

# Icosahedral *Meta*-Carboranes Containing Exopolyhedral B-Se and B-Te Bonds

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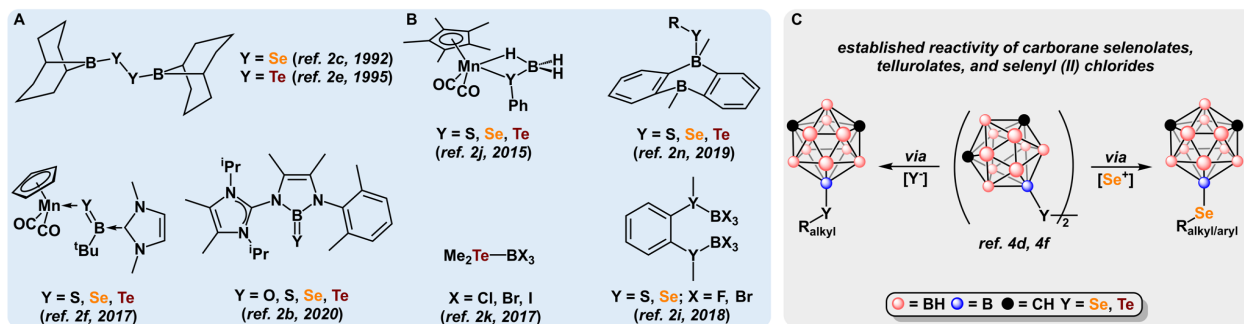
KEYWORDS: carborane, boron cluster, chalcogen, organoselenium, organotellurium

## ***Abstract***

Chalcogen-containing carboranes have been known for several decades and possess stable exopolyhedral B(9)-Se and B(9)-Te  $\sigma$  bonds despite the electron-donating ability of the B(9) vertex. While these molecules are known, little has been done to thoroughly evaluate their electrophilic and nucleophilic behavior. Herein, we report an assessment of the electrophilic reactivity of *meta*-carboranyl selenyl (II), tellurenyl (II), and tellurenyl (IV) chlorides and establish their reactivity pattern with Grignard reagents, alkenes, alkynes, enolates, and electron-rich arenes. These electrophilic reactions afford unique electron-rich B-Y-C (Y = Se, Te) bonding motifs not commonly found before. Furthermore, we show that *meta*-carboranyl selenolate, and even *meta*-carboranyl telluolate, can be competent nucleophiles and participate in nucleophilic aromatic substitution reactions. Arene substitution chemistry is shown to be further extended to electron-rich species via the palladium mediated cross-coupling chemistry.

## Introduction

Organoselenium and organotellurium compounds containing carbon-selenium and -tellurium bonds have been widely studied for the past decades and have recently found a variety of uses in nearly all aspects of chemical research, including: organic synthesis,<sup>1a-f</sup> organometallics,<sup>1g-i</sup> self-assembled and applied materials,<sup>1j-n</sup> photochemistry,<sup>1o-s</sup> and chemical biology.<sup>1t-w</sup> In contrast to organochalcogen compounds, the reactivity of boronochalcogens containing boron-selenium and -tellurium bonds are significantly less established. Of currently known molecules containing boron-selenium or -tellurium bonds, a large portion consist of tricoordinate mononuclear boron centers (Figure 1A).<sup>2a-i</sup>



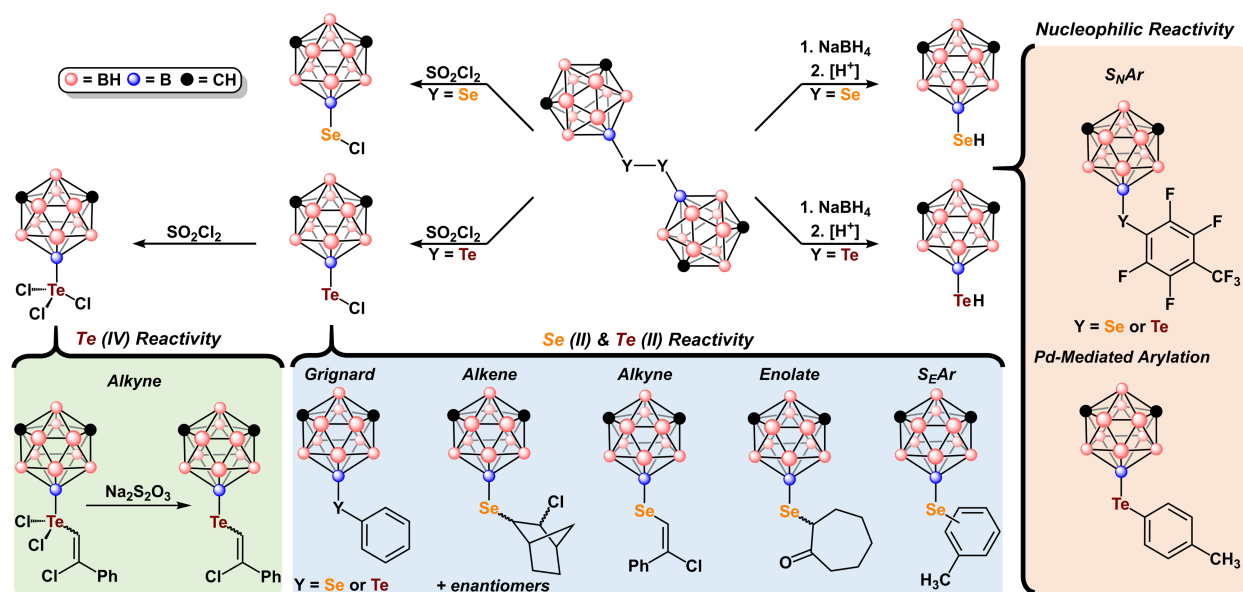
**Figure 1:** **A.** Literature examples of tricoordinate boron centers containing a boron-chalcogen single bond or double bond. **B.** Literature examples of tetracoordinate boron centers containing boron-chalcogen single bonds. **C.** Extent of previous studies regarding the reactivity of B-Se and B-Te containing carboranes. Nucleophilic reactivity has been shown between carboranyl chalcogenolates (Y = Se, Te) and electrophilic reactivity has been shown with carboranyl selenyl (II) chlorides.

Boron sites in these molecules contain a lowest unoccupied molecular orbital (LUMO) capable of accepting some electron density from the bound Se or Te atom, resulting in a shortening of the boron chalcogen bond. Additionally, several examples containing tetracoordinate boron centers<sup>2i-r</sup> exist as well (Figure 1B). In these cases, tricoordinate BR<sub>3</sub> (R: C, F, Cl, Br, I, H) are typically stabilized by coordination of chalcogen-based ligands where lone pair electrons on the chalcogen

are shared with the vacant boron-centered *p*-orbital. Lesser known molecular platforms that can support boron-selenium and -tellurium bonding interactions, are boron-rich clusters.<sup>3</sup> Among these, icosahedral carboranes (C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>) in particular have afforded a unique and stable scaffold for the study of compounds containing boron chalcogen bonds.<sup>4</sup> Similar in size to adamantane, this cluster type exists in three isomeric forms (*ortho*-, *meta*-, *para*-).<sup>5</sup> In all cases,  $\sigma$  electrons responsible for the cluster bonding are delocalized in three dimensions. Given the presence of the carbon vertices and the above delocalization, the resulting asymmetry in the *ortho*- and *meta*-isomers causes boron vertices most distal from the carbon sites to exhibit strong electron-donating character through induction, similar in magnitude to tertiary alkyl groups.<sup>6</sup> Furthermore, electron delocalization in the cluster results in an inaccessible LUMO, affording B-Y single bond character.

Carboranes functionalized with exopolyhedral chalcogens (Se, Te) at these electron-rich boron-vertices were first reported in the early 1980's,<sup>4d-f</sup> but surprisingly little has been established in terms of understanding the reactivity of these compounds. In previous reports, Zakharkin and coworkers have shown examples of nucleophilic reactivity between carborane-based selenolates or tellurolates with alkyl halides, as well as examples of electrophilic reactivity between carborane-based selenyl (II) reagents and Grignard reagents with no reported electrophilic reactivity of the tellurenyl (II) or tellurenyl (IV) congeners (Figure 1C).<sup>4d-f</sup> Notably, the reported compounds have only been characterized by melting point and elemental analysis with no rigorously reported NMR spectroscopy or structural studies. In this work, we report a reactivity map for B(9) functionalized *meta*-carborane, appended with selenium and tellurium-based functional groups (Figure 2). Specifically, we show that B(9)-bound *meta*-carboranyl selenyl (II), tellurenyl (II), and tellurenyl (IV) chlorides participate in electrophilic substitution reactions reminiscent to the established reactivity of analogous carbon-based electrophilic chalcogen reagents.<sup>1a</sup> Furthermore, we show the

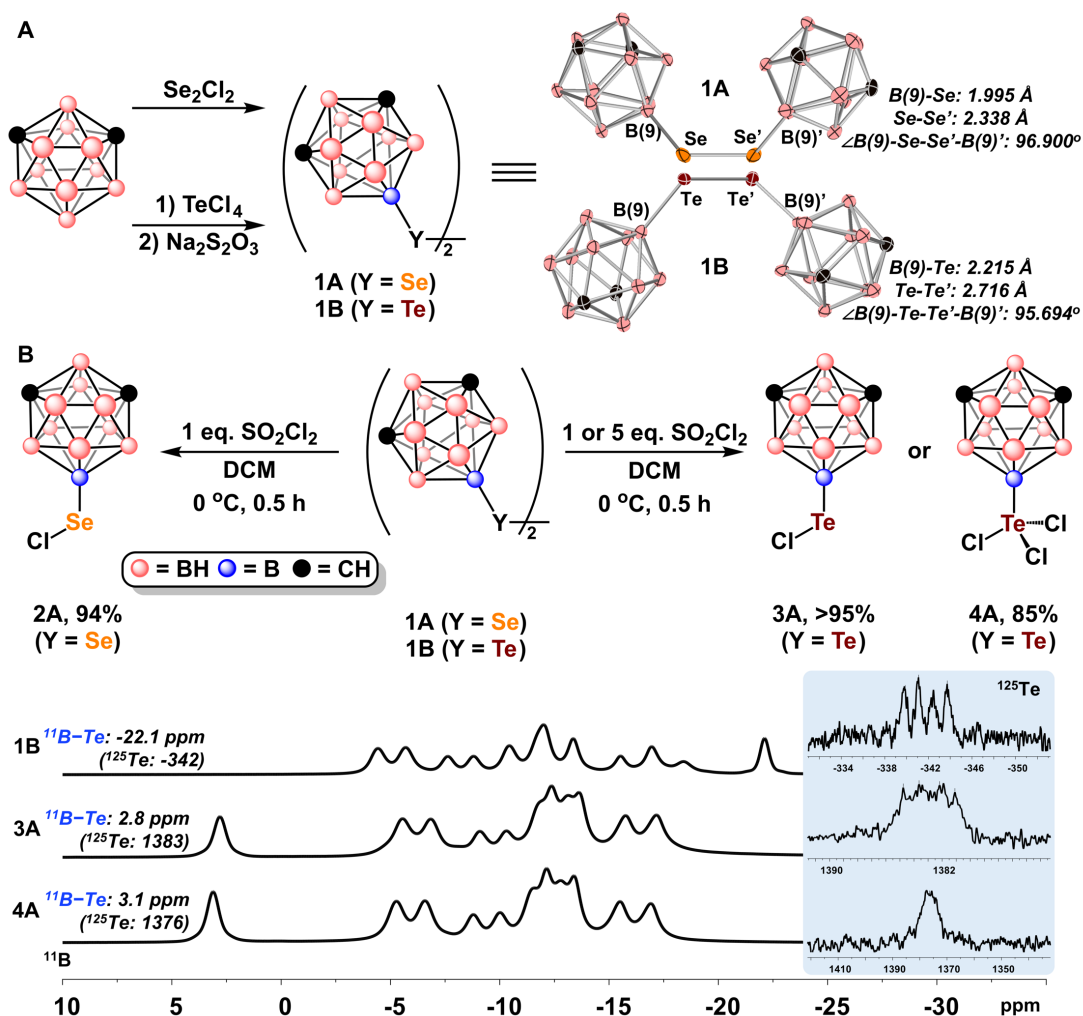
ability of B(9)-bound *meta*-carboranyl selenolates and tellurolates to participate in nucleophilic aromatic substitution reactions as well as the ability of the corresponding tellurol congener to undergo palladium mediated cross-coupling with an aromatic electrophile. For all compounds, we provide full heteronuclear NMR characterization ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{11}\text{B}$ ,  $^{19}\text{F}$ ,  $^{77}\text{Se}$ , and/or  $^{125}\text{Te}$ ) in addition to single-crystal X-ray structural characterization for key intermediates studied in this work (Figure 2). Our findings reveal that the electrophilic and nucleophilic reactivity of selenium- and tellurium-containing *meta*-carboranes is largely analogous to carbon-based reagents.



**Figure 2:** This work, overview of compounds synthesized by the electrophilic and nucleophilic reactions of selenium and tellurium-containing *meta*-carboranes.

## Results and Discussion

To ascertain the electrophilic reactivity of these compounds, we first sought to prepare the 9,9'-*meta*-carboranyl diselenide (**1A**) and ditelluride (**1B**) using modified procedures from previous reports (Figure 3A, SI sec. 3).<sup>4d-f,6b</sup>

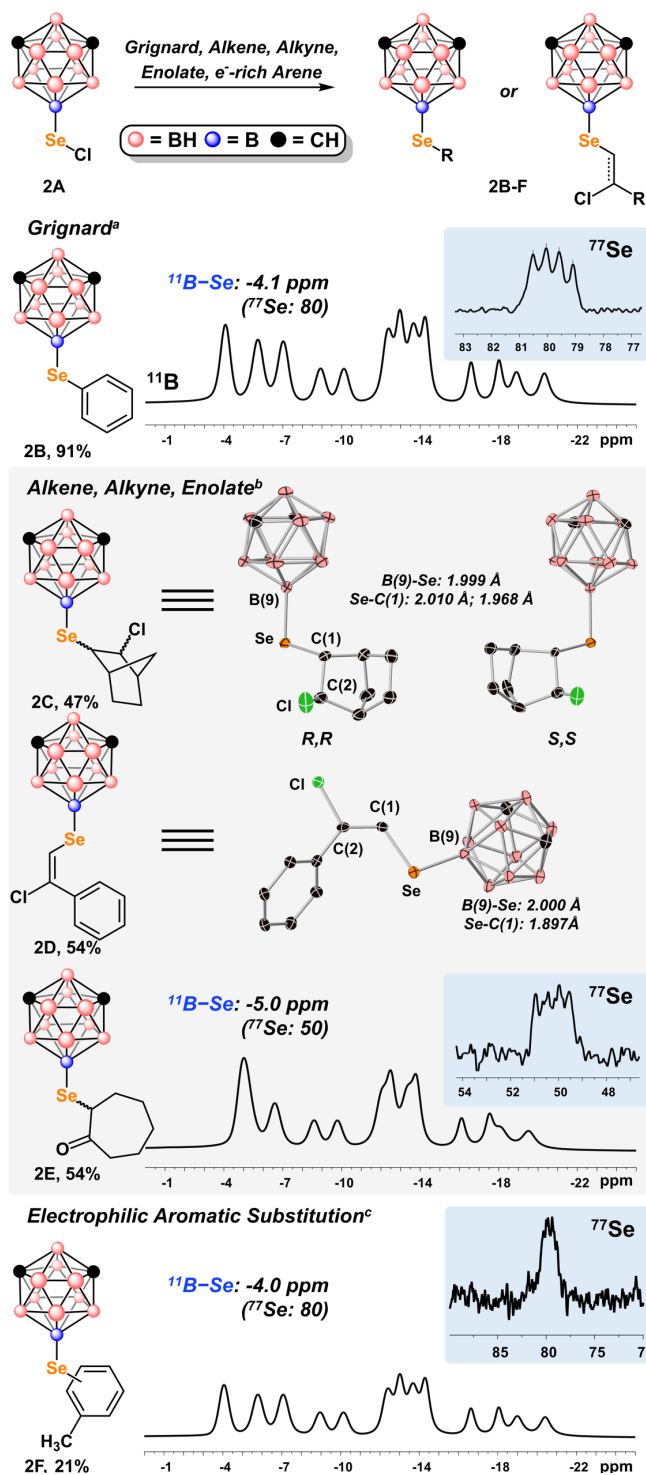


**Figure 3:** **A.** Synthesis of dichalcogenides **1A** and **1B** including their respective crystallographically derived structures. Thermal ellipsoids are drawn at 50% probability, hydrogens are omitted for clarity. **B.** Synthesis of electrophilic selenyl (II), tellurenyl (II), and tellurenyl (IV) reagents **2A**, **3A**, and **4A** from carboranyl dichalcogenides. Comparison of  $^{11}\text{B}$  and  $^{125}\text{Te}$  NMR for compounds **1B**, **3A**, and **4A**.

Analytically pure dichalcogenides **1A** and **1B** were isolated *via* silica gel column chromatography as air stable red-orange and dark red solids, respectively (see SI sec. 3). The isolated dichalcogenides were characterized by heteronuclear NMR spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{11}\text{B}$ ,  $^{77}\text{Se}$ , and/or  $^{125}\text{Te}$ ), revealing diagnostic resonances consistent with the proposed structural formulations.<sup>4d-f,6b</sup> Single crystals suitable for X-ray crystallography of both dichalcogenides were subsequently grown from layered solutions of dichloromethane and hexanes. The crystallographically derived

structures of **1A** and **1B** further corroborate the presence of exopolyhedral B-Y bonds (1.995 Å (Y=Se, **1A**) and 2.215 Å (Y=Te, **1B**) in length respectively) located at the B(9) position of *meta*-carborane (Figure 3A). The measured Y-Y dichalcogenide bond lengths and torsional angles, 2.338 Å/96.900° (Y=Se, **1A**) and 2.716 Å/95.694° (Y=Te, **1B**) are similar in length to other crystallographically characterized dichalcogenides in addition to torsional angles greater than 90° being consistent with more sterically hindered dichalcogenides.<sup>7</sup>

**1A** was then subjected to chlorination by treatment with SO<sub>2</sub>Cl<sub>2</sub> in anhydrous dichloromethane at 0 °C. After stirring the mixture for 30 minutes all volatiles were removed, and NMR spectroscopy revealed full consumption of **1A** as determined by diagnostic downfield shifts in both the <sup>11</sup>B and <sup>77</sup>Se resonances attributed to the exopolyhedral boron-selenium bond. The observed downfield shifts in signal resonances are consistent with an increase in the oxidation state of the bound selenium and confirms the formation of **2A** (Figure 3B, SI sec. 4). By applying similar chlorination procedures to **1B** with varying equivalencies of SO<sub>2</sub>Cl<sub>2</sub>, isolation of tellurenyl (II) chloride (**3A**) and tellurenyl (IV) trichloride (**4A**) was accomplished (Figure 3B, SI sec. 4). Like with **2A**, NMR spectroscopy (<sup>11</sup>B, <sup>125</sup>Te) of **3A** and **4A** revealed significant downfield shifts in the <sup>11</sup>B and <sup>125</sup>Te resonances attributed to the corresponding boron and tellurium nuclei within the exopolyhedral boron-tellurium bond (see Figure 3B for a comparison of <sup>11</sup>B and <sup>125</sup>Te NMR spectra for compounds **1B**, **3A**, and **4A**) and are consistent with an increase in oxidation state at tellurium. While the majority of carbon-based selenyl and tellurenyl chlorides are sensitive to moisture, resulting in seleninic or tellurenic acids,<sup>1a</sup> compounds **2A**, **3A**, and **4A** exhibit improved stability and do not show any signs of decomposition when exposed to an atmosphere of laboratory air on a time scale of several months.



**Figure 4:** Reactions of 2A with common carbon-based nucleophiles. <sup>a</sup>Reaction was performed in anhydrous diethyl ether under an inert atmosphere at r.t.. <sup>b</sup>Reaction was performed in anhydrous dichloromethane at r.t.. <sup>c</sup>Reaction was performed in anhydrous toluene with 2 eq. of AlCl<sub>3</sub> at 50 °C. See SI for full experimental details. Thermal ellipsoids are drawn at 50% probability, hydrogens are omitted for clarity.



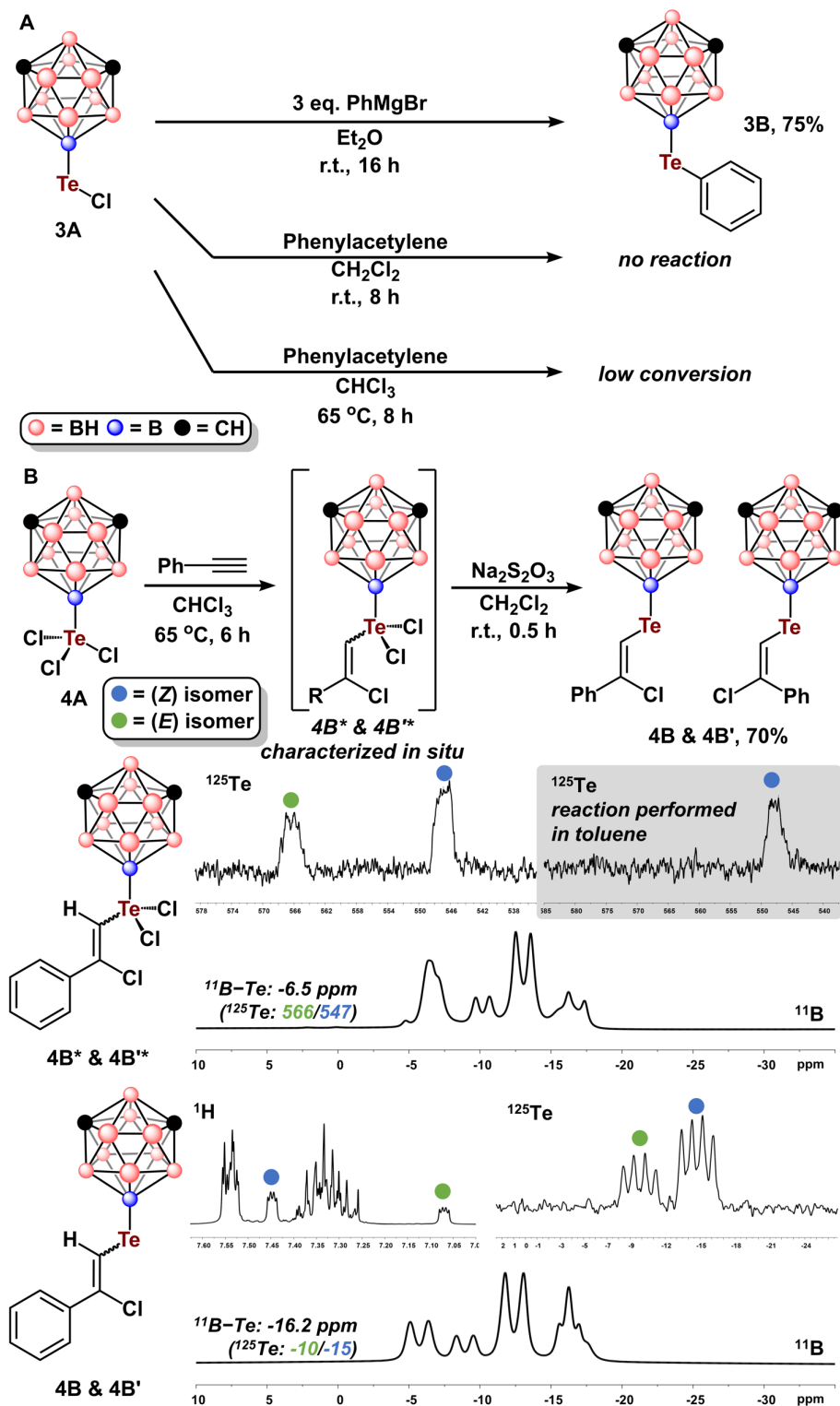
The anticipated electrophilicity of **2A** prompted us to explore its reactivity with several common nucleophiles. Thus, **2A** was treated with an excess of phenylmagnesium bromide in anhydrous diethyl ether at room temperature. After stirring for 16 hours, analysis of the reaction mixture by GC-MS indicated quantitative formation of phenyl selenide (**2B**). The resulting product was then isolated in 91% yield after purification *via* silica gel column chromatography and characterized by heteronuclear NMR spectroscopy (Figure 4, SI sec. 5a). Characterization of **2B** is in agreement with previously reported data of *meta*-carboranyl phenyl selenide obtained *via* an independent chemical route,<sup>8</sup> and confirms the electrophilic behavior of **2A**. Considering the successful outcome of the reaction between **2A** and a model Grignard reagent, we wanted to assess whether less reactive carbon-based nucleophiles would still undergo transformations with **2A**. Previously, researchers have established the reactivity of selenyl chlorides with unsaturated hydrocarbons and enolates.<sup>1a</sup> As such, norbornene, phenylacetylene, and cycloheptanone were chosen as model compounds potentially susceptible to electrophilic substitution by **2A**.

A solution of **2A** in anhydrous dichloromethane was treated with norbornene and the progress of the reaction was monitored by GC-MS. After stirring the mixture overnight, GC-MS indicated the presence of two isomers (**2C** and **2C'**, *m/z*: 352.10, SI sec. 5b,e) approximately in a 1:2 ratio consistent with the anticipated reaction between the electrophilic RSe-Cl fragment in **2A** and the C=C in norbornene, forming a distribution of *endo* and *exo* isomers. Separation of the two isomers *via* silica gel column chromatography proved difficult and thus the products were isolated as a mixture in 47% yield and characterized by heteronuclear NMR spectroscopy. While <sup>13</sup>C, <sup>11</sup>B, and <sup>77</sup>Se NMR spectroscopic data of the isomeric mixture provided little insight on the relationship between **2C** and **2C'**, they confirmed the formation of the anticipated selenium-carbon bond as indicated by the upfield shift in the resonances associated with the exopolyhedral boron-selenium

bond. 600 MHz and 400 MHz  $^1\text{H}$  NMR spectroscopy was used in an attempt to resolve proton resonances in the alkyl region that would correlate to protons bound to the selenium-bound and chlorine-bound carbons of the norbornene (SI sec. 5d). While there was still difficulty resolving  $^1\text{H}$  resonances for individual isomers, the presence of more than just two isomers was evident due to their being multiple unique resonances that integrated together as a single proton, in contrast to the isomer distribution observed by GC-MS. To further understand the substitutional isomers present in the purified product, single crystals suitable for X-ray crystallography were grown from a solution of the isomer mixture in dichloromethane layered with hexanes. The crystallographically derived structure indicated the co-crystallization of enantiomeric **2C'**, revealing the (*R,R*) and (*S,S*) *exo*- products (Figure 4), further confirming the formation of the desired selenium-carbon bond. The measured B(9)-Se and Se-C(1) bond lengths, 1.999 Å and 2.010(*R,R*)/1.968(*S,S*) Å respectively, are typical of other crystallographically measured boron-selenium and selenium-carbon bonds.<sup>9</sup> All characterization of **2C** and **2C'** suggests the formation of both possible diastereomeric products (*endo* and *exo*), resulting from the addition of **2A** across the double bond within norbornene in addition to their corresponding enantiomers (*R,R* and *S,S*), producing four isomers in total. When subjecting **2A** to similar reaction conditions in the presence of phenylacetylene or cycloheptanone, compounds **2D** and **2E** (SI sec. 5c), were both coincidentally isolated in 54% yield (Figure 4).  $^1\text{H}$  NMR spectroscopy of purified **2D** revealed the exclusive formation of a single isomer due to presence of only one olefinic  $^1\text{H}$  resonance. Single crystals of **2D** suitable for X-ray crystallography were then grown from a cold (0 °C) solution of dichloromethane layered with hexanes. The crystallographically derived structure revealed the formation of the *E*-1-SeR-2-Cl-2-Ph isomer (Figure 4), having resulted from Markovnikov, *anti*-addition of **2A** across the carbon-carbon triple bond in phenylacetylene. The formation of the

thermodynamically-favored Markovnikov products from the addition of RSeCl reagents across unsaturated hydrocarbons is expected for this type of process.<sup>1a</sup> In contrast to products **2C** and **2D**, **2E** does not incorporate the chloride of the electrophilic reagent, but still forms the expected selenium-carbon bond as indicated by <sup>11</sup>B and <sup>77</sup>Se NMR spectroscopy (Figure 4).

Beyond reactions of **2A** with alkenes, alkynes, and enolates, we also explored its ability to participate in electrophilic aromatic substitution (S<sub>E</sub>Ar) with toluene. **2A** was treated with an excess of anhydrous toluene and aluminum chloride to catalyze the transformation at 50 °C, with the reaction progress monitored by GC-MS. After stirring the mixture overnight, GC-MS indicated the formation of three isomers consistent (Figure 4) with S<sub>E</sub>Ar occurring between toluene and **2A**. The crude products were then purified *via* silica gel column chromatography, affording a mixture of aryl selenide isomers (**2F**) in 21% isolated yield. In addition to <sup>11</sup>B and <sup>77</sup>Se NMR spectroscopy revealing the formation of the desired aryl selenide, <sup>1</sup>H NMR spectroscopy also indicates the *para* tolyl isomer as the major component in the isomeric mixture (SI sec. 5c), consistent for S<sub>E</sub>Ar mechanisms with toluene. Resolving all three isomers by <sup>1</sup>H NMR spectroscopy proved to be quite difficult not only due to the low abundance of the *ortho*- and *meta*- isomers, but also the prevalence of <sup>1</sup>H resonances attributed to the carborane B-H vertices in the alkyl region. In order to deconvolute the <sup>1</sup>H NMR and obtain a more accurate ratio of isomer, the S<sub>E</sub>Ar between **2A** and toluene was repeated with perdeuterated toluene (SI sec. 5e). <sup>2</sup>H NMR spectroscopy of the isolated product clearly revealed the distribution (*para:ortho/meta*) of isomers to be 89:11, in agreement with the distribution determined by GC-MS.



**Figure 5:** A. Reaction of **3A** with phenylmagnesium bromide in anhydrous  $\text{Et}_2\text{O}$  and phenylacetylene in various solvents. B. Reaction of **4A** with phenylacetylene, including *in situ*  $^{11}\text{B}$  and  $^{125}\text{Te}$  NMR characterization of reaction intermediates, **4B\*** and **4B'**.

With the electrophilicity of **2A** established, we chose next to explore that of **3A**. First, the reaction of **3A** with phenylmagnesium bromide was assessed to confirm the electrophilic character of **3A**. After addition of the Grignard reagent to form the desired phenyl telluride (**3B**), the product was isolated *via* silica gel column chromatography in 75% yield (SI sec. 6a). Importantly, the NMR characterization of **3B** agrees with previously reported characterization by our group of *meta*-carboranyl phenyltelluride obtained *via* an independent chemical route (Figure 5A).<sup>8</sup> We then attempted the reaction of **3A** with phenylacetylene to determine its ability to react with unsaturated hydrocarbons. **3A** was suspended in anhydrous dichloromethane before the addition of phenylacetylene. After stirring the suspension at room temperature for 16 hours, <sup>11</sup>B NMR spectroscopy of the reaction mixture revealed only the presence of **3A** and **1B** as a decomposition product (Figure 5A, see SI sec. 6b). In an attempt to improve conversion to the desired telluride, the reaction was attempted in chloroform at reflux temperature. However, after stirring the reaction mixture for 8 hours, conversion to the desired telluride was lower than anticipated (see SI sec 6c) and contained significant quantities of starting material (**3A**) and **1B** as indicated by <sup>11</sup>B NMR spectroscopy. We attribute this general decrease in reactivity to a combination of both the inherently lower electronegativity of tellurium and the electron donating ability of *meta*-carborane at the B(9) position,<sup>6</sup> resulting in the diminished electrophilicity of **3A**. To test our hypothesis, we attempted the reaction between **4A** and phenylacetylene in refluxing chloroform. In contrast to the selectivity of organic selenyl (II) chlorides and **2A** to form products with unsaturated hydrocarbons resulting from Markovnikov *anti*-addition, the preferred substitution mechanisms of organic tellurenyl (IV) trichlorides are much more difficult to predict, possibly due to the formation of four-centered intermediates (Markovnikov, *syn* in nonpolar solvents), three-centered intermediates (Markovnikov, *anti*), or radical-based intermediates.<sup>1a,10</sup> Notably, the reactions of tellurenyl (IV)

trichlorides with phenylacetylene have typically afforded Markovnikov *syn*-addition products, consistent with the *in situ* formation of a four-centered intermediate, and selectivity for *syn* over *anti*-addition predicated on the polarity of solvent used for the reaction medium. To assess the reactivity of **4A**, it was first suspended in chloroform followed by the addition of phenylacetylene. After stirring the white suspension for 6 hours at reflux (65 °C), a clear, yellow solution remained (SI sec. 7a). *In situ* <sup>11</sup>B NMR spectroscopy of the reaction mixture revealed full consumption of **4A** and a diagnostic upfield shift in the resonance attributed to the exopolyhedral boron-tellurium bond (Figure 5B). This change in resonance chemical shift is consistent with the presence of the key dichlorotelluride intermediate (**4B\***), and suggests the formation of the desired tellurium-carbon bond. However, in contrast to the formation of the selenium-containing congener (**2D**), *in situ* <sup>125</sup>Te NMR spectroscopy revealed the presence of two tellurium-containing isomers with similar chemical shifts approximately in a 2:1 ratio, attributed to **4B\*** and **4B\*' Z/E** isomers. To further understand the reaction mechanism being employed by **4A** in the reaction with phenylacetylene, a series of control reactions were performed to rule out the possible intermediates previously shown to be accessible with tellurenyl (IV) trichlorides *vide supra* (see SI sec. 7b,c)<sup>1a,10</sup> and probed *via in situ* <sup>125</sup>Te NMR spectroscopy. When the reaction was performed in the presence of a radical inhibitor, no significant change in the distribution of **4B\*** and **4B\*' Z/E** was observed, likely ruling out the possibility of a radical-mediated substitution mechanism. However, when the reaction was performed in toluene, a relatively non-polar solvent, **4B\*** was formed exclusively with no measurable amount of **4B\*' Z/E** by <sup>125</sup>Te NMR. This selectivity, as influenced by solvent polarity, is reminiscent to the behavior of four-centered tellurenyl (IV) trichloride intermediates, resulting in selective Markovnikov *syn* addition (**4B\***) of **4A** to phenylacetylene when conducting the reaction in toluene and a mixture of four-centered and three-centered tellurenyl (IV) trichloride

intermediates forming *syn* (**4B\***) and *anti*-addition (**4B\*\***) products when in chloroform. The isomeric mixture of **4B\*** and **4B\*\*** was then reduced to the desired telluride (**4B** and **4B'**) by treatment with an aqueous solution of sodium thiosulfate and the progress of the reduction was monitored by TLC. Once the reduction was complete, **4B** and **4B'** were isolated from the crude reaction mixture *via* silica gel column chromatography as a mixture of Z/E isomers in 70% yield and characterized by heteronuclear NMR spectroscopy to confirm the formation of the desired tellurium-carbon bond. <sup>1</sup>H and <sup>125</sup>Te NMR spectroscopy revealed the isolation of two distinct isomers, **4B** and **4B'** in approximately a 2:1 ratio (Figure 5B, SI sec. 7a). Two broad quartet resonances in the <sup>1</sup>H aromatic region (7.45 and 7.07 ppm) are attributed to the olefinic <sup>1</sup>H's and are used to determine the isomer distribution. Furthermore, <sup>125</sup>Te NMR spectroscopy revealed two <sup>125</sup>Te resonances at -10 and -15 ppm, with approximate relative intensities of 1:2, respectively, and agrees with the distribution observed by <sup>1</sup>H NMR (Figure 5B, see SI sec. 7a). This additional isomer is likely attributed to the formation of *E*-1-TeR-2-Ph-2-Cl (R: *meta*-carboranyl) as the minor product that was enabled by the increased polarity of the reaction solvent. This minor product is produced from a portion of **4A** reacting with phenylacetylene through a three-centered intermediate, similar to the substitution mechanism employed by **2A**.

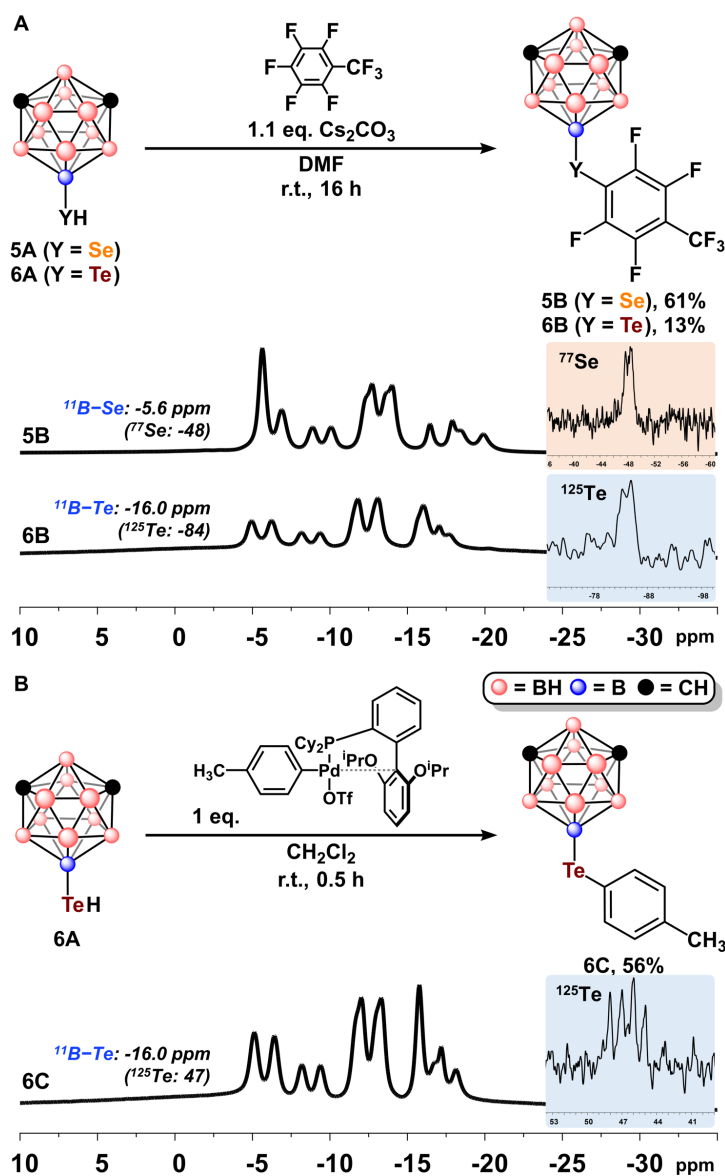
In summary, the assessment of electrophilic behavior for *meta*-carboranyl selenyl (II), tellurenyl (II), and tellurenyl (IV) chlorides reveal that their reactivity is reminiscent to carbon-based reagents. **2A** reacts with Grignard reagents, alkenes, alkynes, enolates, and electron-rich aromatics to form products that would generally be expected for organic selenyl chlorides. Despite, the electron-donating ability of the B(9) position to which the selenyl (II) chloride in **2A** is appended to, no deleterious effects to the overall electrophilic reactivity of **2A** are observed. In contrast, the electrophilic reactivity of the tellurenyl (II) chloride **3A** is significantly dampened,

only showing good reactivity with Grignard reagents. To enhance the electrophilic reactivity, the tellurenyl (IV) chloride **4A** was studied. An increase in oxidation state at tellurium significantly enhanced the electrophilic reactivity and reacts more readily with terminal alkynes. The regioselectivity and stereoselectivity behavior of **4A** when reacting with terminal alkynes in various solvents closely parallels the behavior of organic tellurenyl (IV) chlorides, forming either the *syn* or *anti*-addition products as a function of solvent polarity.

With the electrophilicity of **2A**, **3A**, and **4A** established, we proceeded to expand the nucleophilic substitution chemistry available with selenium and tellurium-containing *meta*-carboranes. The ability of *meta*-carborane-based selenolates and tellurolates to participate in S<sub>N</sub>2 substitution mechanisms with alkyl halides is well established.<sup>4d,f</sup> However, their ability to participate in S<sub>N</sub>Ar substitution mechanisms is not known. To further understand the nucleophilic behavior of boron-bound selenium and tellurium-containing carboranes, we prepared the 9-*meta*-carboranyl selenol (**5A**) and tellurol (**6A**). We envisioned that these compounds, upon deprotonation, would act as precursors to the corresponding nucleophilic chalcogenolates. Selenol (**5A**), was synthesized according to previously reported methods and its spectroscopic characterization is in agreement to the proposed formulation (SI sec. 8a).<sup>4d,6b</sup> While the boron-bound tellurol (**6A**) has not been reported previously, we were able to successfully synthesize **6A** using modified reduction procedures (SI sec. 9a). **6A** is isolated in 67% yield as a colorless, odorless, air sensitive solid that nevertheless can be handled in air for short periods of time (~10 minutes) without significant decomposition. In contrast to all other known carborane chalcogenols, **6A** is light sensitive and reverts to the ditelluride (**1B**) when exposed to ambient light, even when stored in a nitrogen-filled glovebox. The <sup>1</sup>H and <sup>125</sup>Te resonances measured by NMR spectroscopy, -7.15 ppm and -596.5 ppm respectively, are indicative of the exceedingly electron-rich



environment experienced by the tellurol from the B(9) *meta*-carboranyl substituent and are consistent with other reported sterically hindered electron-rich tellurols.<sup>11</sup> This is the first reported synthesis of an isolable carboranyl tellurol, and is a rare example of an isolable tellurol.



**Figure 6:** A.  $S_NAr$  of **5A** and **6A** with perfluorotoluene.  $^{77}Se$  and  $^{125}Te$  NMR of **5B** and **6B**. B. Reaction of **6A** with palladium oxidative addition complex.

$S_NAr$  with the *meta*-carboranyl chalcogenolates was first attempted with **5A** by deprotonating the selenol with  $Cs_2CO_3$  in dimethylformamide (SI sec. 8b). Perfluorotoluene was

then introduced to the mixture as the electrophilic substrate to initiate  $S_NAr$  with the *in situ* generated selenolate. After stirring the mixture overnight, GC-MS indicated full conversion to a single isomer with an  $m/z$  (223.20) consistent with the formation of the desired aryl selenide (**5B**). The compound was subsequently purified from the crude reaction mixture *via* silica gel column chromatography in 61% isolated yield and characterized by NMR spectroscopy.  $^{19}F$  NMR revealed a diagnostic resonance pattern consistent with mono-substituted perfluorotoluene in the *para*-position and is in agreement with the proposed structure formulation. Furthermore,  $^{77}Se$  NMR showed a downfield shift in the resonance attributed to the exopolyhedral boron-selenium bond found in **5B**, and is consistent with the formation of an aryl selenide (Figure 6A).  $S_NAr$  was then attempted with the tellurol (**6A**) using similar conditions, though taking additional precautions to limit exposure to light and oxygen (SI sec. 9b). Following similar isolation procedures to **5B**, the desired aryl telluride (**6B**) was isolated in small yield (13%), sufficient for full characterization by NMR spectroscopy. Due to the general instability of the *in situ* generated tellurolate under the reaction conditions, ditelluride (**1B**) was a major byproduct formed during the reaction between **6A** and perfluorotoluene (SI sec. 9d).

To study the reactivity of **6A** further with more electron-rich aryl-based electrophiles, we attempted arylation with a stoichiometric palladium-based oxidative addition complex. These oxidative addition complexes are typically used stoichiometrically for the arylation of sensitive substrates due to their high degree of selectivity for chalcogenols and ease of preparation.<sup>12</sup> A solution of **6A** in dichloromethane was prepared in a dark, nitrogen filled glovebox without the addition of base to avoid incompatibilities of the tellurolate with the oxidative addition complex (SI sec. 9c). Subsequently, [4-tolyl-PdRuPhos][OTf] (Figure 6B) was added and the reaction progress was monitored by GC-MS. After 30 minutes, GC-MS indicated the formation of a

compound with an  $m/z$  of 363.20, suggesting the formation of the desired tolyl telluride (**6C**). **6C** was isolated from the crude reaction mixture *via* silica gel column chromatography in 56% yield and characterized by NMR spectroscopy.  $^{125}\text{Te}$  NMR revealed a resonance with a chemical shift of 46.5 ppm, similar to that of **3A** (Figure 5, 6B). Overall, these studies indicate that B(9) *meta*-carboranyl selenolate and tellurolate can be competent nucleophiles and are able to participate in  $\text{S}_{\text{N}}\text{Ar}$  and Pd-mediated arylation processes, leading to the formation of selenoether and telluroether moieties with B-Y-C connectivity.

## Conclusions

In conclusion, B(9)-connected *meta*-carboranyl selenyl and tellurenyl reagents have been shown to participate in electrophilic substitution reactions with unsaturated hydrocarbons, including alkenes, alkynes, enolates, and aromatic substrates; reminiscent to other electrophilic organochalcogen compounds. We further show the first examples of nucleophilic aromatic substitution with carborane selenolates and tellurolates as well as the first use of palladium-based oxidative addition complexes for the arylation of a free tellurol. All formed products contained the unique B-Se-C or B-Te-C bonding motifs and are stable in air despite the exceedingly electron-rich environment experienced by either the selenium or tellurium nucleus as suggested by the  $^{77}\text{Se}$  and  $^{125}\text{Te}$  NMR spectroscopic experiments. The reactivity map developed in this work serves as an expansion of available modification reactions for carboranes and other polyhedral boron clusters containing C- or B-connected exopolyhedral heteroatom substituents,<sup>13</sup> as well as benchmarks similarities and differences in terms of reactivity and stability with the fundamental chemistry of electron-rich chalcogen-containing molecules.<sup>1a,10,11,14</sup>

## ***ASSOCIATED CONTENT***

Crystallographic data are available from the Cambridge Crystallographic Data Centre, under reference numbers CCDC 2105009 (***1A***), 2105007 (***1B***), 2105010 (***2C***), and 2105008 (***2D***).

The following files are available free of charge.

Full synthetic procedures, spectroscopic data (PDF).

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### ***Notes***

The authors declare no competing financial interests

## ACKNOWLEDGMENTS

A. M. S. thanks NIGMS (R35GM124746) for supporting this work. H. A. M. is a recipient of the UCLA Dissertation Year Fellowship. F. A. is a recipient of Arthur Furst Summer Undergraduate Research Fellowship and Raymond and Dorothy Wilson Fellowship. A. M. S. is a Research Corporation for Science Advancement (RCSA) Cottrell Scholar and a Dreyfus Foundation Camille Dreyfus Teacher Scholar.

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**Graphical Abstract (TOC):**

