**1**) in unbuffered 1 M $NaClO_4$ (Figure 1B). Each showed irreversible oxidations with peak potentials of 1.05, 0.52, and ~2.0 V vs SCE, respectively. Importantly, each pseudohalide salt oxidizes at a potential that is more negative than that of $[B_{12}H_{12}]^{2-}$ (~2.0 V), indicating that under highly oxidizing conditions, the pseudohalides will be oxidized before the boron cluster.

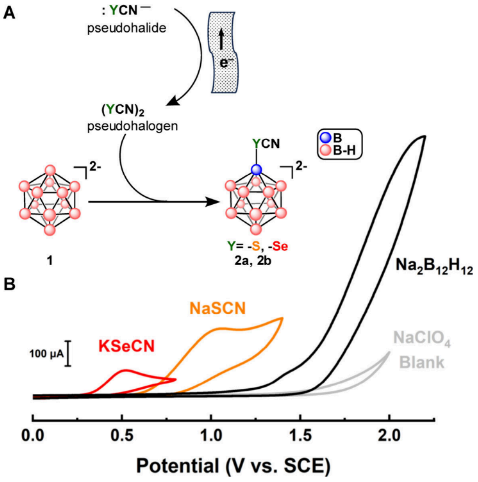

Figure 1. (A) Oxidation of pseudohalide to pseudohalogen, which reacts with **1**, forming pseudohalogenated products **2a** and **2b**. (B) Cyclic voltammograms of KSeCN (red), NaSCN (orange), and **1** (black) in unbuffered 1 M $NaClO_4$ in H_2O (gray) on a 3 mm glassy carbon disk electrode.

Leveraging the reactivity of the pseudohalogens with boron clusters (Figure 1A), we reasoned that the electrolytically generated $(SCN)_2$ and $(SeCN)_2$ would react with **1** to form the desired products **2a** and **2b**. Using a divided cell, solutions of **1** and NaSCN or KSeCN in water were electrolyzed at 100 mA constant current using a carbon cloth working electrode and copper wire counter electrode. The counter electrode compartment contained a 4 M solution of $CuCl_2$ in 1 M KCl, and a Nafion membrane separated the solutions. The reactions were monitored by ^{11}B NMR spectroscopy and showed complete conversion to single products after about three molar equivalents of electrons were passed per equivalent of **1**. Products **2a** and **2b** were isolated in 90% and 82% yields, respectively. The ^{11}B and $^{13}C\{^1H\}$ NMR spectra of **2a** were consistent with the presence of a single exopolyhedral $-SCN$ substituent on a *closo*-dodecaborate cluster.[12] In the case of **2b**, the product similarly showed a diagnostic ^{11}B NMR spectrum for a singly substituted boron cluster. The ^{77}Se NMR spectrum for this compound shows a broad resonance at −20 ppm with a fwhm (full width at half maximum) of 90 Hz, which is significantly broader than the ^{77}Se resonance for KSeCN in D_2O at −325 ppm with a fwhm of 4.5 Hz. The chemical shift of the **2b** is upfield shifted compared to other selenocyanates with PhSeCN found at 328 ppm.[29] An attempt was made to further substitute **1** with more than one -SCN substituent by treating it with 36 mol equiv of NaSCN and electrolyzing with 72 mol equiv of electrons, and ^{11}B NMR spectra of the reaction mixture suggested the presence of a mixture of *ortho*-, *meta*-, and *para*-disubstituted $[B_{12}H_{10}(SCN)_2]^{2-}$ (Figures S55−S56). A small amount of *para*-substituted isomer was recrystallized from the reaction mixture, and a single crystal X-ray structure is shown in Figure S95.

Reductions of alkyl and aryl thiocyanates have previously been shown to convert to the corresponding thiols using strong hydride donors[30] and other strong reducing conditions, including the classical Birch reduction conditions with elemental sodium in liquid ammonia.[31] More recently, phosphorus pentasulfide (P_2S_5) was shown to facilitate the reduction of thiocyanates under mild conditions.[32] Thus, we explored the reduction of **2a** and **2b** using both P_2S_5 and Birch reduction conditions. Using P_2S_5, we were able to show quantitative conversion of **2a** to **3a** on a 100 mg scale under microwave irradiation. Characterization of BSH product by $^{11}B\{^1H\}$ NMR spectroscopy in D_2O showed resonances at −8.8, −13.3, −15.5, and −19.1 ppm, consistent with previous literature.[33] The mechanism of the conversion of thiocyanates to thiols using P_2S_5 is thought to involve the formation of a dithiocarbamate, which hydrolyzes on aqueous workup to form the thiol and thiocarbamic acid. In our attempts to perform the same reaction on the selenocyanated boron cluster, the desired **3b** product was not formed. ^{13}C NMR spectroscopy suggested the selenothiocarbamate intermediate that is formed in the reaction with P_2S_5 remained present after aqueous workup.

While using P_2S_5 is an effective method for the reduction of a thiocyanate, differing conditions were deemed necessary to reduce **2b**. We found that sodium metal in liquid ammonia was a general method of decyanation of both the thiocyanate and the selenocyanate (Figure 2A). After condensation of liquid ammonia using a dry ice/acetone-filled condenser into a flask containing **2b** cooled by a dry ice/acetone bath, pieces of sodium metal were added until the solution remained a deep blue color (~3 equiv). After 2 h, the mixture was quenched by dropwise addition of a CsCl solution in water and allowed to warm to room temperature, affording a light gray powder, which was filtered in air. After filtration, the powder showed a color change to light orange. $^{11}B\{^1H\}$ NMR spectroscopy of this compound (Figure 2B) showed predominantly a 1-substituted boron cluster that is distinct from the **2b** with a minor impurity. We believe the potently oxygen-sensitive product formed under Birch reduction conditions[34] is **4b** with an impurity of the oxidized diselenide, **7b**. Further characterization of this selenide product by ^{77}Se NMR spectroscopy was inconclusive, and we were unable to locate a resonance attributable to **4b** between −2000 and 2000 ppm. Acidification of a suspension of **4b** in water under rigorously oxygen-free conditions formed a new compound with a diagnostic ^1H NMR resonance at −3.07 ppm assigned to the selenol hydrogen atom (Figure S25).

Exposure of a colorless aqueous solution of **4b** to air led to an orange solution of the impurity seen in the $^{11}B\{^1H\}$ NMR spectrum of **4b** and the appearance of a new ^{77}Se NMR resonance at 40 ppm (Figure 2B). The chemical shift of this resonance is distinct from most diselenides that fall between

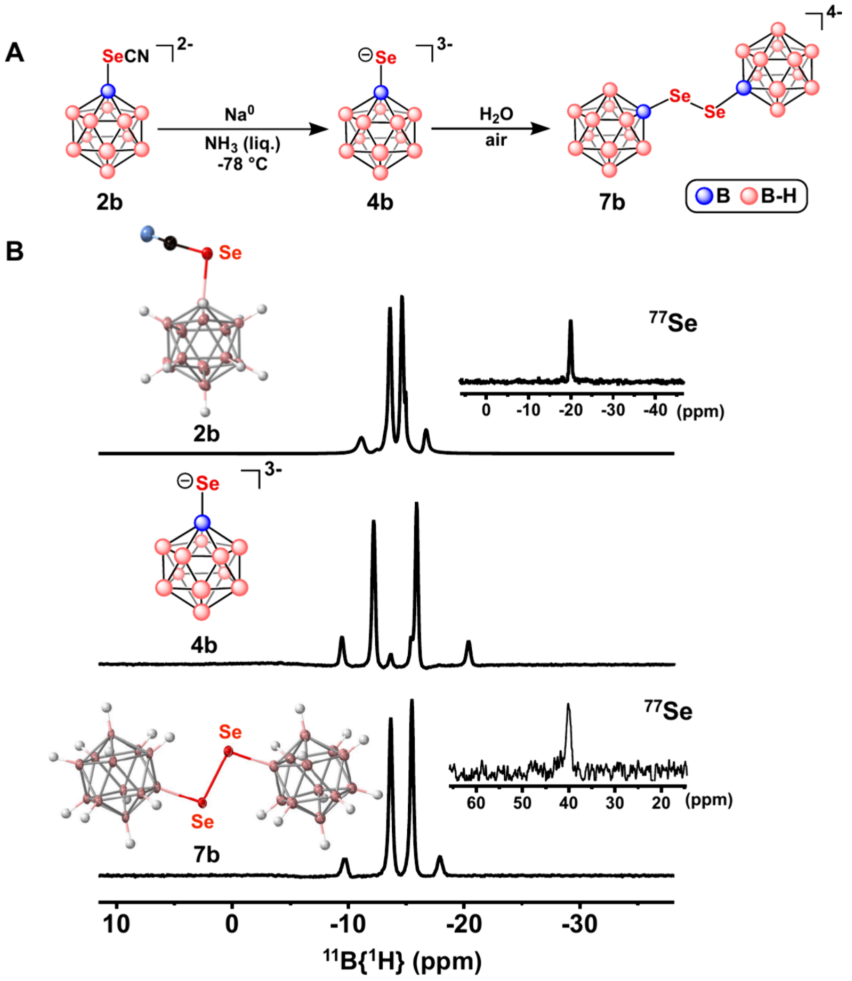

Figure 2. (A) Reaction of **2b** under Birch reduction conditions to form **4b**, which is oxidized by air to form **7b**. (B) $^{11}B\{^{1}H\}$ of **4b** in D_2O and $^{11}B\{^{1}H\}$ and ^{77}Se NMR spectra of **2b** and **7b** in D_2O. Countercations and solvent molecules removed for clarity.

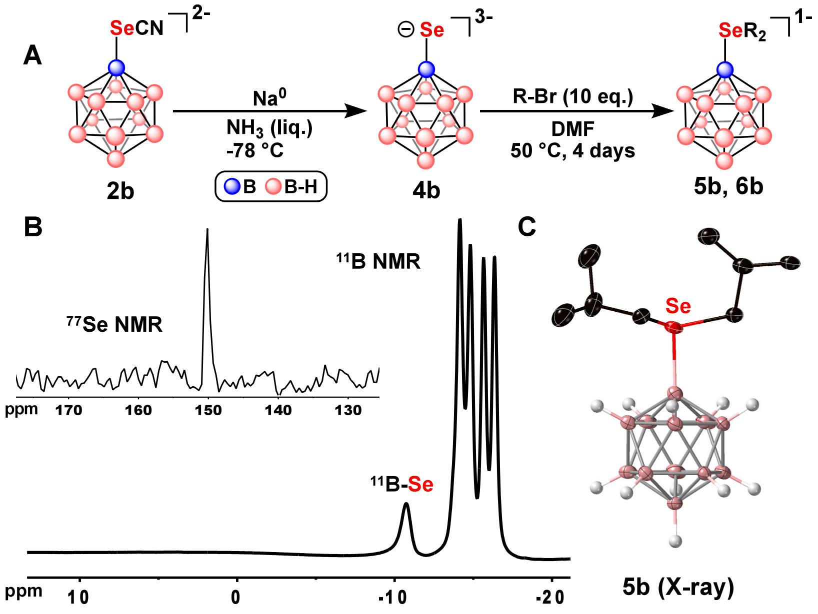

Figure 3. (A) Reaction scheme showing the disubstitution of selenide **4b** forming selenonium products **5b** and **6b** with R-Br = $^{i}BuBr$ and cyclopropylmethyl bromide, respectively. (B) ^{11}B and ^{77}Se NMR spectra of **5b**. (C) Single crystal X-ray structure of anionic **5b**. Cs^{+} countercation and hydrogen atoms on carbons removed for clarity. Ellipsoids shown at 50%.

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300 and 500 ppm in ^{77}Se NMR. Single crystal X-ray analysis of red-orange crystals grown from DMF and Et_2O showed the diselenide product, **7b**, crystallized in the less common *trans* configuration (dihedral = 179.8(7)°) due to weakly bound Cs^+ cations on each side of the diselenide bond. The Se−Se bond length was found to be 2.353(2) Å, similar to the 2.338 Å found in 9,9′-*m*-carboranyl diselenide.[35]

To confirm the presence of **4b**, we turned to its reactivity, as shown in Figure 3. Using **4b** as a nucleophile with ^{i}BuBr (isobutyl bromide), we found that after 4 days in DMF, the ^{11}B NMR showed conversion to a single product that showed a ^{77}Se resonance at 150 ppm. Integrations of the resonances in the ^{1}H NMR spectrum suggested that the ^{i}BuBr substituted twice onto the boron cluster. Single crystals of the Cs^+ salt of this compound were grown from CH_3CN and Et_2O, which showed that the selenide formed an air-stable zwitterionic selenonium compound, **5b**. Using cyclopropylmethyl bromide as an electrophile, we synthesized **6b** and support that this reaction proceeds through a simple S_N2-like displacement reaction. Notably, the treatment of **4a** (which is a sulfur-based congener of **4b**, see SI) with ^{i}BuBr under the same conditions also forms sulfonium **5a**, which has previously been observed.[36]

Alkyl and aryl/alkyl sulfonium and selenonium salts can be prepared from the corresponding thioethers and selenoethers using high temperatures or halide scavengers like Ag^+.[37−41] Because our conditions contain no halide scavengers and use mild heat, we support that the dianionic boron cluster increases the nucleophilicity of the sulfide and selenide. To test this, we subjected 9-*m*-carboranylselenol to the same conditions as before with ^{i}BuBr as the electrophile with CsOAc as a base, and integrations of the ^{1}H resonances in the ^{1}H NMR spectra are consistent with only single substitution forming the selenoether with ^{i}BuBr rather than a selenonium compound as with **4b** (Figures S50−S52). A single nucleophilic substitution of the 9-*m*-carboranyl selenol with the alkyl bromide confirms that **4b** is significantly more nucleophilic due to its charge rather than electronic effects imparted by the boron cluster.

Finally, we determined the pK_a values of **3a** and **3b** through potentiometric titrations in aqueous solutions. We found pK_a values of 13.3 for **3a** and 10.7 for **3b** (Figures S51 and S52). The value found for **3a** is consistent with the previously found value of 13.4 by spectrophotometric titration.[36] The pK_a value of 10.7 for selenol **3b** is significantly more basic than other reported selenols, making this the most basic selenol reported to date.[42,43] These observations further reinforce the notion that polyhedral boron clusters can feature extreme electronic properties when attached to heteroatom sites.[44−51]

Using electrochemical methods, we have synthesized pseudohalide-substituted *closo*-dodecaborate clusters. We propose that these reactions proceed through direct electrophilic addition of thiocyanogen or selenocyanogen to the cage as with other halides, but we cannot rule out reactions with other species associated with aqueous $(SCN)_2$ and $(SeCN)_2$ decomposition[52,53] that nevertheless form the desired pseudohalogenated product. The pseudohalogenated compounds undergo reduction to form BSH and its selenolated analog, BSeH, which is the first anionic polyhedral boron cluster-based selenol. The basicity and further reactivity of these compounds underpin the highly nucleophilic nature of the associated chalcogenides. Overall, this work provides an effective and high-yielding method to synthesize BSH and other chalcogenated boron clusters that may appeal to the medical community as potential BNCT agents.[54] Furthermore, the work highlights how boron clusters can exhibit an extreme electron-donating character to the heteroatoms attached directly to a boron vertex, as exemplified by the newly synthesized BSeH compound which is the most basic selenol reported to date.[55]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.5c00469.

Detailed experimental procedures, characterization data, crystallographic, and spectroscopy (PDF)

Accession Codes

Deposition Numbers 2415058−2415062 and 2426011 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

■ AUTHOR INFORMATION

Corresponding Author

Alexander M. Spokoyny − *Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095, United States; California NanoSystems Institute (CNSI), University of California, Los Angeles, Los Angeles, California 90095, United States;* orcid.org/0000-0002-5683-6240; Email: spokoyny@ucla.edu

Authors

Tyler A. Kerr − *Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095, United States*

Yessica A. Nelson − *Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095, United States*

Nicholas A. Bernier − *Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095, United States;* orcid.org/0000-0002-4474-8665

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.5c00469

Author Contributions

‡T. A. K. and Y. A. N. contributed equally.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Soloway, A. H.; Tjarks, W.; Barnum, B. A.; Rong, F.-G.; Barth, R. F.; Codogni, I. M.; Wilson, J. G. The Chemistry of Neutron Capture Therapy. *Chem. Rev.* **1998**, *98* (4), 1515−1562.

(2) Ho, S. L.; Yue, H.; Tegafaw, T.; Ahmad, M. Y.; Liu, S.; Nam, S.-W.; Chang, Y.; Lee, G. H. Gadolinium Neutron Capture Therapy (GdNCT) Agents from Molecular to Nano: Current Status and Perspectives. *ACS Omega* **2022**, *7* (3), 2533−2553.

(3) Hamdaoui, M.; Liu, F.; Cornaton, Y.; Lu, X.; Shi, X.; Zhang, H.; Liu, J.; Spingler, B.; Djukic, J.-P.; Duttwyler, S. An Iridium-Stabilized Borenium Intermediate. *J. Am. Chem. Soc.* **2022**, *144* (40), 18359−18374.

(4) Barba-Bon, A.; Salluce, G.; Lostalé-Seijo, I.; Assaf, K. I.; Hennig, A.; Montenegro, J.; Nau, W. M. Boron Clusters as Broadband Membrane Carriers. *Nature* **2022**, *603* (7902), 637−642.

(5) Zhou, T.; Igawa, K.; Kasai, T.; Sadahira, T.; Wang, W.; Watanabe, T.; Bekku, K.; Katayama, S.; Iwata, T.; Hanafusa, T.; Xu, A.; Araki, M.; Michiue, H.; Huang, P. The Current Status and Novel Advances of Boron Neutron Capture Therapy Clinical Trials. *Am. J. Cancer Res.* **2024**, *14* (2), 429−447.

(6) Farr, L. E.; Sweet, W. H.; Robertson, J. S.; Foster, C. G.; Locksley, H. B.; Sutherland, D. L.; Mendelsohn, M. L.; Stickley, E. E. Neutron Capture Therapy with Boron in the Treatment of Glioblastoma Multiforme. *Am. J. Roentgenol. Radium Ther. Nucl. Med.* **1954**, *71* (2), 279−293.

(7) Yanagie, H.; Higashi, S.; Seguchi, K.; Ikushima, I.; Fujihara, M.; Nonaka, Y.; Oyama, K.; Maruyama, S.; Hatae, R.; Suzuki, M.; Masunaga, S.; Kinashi, T.; Sakurai, Y.; Tanaka, H.; Kondo, N.; Narabayashi, M.; Kajiyama, T.; Maruhashi, A.; Ono, K.; Nakajima, J.; Ono, M.; Takahashi, H.; Eriguchi, M. Pilot Clinical Study of Boron Neutron Capture Therapy for Recurrent Hepatic Cancer Involving the Intra-Arterial Injection of a ^{10}BSH-Containing WOW Emulsion. *Appl. Radiat. Isot.* **2014**, *88*, 32−37.

(8) Barth, R. F.; Coderre, J. A.; Vicente, M. G. H.; Blue, T. E. Boron Neutron Capture Therapy of Cancer: Current Status and Future Prospects. *Clin. Cancer Res.* **2005**, *11* (11), 3987−4002.

(9) International Atomic Energy Agency. *Compact Accelerator Based Neutron Sources*, 2021. https://www.iaea.org/publications/14948/compact-accelerator-based-neutron-sources (accessed 2024−06−17).

(10) Gu, W.; Ozerov, O. V. Exhaustive Chlorination of $[B_{12}H_{12}]^{2-}$ without Chlorine Gas and the use of $[B_{12}Cl_{12}]^{2-}$ as a Supporting Anion in Catalytic Hydrodefluorination of Aliphatic C−F Bonds. *Inorg. Chem.* **2011**, *50* (7), 2726−2728.

(11) Axtell, J. C.; Saleh, L. M. A.; Qian, E. A.; Wixtrom, A. I.; Spokoyny, A. M. Synthesis and Applications of Perfunctionalized Boron Clusters. *Inorg. Chem.* **2018**, *57* (5), 2333−2350.

(12) Lepšík, M.; Srnec, M.; Plešek, J.; Buděšínský, M.; Klepetářová, B.; Hnyk, D.; Grüner, B.; Rulíšek, L. Thiocyanation of *closo*-Dodecaborate $B_{12}H_{12}^{2-}$. A Novel Synthetic Route and Theoretical Elucidation of the Reaction Mechanism. *Inorg. Chem.* **2010**, *49* (11), 5040−5048.

(13) Srebny, H.-G.; Preetz, W. Darstellung und Charakterisierung von Thiocyanatderivaten der Hydroboratanionen $B_{10}H_{10}^{2-}$ und $B_{12}H_{12}^{2-}$. *Z. Für Anorg. Allg. Chem.* **1984**, *513* (6), 7−14.

(14) Nachtigal, C.; Steuer, B.; Preetz, W. Selenocyanato Derivatives of Hydro-*closo*-borates: Syntheses and Crystal Structures of $(PPh_4)_2[(SeCN)B_nH_{n-1}]$ (n = 6, 10, 12). *Chem. Ber.* **1996**, *129* (12), 1531−1534.

(15) Knoth, W. H.; Sauer, J. C.; England, D. C.; Hertler, W. R.; Muetterties, E. L. Chemistry of Boranes XIX ^{1} Derivative Chemistry of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$. *J. Am. Chem. Soc.* **1964**, *86* (19), 3973−3983.

(16) Tolpin, E. I.; Wellum, G. R.; Berley, S. A. Synthesis and Chemistry of Mercaptoundecahydro-*closo*-dodecaborate(2-). *Inorg. Chem.* **1978**, *17* (10), 2867−2873.

(17) Hamilton, E. J. M.; Jordan; Meyers, E. A.; Shore, S. G. One-Step Preparation of Dimethyl Sulfide Substituted Icosahedral Boranes: The Crystal and Molecular Structures of 1,7-$(SMe_2)_2B_{12}H_{10}$, 1,12-$(SMe_2)_2B_{12}H_{10}$, and $[SMe_3][B_{12}H_{11}(SMe_2)]$·MeCN. *Inorg. Chem.* **1996**, *35* (18), 5335−5341.

(18) Kultyshev, R. G.; Liu, S.; Shore, S. G. Reduction of Inner Sulfonium Salts, Thioethers, and Sulfones Derived from *closo*-$[B_{12}H_{12}]^{2-}$ by Lithium in Methylamine: A New Route to Mercaptododecaborates. *Inorg. Chem.* **2000**, *39* (26), 6094−6099.

(19) Olid, D.; Núñez, R.; Viñas, C.; Teixidor, F. Methods to Produce B−C, B−P, B−N and B−S Bonds in Boron Clusters. *Chem. Soc. Rev.* **2013**, *42* (8), 3318−3336.

(20) Horn, E. J.; Rosen, B. R.; Baran, P. S. Synthetic Organic Electrochemistry: An Enabling and Innately Sustainable Method. *ACS Cent. Sci.* **2016**, *2* (5), 302−308.

(21) Zhu, C.; Ang, N. W. J.; Meyer, T. H.; Qiu, Y.; Ackermann, L. Organic Electrochemistry: Molecular Syntheses with Potential. *ACS Cent. Sci.* **2021**, *7* (3), 415−431.

(22) Rafiee, M.; Abrams, D. J.; Cardinale, L.; Goss, Z.; Romero-Arenas, A.; Stahl, S. S. Cyclic Voltammetry and Chronoamperometry: Mechanistic Tools for Organic Electrosynthesis. *Chem. Soc. Rev.* **2024**, *53* (2), 566−585.

(23) Lehnherr, D.; Chen, L. Overview of Recent Scale-ups in Organic Electrosynthesis (2000−2023). *Org. Process Res. Dev.* **2024**, *28* (2), 338−366.

(24) Xie, H.; Gao, X.; Dong, B.; Wang, H.; Spokoyny, A. M.; Mu, X. Electrochemical Deconstruction of Alkyl Substituted Boron Clusters to Produce Alkyl Boronate Esters. *Chem. Commun.* **2024**, *60* (81), 11548−11551.

(25) Morris, J. H.; Brattsev, V. A.; Gaines, D. F. Thio- and Selenocyanation of $[B_{12}H_{12}]^{2-}$ Under Conditions of Electrochemical and Chemical Oxidation. In *Advances in Boron Chemistry*; Royal Chem. Soc.: Cambridge, 1997; pp 434−437.

(26) Sivaev, I. B.; Bregadze, V. I.; Sjöberg, S. Chemistry of *closo*-Dodecaborate Anion $[B_{12}H_{12}]^{2-}$: A Review. *Collect. Czechoslov. Chem. Commun.* **2002**, *67* (6), 679−727.

(27) Sivaev, I. B.; Bregadze, V. I.; Kuznetsov, N. T. Derivatives of the *closo*-Dodecaborate Anion and Their Application in Medicine. *Russ. Chem. Bull.* **2002**, *51* (8), 1362−1374.

(28) Kaszynski, P. Four Decades of Organic Chemistry of *closo*-Boranes: A Synthetic Toolbox for Constructing Liquid Crystal Materials. A Review. *Collect. Czechoslov. Chem. Commun.* **1999**, *64* (6), 895−926.

(29) Poleschner, H.; Radeglia, R.; Kuprat, M.; Richter, A. M.; Fanghänel, E. Organylselenoacetylene und Selenocyanate; ^{77}Se- und ^{13}C-NMR-chemische Verschiebungen und ^{77}Se- ^{13}C-spin-kopplungskonstanten. *J. Organomet. Chem.* **1987**, *327* (1), 7−15.

(30) O'Connor, G. L.; Nace, H. R. Further Studies on the Chugaev Reaction and Related Reactions. *J. Am. Chem. Soc.* **1953**, *75* (9), 2118−2123.

(31) Erian, A. W.; Sherif, S. M. The Chemistry of Thiocyanic Esters. *Tetrahedron* **1999**, *55* (26), 7957−8024.

(32) Maurya, C. K.; Mazumder, A.; Gupta, P. K. Phosphorus Pentasulfide Mediated Conversion of Organic Thiocyanates to Thiols. *Beilstein J. Org. Chem.* **2017**, *13* (1), 1184−1188.

(33) Schmid, G.; Pugin, R.; Meyer-Zaika, W.; Simon, U. Clusters on Clusters: *closo*-Dodecaborate as a Ligand for Au_{55} Clusters. *Eur. J. Inorg. Chem.* **1999**, *1999* (11), 2051−2055.

(34) Rabideau, P. W.; Marcinow, Z. The Birch Reduction of Aromatic Compounds. In *Organic Reactions*; John Wiley & Sons, Ltd, 2004; pp 1−334. DOI: 10.1002/0471264180.or042.01.

(35) Mills, H. A.; Alsarhan, F.; Ong, T.-C.; Gembicky, M.; Rheingold, A. L.; Spokoyny, A. M. Icosahedral *m*-Carboranes Containing Exopolyhedral B−Se and B−Te Bonds. *Inorg. Chem.* **2021**, *60* (24), 19165−19174.

(36) Gabel, D.; Moller, D.; Harfst, S.; Roesler, J.; Ketz, H. Synthesis of S-Alkyl and S-Acyl Derivatives of Mercaptoundecahydrododecaborate, a Possible Boron Carrier for Neutron Capture Therapy. *Inorg. Chem.* **1993**, *32* (11), 2276−2278.

(37) Kozhushkov, S. I.; Alcarazo, M. Synthetic Applications of Sulfonium Salts. *Eur. J. Inorg. Chem.* **2020**, *2020* (26), 2486−2500.

(38) Kemp, D. S.; Vellaccio, F. Studies toward Practical Thioxanthene-Derived Protective Groups. 9,10-Propanothioxanthylium Salts. *J. Org. Chem.* **1981**, *46* (9), 1807−1810.

(39) Trost, B. M.; Bogdanowicz, M. J. Preparation of Cyclopropyldiphenylsulfonium and 2-Methylcyclopropyldiphenylsulfonium Fluoroborate and Their Ylides. Stereochemistry of Sulfur Ylides. *J. Am. Chem. Soc.* **1973**, *95* (16), 5298−5307.

(40) Magdesieva, N. N. Selenonium Compounds and Their Applications in Synthesis. *Russ. Chem. Rev.* **1988**, *57* (2), 161.

(41) Lenardão, E. J.; Mendes, S. R.; Ferreira, P. C.; Perin, G.; Silveira, C. C.; Jacob, R. G. Selenium- and Tellurium-Based Ionic Liquids and Their Use in the Synthesis of Octahydroacridines. *Tetrahedron Lett.* **2006**, *47* (42), 7439−7442.

(42) Thapa, B.; Schlegel, H. B. Theoretical Calculation of p*K*a's of Selenols in Aqueous Solution Using an Implicit Solvation Model and Explicit Water Molecules. *J. Phys. Chem. A* **2016**, *120* (44), 8916−8922.

(43) Zhu, D.; Zheng, W.; Chang, H.; Xie, H. A Theoretical Study on the p*K*a Values of Selenium Compounds in Aqueous Solution. *New J. Chem.* **2020**, *44* (20), 8325−8336.

(44) Spokoyny, A. M.; Lewis, C. D.; Teverovskiy, G.; Buchwald, S. L. Extremely Electron-Rich, Boron-Functionalized, Icosahedral Carborane-Based Phosphinoboranes. *Organometallics* **2012**, *31* (24), 8478−8481.

(45) Mills, H. A.; Jones, C. G.; Anderson, K. P.; Ready, A. D.; Djurovich, P. I.; Khan, S. I.; Hohman, J. N.; Nelson, H. M.; Spokoyny, A. M. Sterically Invariant Carborane-based Ligands for the Morphological and Electronic Control of Metal−organic Chalcogenolate Assemblies. *Chem. Mater.* **2022**, *34* (15), 6933−6943.

(46) Spokoyny, A. M. New Ligand Platforms Featuring Boron-Rich Clusters as Organomimetic Substituents. *Pure Appl. Chem.* **2013**, *85* (5), 903−919.

(47) Spokoyny, A. M.; Machan, C. W.; Clingerman, D. J.; Rosen, M. S.; Wiester, M. J.; Kennedy, R. D.; Stern, C. L.; Sarjeant, A. A.; Mirkin, C. A. A Coordination Chemistry Dichotomy for Icosahedral Carborane-Based Ligands. *Nat. Chem.* **2011**, *3* (8), 590−596.

(48) Schulz, J.; Clauss, R.; Kazimir, A.; Holzknecht, S.; Hey-Hawkins, E. On the Edge of the Known: Extremely Electron-Rich (Di)Carboranyl Phosphines. *Angew. Chem., Int. Ed.* **2023**, *62* (14), No. e202218648.

(49) Akram, M. O.; Tidwell, J. R.; Dutton, J. L.; Martin, C. D. Tris(*ortho*-Carboranyl)Borane: An Isolable, Halogen-Free, Lewis Superacid. *Angew. Chem., Int. Ed.* **2022**, *61* (46), No. e202212073.

(50) Lavallo, V.; Wright II, J. H.; Tham, F. S.; Quinlivan, S. Perhalogenated Carba-*closo*-Dodecaborate Anions as Ligand Substituents: Applications in Gold Catalysis. *Angew. Chem., Int. Ed.* **2013**, *52* (11), 3172−3176.

(51) Zhang, C.; Liu, X.; Wang, J.; Ye, Q. A Three-Dimensional Inorganic Analogue of 9,10-Diazido-9,10-Diboraanthracene: A Lewis Superacidic Azido Borane with Reactivity and Stability. *Angew. Chem., Int. Ed.* **2022**, *61* (36), No. e202205506.

(52) Barnett, J. J.; McKee, M. L.; Stanbury, D. M. Acidic Aqueous Decomposition of Thiocyanogen. *Inorg. Chem.* **2004**, *43* (16), 5021−5033.

(53) Martins, M. E.; Castellano, C. E.; Calandra, A. J.; Arvia, A. J. Electrochemical Behavior of the Selenocyanate/Triselenocyanate Redox Couple in Acetonitrile on Platinum Electrodes. *Anal. Chem.* **1978**, *50* (2), 229−231.

(54) *Boron Science: New Technologies and Applications*; Hosmane, N. S., Ed.; CRC Press: Boca Raton, 2012. DOI: 10.1201/b11199.

(55) Kerr, T.; Nelson, Y.; Bernier, N.; Spokoyny, A. An Electrochemical Strategy for Chalcogenation of *closo*-Dodecaborate $(B_{12}H_{12})^{2-}$ Anion. *ChemRxiv Preprint* **2025**, DOI: 10.26434/chemrxiv-2025-t38ql.