

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

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

Fu An Tsao,^a Alan. J. Lough^a and Douglas W. Stephan^{*a,b}

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

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

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 Erker⁶ 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 cyclopentadienes, including phospholes,⁸ boroles⁹ and plumboles.¹⁰ More recently this reactivity has also been employed to generate sulfur-substituted vinyl species,¹¹ while we have recently shown that 1,1-carboration of tellurium-monoacetylides afford boron-substituted vinyltelluroethers.¹² In this communication, we explore related 1,1-carboration reactions of boranes with $\text{Te}(\text{CCPh})_2$. These reactions are shown to proceed via doublecarboration and Te/B frustrated Lewis pair (FLP) additions reactions, affording 1-bora-4-tellurocyclohexa-2,5-diene and tricyclic Te/B heterocycles, respectively.

The *bis*(phenylethynyl)telluroether $\text{Te}(\text{CCPh})_2$ **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 ¹¹B 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 (Figure 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, 1.551(3) Å and 1.577(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 *intermolecular* 1,1-carboboration of **1**, followed by an *intramolecular* 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 $(\text{CH}_2)_5\text{Sn}(\text{HC}=\text{C}(\text{Ph}))_2\text{BPh}$ ⁴ is the only other reported analogous 6-membered heterocycle that has been crystallographically characterized.^{4,14}

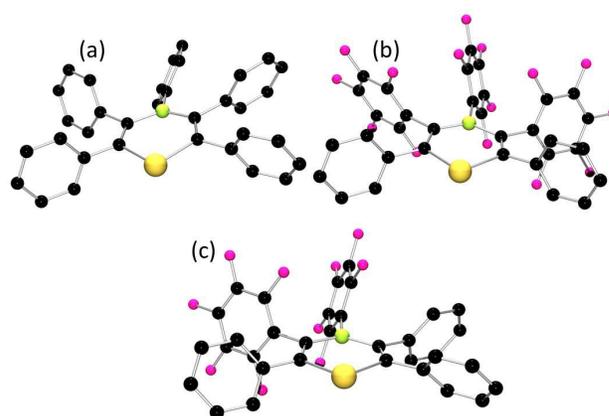


Figure 1. POV-ray depiction of (a) **2**, (b) **4** and (c) **6**. C: black, Te: gold, B: yellow-green, F: pink. Hydrogen atoms have been omitted for clarity.

The corresponding addition of a slurry of **1** in pentane to $\text{B}(\text{C}_6\text{F}_5)_3$ at -35 °C resulted in the immediate color change from yellow to dark red. The ¹⁹F NMR spectrum showed complete consumption of the starting material and the formation of a minor product **3** which exhibited a sharp ¹¹B peak at -4.2 ppm. A major product **4** was also seen to exhibit two sets ¹⁹F 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 ¹¹B 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** (Figure 2(b)).

The corresponding reaction of $\text{PhB}(\text{C}_6\text{F}_5)_2$ and **1** gave about a 1:1 mixture of two species, **5** and **6** as evidenced by ¹¹B and ¹⁹F

NMR spectra. Again heating the solution to 80 °C for 8 h resulted in the formation of **6**. The species **6** was confirmed to be the 6-membered ring analogous to **2** and **4** (Figure 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(CH₂)₂TeC(Ph)C(C₆F₅)B(C₆F₅)₂(OCHPh) (2.126(2), Te-C(15): 2.151(3) Å)¹² indicative some degree of delocalization. However, the ¹³C 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 that expected for aryl substituents on aromatic fragments (□ 136.6 - 138.1 ppm).¹⁵ Thus, the cyclic compounds **2**, **4** and **6** cannot be considered aromatic.

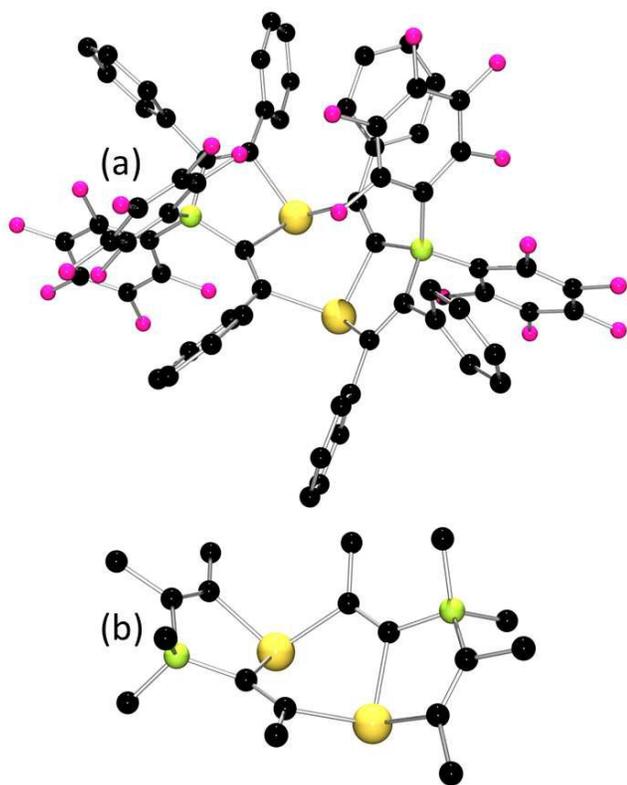
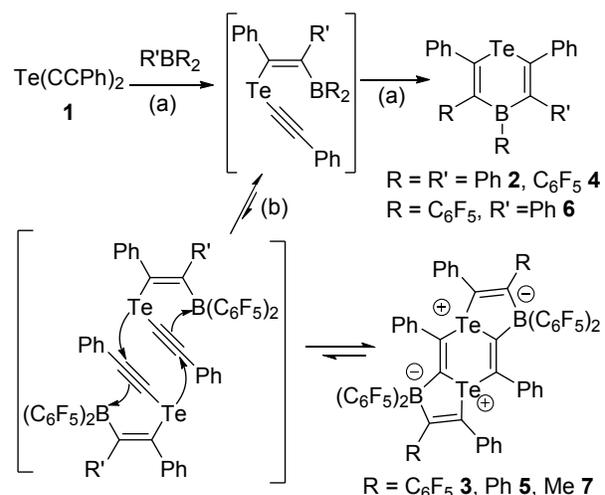


Figure 2. POV-ray depiction of (a) **5**, (b) core of **5**; C: black, Te: gold, B: yellow-green, F: pink, Hydrogen atoms have been omitted for clarity.

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(C₆F₅)₃ to a 1:4 mixture of CH₂Cl₂: pentane resulted in the precipitation of a yellow powder in 47% yield. This species was confirmed to be exclusively **3** as evidenced by the ¹¹B{¹H} resonance (-4.1). ¹⁹F{¹H} NMR data for **3** showed 15 discrete signals suggestive of both inequivalence and hindered rotation of the C₆F₅ rings. In a similar fashion, species **5** exhibits eight distinct ¹⁹F resonances in addition to a ¹¹B 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 for 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 rings which incorporated the 4 coordinate B centers (Figure 2). It is also noteworthy that the corresponding reaction of MeB(C₆F₅)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 [(C₆F₅)₂BC(Me)=C(Ph)TeC(CPh)]₂



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

The formation of the above compounds from **1** are consistent with two reaction pathways involving an initial 1,1-carboration 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-addition¹⁷ 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(C₆F₅)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 *intramolecular* 1,1-carbaboration are observed to be in competition with *intermolecular* FLP addition.

Conclusions

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-carbaboration, the intermediate can either undergo intramolecular 1,1-carbaboration 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 ring. These facile and high-yielding syntheses are especially attractive for future applications in optoelectronic materials. Such investigations are currently underway in our laboratory.

Notes and references

NSERC of Canada is thanked for financial support. DWS is grateful for the award of a Canada Research Chair. FAT is grateful for an NSERC CGS-D.

^a Department of Chemistry, 80 St. George Street, University of Toronto, Toronto, Ontario, Canada, M5S 3H6.

E-mail: dstephan@chem.utoronto.ca

^b Chemistry Department, Faculty of Science, King Abdulaziz University (KAU), Jeddah 21589, Saudi Arabia.

† Electronic Supplementary Information (ESI) available: Synthetic and spectroscopic details are deposited Crystallographic data have been deposited in the Cambridge database. see DOI: 10.1039/b000000x/. CCDC 1033757-1033760 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

- (a) A. A. Jahnke and D. S. Seferos, *Macromol. Rapid Commun.*, 2011, **32**, 943-951; (b) T. Baumgartner, *Acc. Chem. Res.*, 2014, **47**, 1613.
- (a) G. He, W. T. Delgado, D. J. Schatz, C. Merten, A. Mohammadpour, L. Mayr, M. J. Ferguson, R. McDonald, A. Brown, K. Shankar and E. Rivard, *Angew. Chem. Int. Ed.*, 2014, **53**, 4587-4591; (b) G. He, L. Kang, W. T. Delgado, O. Shynkaruk, M. J. Ferguson, R. McDonald and E. Rivard, *J. Am. Chem. Soc.*, 2013, **135**, 5360-5363.
- (a) E. I. Carrera, T. M. McCormick, M. J. Kapp, A. J. Lough and D. S. Seferos, *Inorg. Chem.*, 2013, **52**, 13779-13790; (b) E. I. Carrera and D. S. Seferos, *Dalton Trans.*, 2014; (c) T. M. McCormick, E. I. Carrera, T. B. Schon and D. S. Seferos, *Chem. Commun.*, 2013, **49**, 11182-11184.
- B. Wrackmeyer, P. Thoma, S. Marx, G. Glatz and R. Kempe, *Z. Anorg. Allg. Chem.*, 2013, **639**, 1205-1213.
- C. F. Jiang, O. Blacque and H. Berke, *Organometallics*, 2010, **29**, 125-133.
- G. Kehr and G. Erker, *Chem. Commun.*, 2012, **48**, 1839-1850.
- R. L. Melen, *Chem. Commun.*, 2014, **50**, 1161-1174.
- J. Mobus, Q. Bonnin, K. Ueda, R. Fröhlich, K. Itami, G. Kehr and G. Erker, *Angew. Chem. Int. Ed.*, 2012, **51**, 1954-1957.
- (a) A. Feldmann, A. Iida, R. Fröhlich, S. Yamaguchi, G. Kehr and G. Erker, *Organometallics*, 2012, **31**, 2445-2451; (b) F. Ge, G. Kehr, C. G. Daniliuc and G. Erker, *J. Am. Chem. Soc.*, 2014, **136**, 68-71.
- B. Wrackmeyer and K. Horchler, *J. Organomet. Chem.*, 1990, **399**, 1-10.
- C. Eller, G. Kehr, C. G. Daniliuc, R. Fröhlich and G. Erker, *Organometallics*, 2013, **32**, 384-386.
- F. A. Tsao and D. W. Stephan, *Dalton Trans.*, 2014, DOI: 10.1039/C1034DT03241A.

- M. J. Dabdoub and J. V. Comasseto, *Organometallics*, 1988, **7**, 84-87.
- (a) L. Killian and B. Wrackmeyer, *J. Organomet. Chem.*, 1978, **153**, 153-164; (b) B. Wrackmeyer, K. Horchler and R. Boese, *Angew. Chem. Int. Ed.*, 1989, **28**, 1500-1502; (c) B. Wrackmeyer and G. Kehr, *Polyhedron*, 1991, **10**, 1497-1506; (d) R. Koster, G. Seidel, I. Klopp, C. Kruger, G. Kehr, J. Suss and B. Wrackmeyer, *Chem. Ber-Recl.*, 1993, **126**, 1385-1396; (e) B. Wrackmeyer, S. Kundler and R. Boese, *Chem. Ber-Recl.*, 1993, **126**, 1361-1370; (f) B. Wrackmeyer, G. Kehr and D. Wettinger, *Inorg. Chim. Acta*, 1994, **220**, 161-173; (g) B. Wrackmeyer, S. Kundler, W. Milius and R. Boese, *Chem. Ber.*, 1994, **127**, 333-342; (h) B. Wrackmeyer, S. Kundler and A. Arizacastolo, *Phosphorus Sulfur*, 1994, **91**, 229-239; (i) B. Wrackmeyer, A. Pedall, W. Milius, O. L. Tok and Y. N. Bubnov, *J. Organomet. Chem.*, 2002, **649**, 232-245; (j) B. Wrackmeyer, B. H. Kenner-Hofmann, W. Milius, P. Thoma, O. L. Tok and M. Herberhold, *Eur. J. Inorg. Chem.*, 2006, 101-108.
- Z. Garkani-Nejad and M. Poshteh-Shirani, *Can. J. Chem.*, 2011, **89**, 598-607.
- (a) J. Beck, *Chem. Ber.*, 1995, **128**, 23; (b) J. Beck and K. Mueller-Buschbaum, *Z. Anorg. Allg. Chem.*, 1997, **623**, 409.
- (a) M. A. Dureen, C. C. Brown and D. W. Stephan, *Organometallics*, 2010, **29**, 6594-6607; (b) M. A. Dureen, C. C. Brown and D. W. Stephan, *Organometallics*, 2010, **29**, 6422-6432; (c) M. A. Dureen and D. W. Stephan, *J. Am. Chem. Soc.*, 2009, **131**, 8396-8397.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Graphical TOC

