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Intramolecular 1,1-carboboration *versus* intermolecular FLP addition in reactions of boranes and bis(phenylethynyl)telluroether†

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Reactions of boranes with Te(CCPh)$_2$ proceed *via* initial intermolecular 1,1-carboboration followed by either an intramolecular carboboration or an FLP addition to a second molecule of the intermediate, yielding 1-bora-4-tellurocyclohexa-2,5-diene heterocycles or tricylic derivatives of 1,4-ditellurocyclohexa-2,5-diene, respectively. The latter species is also shown to convert to the former upon heating.

The incorporation of tellurium into heterocycles and polymeric materials has garnered recent attention for applications in new optoelectronic materials.[1] However, the laborious and low-yielding (<40%) nature of the syntheses of Te-containing heterocycles have been noted by many authors in the literature.[2,3] Indeed, the development of new tellurium-containing heterocycles has been hampered by the lack of synthetic methodologies.

Recognizing that unsaturated heterocycles that incorporated donor and acceptors sites would be of interest, we considered new synthetic avenues to Te–B heterocycles. The research groups of Wrackmeyer,[4] Berke,[5] and Erker[6] have exploited the reactions of alkynes with electrophilic boranes to effect 1,1-carboborations.[6,7] The reactivity affords vinyl-boranes but can be extended to prepare a variety of boryl-substituted cyclopentandienes, including phospholes,[8] boroles,[9] and plumboles.[10] More recently this reactivity has also been employed to generate sulfur-substituted vinyl species,[11] while we have shown that 1,1-carboration of tellurium-monoacetylides afford boron-substituted vinyl telluroethers.[12] In this communication, we explore related 1,1-carboration reactions of boranes with Te(CCPh)$_2$. These reactions are shown to proceed *via* double carboboration and Te/B frustrated Lewis pair (FLP) additions reactions, affording 1-bora-4-tellurocyclohexa-2,5-diene and tricylic Te/B heterocycles, respectively.

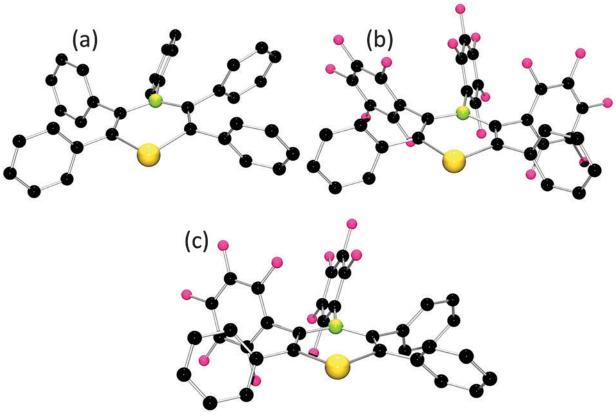

Fig. 1 POV-ray depiction of (a) **2**, (b) **4** and (c) **6**. C: black, Te: gold, B: yellow-green, F: pink. Hydrogen atoms have been omitted for clarity.

The bis(phenylethynyl)telluroether Te(CCPh)$_2$ **1**, was prepared by a modified literature procedure.[13] The addition of a slurry of **1** in pentane to BPh$_3$ at room temperature was stirred for 16 hours affording the product **2** which was isolated in 93% yield. The ^{11}B NMR spectrum of **2** showed a single peak at 53.3 ppm. Single crystals of **2** suitable for X-ray analysis grown from a saturated pentane solution confirmed the structure of **2** to be a planar six-membered 1-bora-4-tellurocyclohexa-2,5-diene heterocycle (Fig. 1(a)). Phenyl-substituents are found on each of the linking olefinic carbons and on the B atom. The Te–C and B–C distances are 2.075(2) Å, 2.087(2) Å and 1.559(3) Å, 1.552(3) Å and 1.576(3) Å, respectively while the intra-ring C–Te–C and C–B–C angles were found to be 97.08(9)° and 124.3(2)°, respectively. The formation of **2** is thought to result from an initial *inter*molecular 1,1-carboboration of **1**, followed by an *intra*molecular 1,1-carboboration of the remaining acetylenic group on Te affording the six-membered ring (Scheme 1). Even though 1,1-carboboration has been documented extensively, the species (CH$_2$)$_5$Sn(HC=C(Ph))$_2$BPh.[4] is the only other reported analogous 6-membered heterocycle that has been crystallographically characterized.[4,14]

The corresponding addition of a slurry of **1** in pentane to B(C$_6$F$_5$)$_3$ at −35 °C resulted in the immediate color change from

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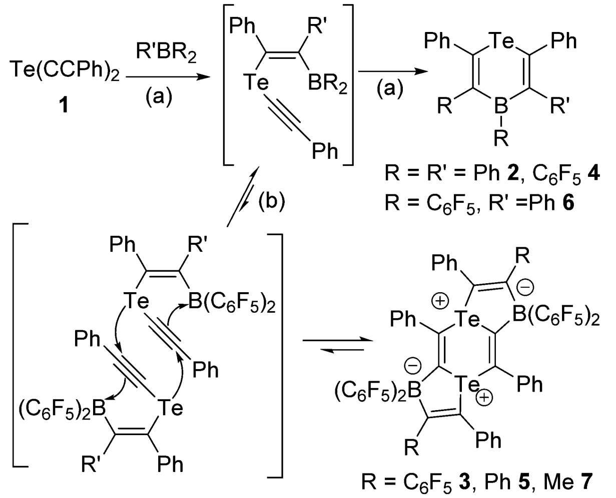

Scheme 1 Proposed reaction pathways to **2–7** *via* (a) 1,1 carboboration, (b) FLP addition.

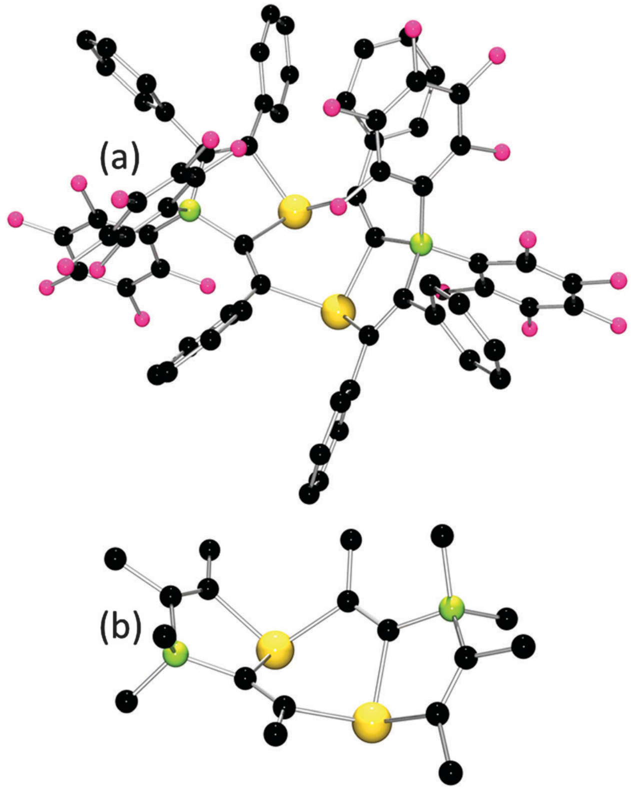

Fig. 2 POV-ray depiction of (a) **5**, (b) core of **5**; C: black, Te: gold, B: yellow-green, F: pink, Hydrogen atoms have been omitted for clarity.

yellow to dark red. The ^{19}F NMR spectrum showed complete consumption of the starting material and the formation of a minor product **3** which exhibited a sharp ^{11}B peak at −4.1 ppm. A major product **4** was also seen to exhibit two sets ^{19}F signals resulting from C_6F_5 rings in a 2 : 1 intensity ratio (−139.7 −161.9 −163.2, and −132.9, −153.4 −155.9 ppm, respectively) and a broad ^{11}B peak at 49.5 ppm. Heating this mixture to 80 °C for 8 h resulted in the complete disappearance of **3** suggesting that this species was converted to the thermodynamic product **4**. On work-up, the product **4** was isolated in 57% yield. An X-ray diffraction study revealed that **4** is directly analogous to **2** with C_6F_5 rings replacing the Ph substituents of **2** (Fig. 2(b)).

The corresponding reaction of $PhB(C_6F_5)_2$ and **1** gave about a 1 : 1 mixture of two species, **5** and **6** as evidenced by ^{11}B and ^{19}F NMR spectra. Again heating the solution to 80 °C for 8 h resulted in the conversion of **5** to **6**. The species **6** was confirmed to be the 6-membered ring analogous to **2** and **4** (Fig. 1(c)). The solid-state structures of **2**, **4** and **6** are directly analogous, featuring a central 6-membered 1-bora-4-tellurocyclohexa-2,5-diene ring with various aryl substituents. The B–C and C═C bond lengths in the central ring of **6** are 1.559(3) Å and 1.552(3) Å and 1.360(3) Å and 1.363(3) Å, respectively, suggesting some delocalization over the C–C–B–C–C fragment. The Te–C bond distances in **2**, **4** and **6** fall in the range of 2.063(3)–2.087(2) Å which is significantly shorter than those seen in $Ph(CH_2)_2TeC(Ph)C(C_6F_5)B(C_6F_5)_2(OCHPh)$ (2.126(2), Te–C(15): 2.151(3) Å)[12] indicative of some degree of delocalization within the 6-membered heterocycle. However, the ^{13}C shifts of the *ipso*-Ph(Te)C═C phenyl rings in **2**, **4**, and **6** are −143.9, −141.4 and −141.4/143.5 ppm, respectively. These values deviate significantly from those expected for aryl substituents on aromatic fragments (−136.6 to 138.1 ppm).[15] Thus, the cyclic compounds **2**, **4** and **6** cannot be considered fully aromatic.

The nature of the minor products **3** and **5** were probed. Interestingly, adjusting the polarity of the solvent of the initial reaction of **1** with $B(C_6F_5)_3$ to a 1 : 4 mixture of CH_2Cl_2 : pentane resulted in the precipitation of a yellow powder in 47% yield. This species was confirmed to be exclusively **3** as evidenced by the $^{11}B\{^1H\}$ resonance (−4.1). $^{19}F\{^1H\}$ NMR data for **3** showed 15 discrete signals suggestive of both inequivalence and hindered rotation of the C_6F_5 rings. In a similar fashion, species **5** exhibits eight distinct ^{19}F resonances in addition to a ^{11}B resonance at −3.5 ppm consistent with a 4-coordinate boron centre. While **3** could not be unambiguously formulated, an X-ray crystallographic study of **5** revealed it to be a species consisting of three fused 5–6–5 rings featuring a central 1,4-ditellurocyclohexa-2,5-diene heterocycle. The tellurium centers of compound **5** both adopt distorted trigonal pyramidal geometry and are separated by 3.2896(7) Å which is within the range previously reported Te–Te interactions in Te(IV)-based heterocycles (3.15–3.28 Å).[16] Fused to the Te–C bonds of the central rings are adjacent 5-membered $TeCBC_2$ rings which incorporated the 4 coordinate B centers (Fig. 2). It is also noteworthy that the corresponding reaction of $MeB(C_6F_5)_2$ with **1** affords exclusively the product **7** which exhibits similar spectral parameters to **3** and **5**, consistent with the analogous formulation of **7** as $[(C_6F_5)_2BC(Me){=}C(Ph)TeC(CPh)]_2$.

The formation of the above compounds from **1** are consistent with two reaction pathways involving an initial 1,1-carboboration of one of the alkynyl fragments on Te. A second intramolecular carboboration accounts for the formation of 1-bora-4-tellurocyclohexa-2,5-diene heterocycles **2**, **4** and **6** (Scheme 1). Alternatively, the intermediate Te–B species can undergo an FLP-addition[17] in which the Te of one molecule and B of another add across alkynyl fragments affording the tricyclic species with the central 1,4-ditellurocyclohexa-2,5-diene ring as in **5** (Scheme 1). It is important to note that the thermal conversion (80 °C) of **3** to **4** and

5 to **6** illustrate that the FLP addition to alkyne is reversible presumably a result of destabilizing steric congestion prompting formation of the thermodynamically stable **4** and **6**. It is also noteworthy that the FLP addition products were only observed for the systems where the transient B/Te species contains electrophilic $B(C_6F_5)_2$ fragments, suggesting that only the more Lewis acidic systems can effect FLP additions. In the case of **7**, apparently the reduced steric congestion in the FLP addition product and the increased basicity of the Te center garners stability. Effects to convert **7** to the analogous 1-bora-4-tellurocyclohexa-2,5-diene heterocycle were unsuccessful, leading only to thermal degradation and a mixture of unidentified products. Nonetheless, to the best of our knowledge, the reactions described herein are the first examples in which that *intra*molecular 1,1-carboboration are observed to be in competition with *inter*molecular FLP addition.

In summary, we have demonstrated that the reaction between bis(phenylethynyl)telluroether and a series of boranes leads to two products. Following initial intermolecular 1,1-carboboration, the intermediate can either undergo intramolecular 1,1-carboboration or intermolecular FLP addition. Compounds **2**, **4** and **6** are of particular interest as they present new tellurium-containing heterocycles with an electrophilic element embedded within the heterocycle. These facile and high-yielding syntheses are especially attractive for future applications in optoelectronic materials. Such investigations are currently underway in our laboratory.

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