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Highly Strained Heterocycles Constructed from Boron–Boron Multiple Bonds and Heavy Chalcogens

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Abstract: *The reactions of a diborene with elemental selenium or tellurium are shown to afford a diboraselenirane or diboratellurirane, respectively. These reactions are reminiscent of the sequestration of subvalent oxygen and nitrogen in the formation of oxiranes and aziridines; however, such reactivity is not known between alkenes and the heavy chalcogens. Although carbon is too electronegative to affect the reduction of elements with lower relative electronegativity, the highly reducing nature of the B=B double bond enables reactions with* Se^0 *and* Te^0*. The capacity of multiple bonds between boron atoms to donate electron density is highlighted in reactions where diborynes behave as nucleophiles, attacking one of the two Te atoms of diaryltellurides, forming salts consisting of diboratellurenium cations and aryltelluride anions.*

The energy stored in small, highly strained cyclic molecules has made them an integral part of modern synthetic chemistry. Since this "strain energy" increases with decreasing ring size, it is greatest for three-membered rings, and when these rings are heterocyclic, the charge asymmetry induced in the molecule provides sites ready for reaction. Accordingly, an enormous amount of research has gone into both the synthetic paths to, and reactions of, members of this class of compounds, most prominently oxiranes (C_2O rings) and aziridines (C_2N rings). The most common route to these materials is the oxidation of olefins by using, in the case of oxirane formation, subvalent oxygen species such as O_2, peroxides, peroxyacids, and ozone, or with reagents that impart a degree of electron deficiency to an oxygen atom, for example, chlorite or iodosylbenzene.[1] Aziridination of olefins is most frequently accomplished through the in situ generation of nitrenes from azides or other electron-deficient nitrogen sources such as iodinanes, hydroxylamines, and hydrazines.[1a,2] These alkene oxidations are made possible by the relatively high electronegativity of oxygen and nitrogen ($\chi_{\text{Pauling}} = 3.44$ and 3.04, respectively) relative to carbon ($\chi_{\text{Pauling}} = 2.55$).

Thiiranes (C_2S rings) are comparatively less common, and although examples of the direct addition of elemental sulfur to alkenyl double bonds are not unknown,[3] their syntheses are more likely than their first row neighbors to involve nonredox routes.[4] The similarity in the electronegativities of carbon and sulfur ($\chi_{\text{Pauling}} = 2.58$) decreases the thermodynamic driving force for alkene oxidation, further exemplified by the noted willingness of thiiranes to thermally extrude atomic sulfur[5] and by their utility as sulfur atom transfer reagents.[6] Three-membered heterocycles featuring heavier chalcogens (Se and Te) are even less prevalent. Although seleniranes have been proposed as reactive intermediates in a handful of transformations,[7] examples of isolated compounds are few and none have been verified crystallographically.[8] To date, there are no known examples of telluriranes. The heavy chalcogens have roughly equal ($\chi_{\text{Se}} = 2.55$) or smaller ($\chi_{\text{Te}} = 2.10$) electronegativities than carbon. As such, there is little or no driving force for the transfer of electron density from the alkene to form C_2Se or C_2Te rings, and hypothetical seleniranes or telluriranes would logically be thermodynamically unstable toward the alkene reclaiming its electrons by expelling the electropositive chalcogen.

For some time our group has been interested in the syntheses and utilities of diborenes.[9] In comparison to alkenes, the B=B bonds of diborenes have been found to be exceptionally reducing,[10] which is not surprising when considering both the +I oxidation state of boron (rather than the more common +III) and the lower electronegativity of boron ($\chi_{\text{Pauling}} = 2.04$) than carbon. Indeed, although direct oxidation of alkenes to thiiranes with elemental sulfur is rare, the reaction of diborenes with S_8 results in the transfer of all four reducing equivalents of the double bond to three sulfur atoms during the formation of five-membered trisulfidodiborolane.[11]

The following question can then be asked: might these highly reductive double bonds be capable of reacting with elemental Se and Te to form stable diboraseleniranes and diboratelluriranes?

When a thienyl-substituted, N-heterocyclic carbene (NHC) stabilized diborene (**1**, $IMe_2[5\text{-}(Me_3Si)C_4H_2S]_2B_2$, IMe = 1,3-dimethylimidazol-2-ylidene) was treated with

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excess elemental selenium in benzene, a color change from the deep purple of **1** to yellow was observed, along with the emergence of a new signal at −14 ppm in its ^{11}B NMR spectrum. An equivalent reaction with elemental tellurium showed a similar change, with the emergence of a signal at −13 ppm in the ^{11}B NMR spectrum concomitant with a similar change of color from purple to yellow. After filtration to remove the excess chalcogen, recrystallization from acetonitrile yielded pure **2** and **3**, the desired diboraselenirane and diboratellurirane, respectively (Figure 1). Both were structurally characterized by single-crystal X-ray crystallography.[12]

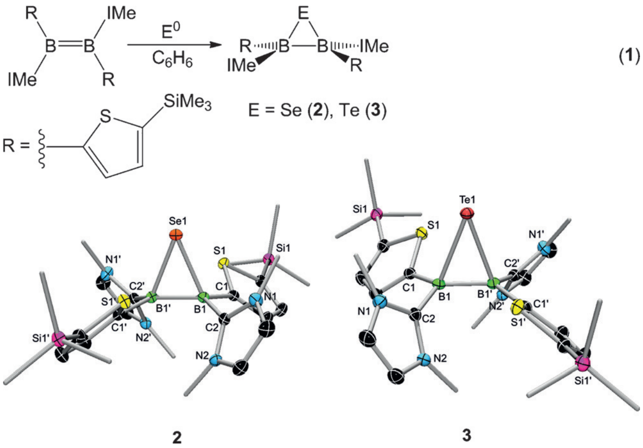


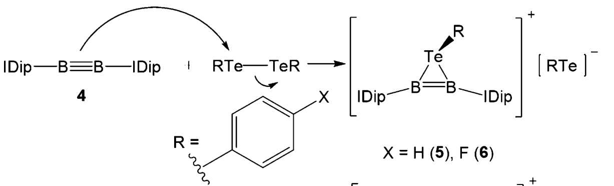
Figure 1. Synthesis and crystallographically determined structures of **2** and **3**.[28] The ellipsoids represent 50% probability, and have been omitted from the ligand periphery. For clarity, all hydrogen atoms are likewise omitted. Selected bond lengths [Å]: **2**: B1-B2 1.707(3), C2-B1 1.604(2), C1-B1 1.586(2), B1-Se1 2.115(2). **3**: B1-B2 1.713(5), C1-B1 1.584(4), C2-B1 1.598(4), B1-Te1 2.360(3).

Although neither ^{77}Se nor ^{125}Te nuclei could be detected by NMR spectroscopy of **2** and **3**, likely a result of extensive quadrupolar broadening induced by proximity to multiple boron nuclei, the ^{1}H NMR spectra of the compounds are consistent with the solid-state structures. Similarly, the upfield shift of the ^{11}B NMR resonances from the resonance at 22 ppm found for **1** is indicative of an increase in the coordination number at boron.

The B−B bonds in **2** (1.707(3) Å) and **3** (1.713(5) Å) are elongated with respect to the normal range of B=B lengths in diborene compounds (ca. 1.58–1.61 Å),[10,13] falling slightly short of the normal range for B−B single bonds in base-stabilized neutral diboranes (1.72–1.84).[13,14] This mirrors the geometries of oxiranes, which tend to have C−C bond distances (1.438(4) Å, ethylene oxide)[15] between those of alkanes (1.532 Å, ethane)[16] and alkenes (1.3142(3) Å, ethylene).[17] The typical C−C bonds in aziridines (ca. 1.48 Å) and thiirane (ca. 1.49 Å) are similarly situated between those of ethane and ethylene.[18]

Diborynes, molecules containing a boron–boron triple bond,[19] are likewise known to be highly reducing.[11,19,20] In fact, the reaction of the bis-NHC-stabilized diboryne B_2IDip_2 (**4**, IDip = 1,3-(diisopropylphenyl)imidazol-2-ylidene) with elemental selenium was previously reported to result in a six-electron reduction with insertion of five selenium atoms between the two boron atoms and formation of a bicyclic compound consisting of two conjoined triselenadiborolane rings.[11]

An equivalent reaction with elemental tellurium resulted in a complicated mixture of products from which no single major product could be isolated. In the hope of increasing the selectivity of the reaction by decreasing the oxidative power of the chalcogen, **4** was treated with 1,2-diphenylditelluride [Eq. (2)]. When the components were combined in benzene, a yellow precipitate was formed, which was isolated by filtration. The ^{11}B NMR spectrum of this material showed one signal at 0 ppm, while the ^{125}Te NMR spectrum showed two very different signals at 30 and −328 ppm. The ^{1}H NMR spectrum of the product indicated two different phenyl environments. Single-crystal X-ray analysis showed the formation of a salt complex (**5**) consisting of a cationic diboraphenyltellurirenium fragment and a spatially separated anionic phenyltelluride. An equivalent reaction utilizing the more electron-poor di-(4-fluorophenyl)-ditelluride showed identical reactivity, thus allowing the isolation and characterization of **6**.



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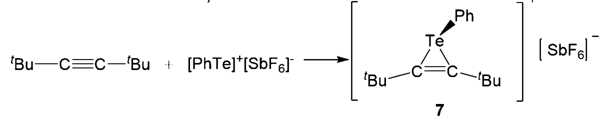

(3)

Similar organic three-membered tellurirenium ions [**7**, Eq. (3)] were previously demonstrated by Poleschner and Seppelt;[21] however, the reaction pathway to these products is notably different. In this reaction, an $[ArTe]^{+}$ fragment is generated by oxidation of a ditelluride and subsequently treated with an alkyne [Eq. (3)]. It seems that the tellurium must be cationic to facilitate the reaction with the more highly electronegative carbon atoms of the alkyne. In the diboryne reaction, the presence of the anionic phenyltelluride in the product indicates a reaction pathway wherein the B≡B bond acts as a nucleophile, attacking one of the tellurium atoms of the ditelluride and forcing out a $[PhTe]^{-}$ leaving group. Such a process has been suggested as the pathway for the epoxidation of alkenes with peracids,[22] although controversy surrounding this assertion still exists.[23]

The boron–boron bond lengths in **5** and **6** were found to be 1.490(6) Å and 1.494(10) Å, respectively (Figure 2). These are moderately longer than the B≡B length in **4** (1.449-(3) Å),[19] yet substantially shorter than those typically found in diborenes (ca. 1.58–1.61 Å).[10,13] Similar structural features are found in the organic tellurirenium, which has a central C−C bond measuring 1.288(14) Å[21a]—longer than the central

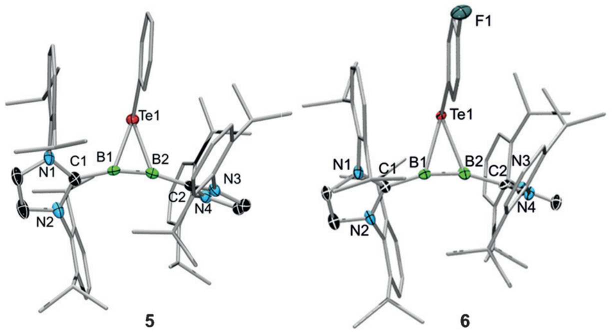

Figure 2. Crystallographically determined structures of $[\mathbf{5}]^+$ and $[\mathbf{6}]^+$ (aryltelluride anions have been omitted).[28] The ellipsoids represent 50% probability, and have been omitted from the ligand periphery. For clarity, all hydrogen atoms are likewise omitted. Selected bond lengths [Å] and angles [°]: $[\mathbf{5}]^+$: B1-B2 1.490(6), C1-B1 1.551(5), C2-B2 1.552(5), B1-Te1 2.260(4), B2-Te1 2.247(4); C1-B1-B2 165.0(4), C2-B2-B1 164.1(3), C1- B1- Te1 123.9(3), C2- B2-Te1 124.8(2). $[\mathbf{6}]^+$: B1-B2 1.494(10), C1-B1 1.545(9), C2-B2 1.559(10), B1-Te1 2.254(7), B2-Te1 2.243(8); C1-B1-B2 164.7(7), C2-B2-B1 163.6(7), C1-B1-Te1 123.7(5), C2-B2-Te1 125.4(5).

bond in di-*tert*-butylacetylene (1.202(2) Å),[24] but significantly shorter than a typical double bond in alkenes (ca. 1.34 Å).[25] The B−B−C angles in **5** and **6** (ca. 163–165°) are only slightly bent from linearity, although it is possible that the steric bulk of the two IDip groups prevents more acute bending. These angles are slightly more linear than the $C{-}C{-}C_{tBu}$ angles in **7**, which measure 155.5(10)° and 157.6(9)°.[21a] The Te atoms of **5** and **6** are highly pyramidalized, which is unsurprising since a planar tricoordinate Te atom would necessarily place two electrons into the π system between the boron atoms, thereby resulting in an antiaromatic system with four electrons.[26]

The relatively slight deviation from linearity induced by the complexation of $[\mathrm{PhTe}]^+$ led us to seek additional information about the boron–boron bonds in **5** and **6**. The Raman spectrum of **4**, previously used to study the strength of the B≡B bond,[27] shows identifiable peaks at 1628, 1657, and 1685 cm^{-1} that correspond to the symmetric stretch of the three possible isotopologic combinations of ^{11}B and ^{10}B. The spectra recorded with **5** and **6** showed a similar diagnostic isotopic pattern, shifted to lower wavenumbers as a result of bond lengthening and a decrease in bond order. The spectrum of **5**, in combination with the predicted spectra of its isotopologues, is presented in Figure 3, and shows B≡B frequencies of 1511, 1531, and 1555 cm^{-1} (tentatively) for the ^{11}B/^{11}B, ^{11}B/^{10}B, and ^{10}B/^{10}B isotopomers, respectively. Compound **6** showed a very similar spectrum (see Figure S3). For comparison, the stretching frequencies attributed to the B≡B stretch in **4** are given in Figure 3 in green. Although direct comparison to organic tellurirenium species such as **7** was not possible, as these compounds lack Raman data, the red-shift of the B_2 stretch ($\Delta\nu \approx 120\ \mathrm{cm}^{-1}$) upon going from **4** to **5** is significantly smaller than the red-shift observed between C≡C bonds and the central C_2 stretch in similarly structured selenirenium ions ($\Delta\nu \approx 380\ \mathrm{cm}^{-1}$).[21a]

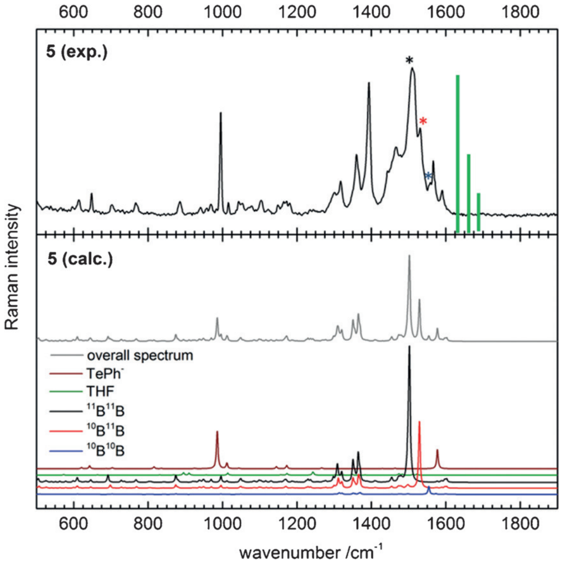

Figure 3. Comparison of the experimentally measured and DFT simulated Raman spectrum of **5**. The multicolored spectra represent the calculated Raman spectra for the three constitutive isotopologues of **5** as well as THF bound in the crystal. The gray line represents the summation of the five listed spectra. The green vertical lines in the experimental spectrum (top) represent the positions of the Raman peaks previously reported for **4**.[27]

In conclusion, the use of highly reducing boron–boron multiple bonds has enabled the formation of new, small heterocycles incorporating heavy chalcogens, which are too electropositive to form similar compounds with carbon. The willingness of the π bonds between boron atoms to donate electrons was explicitly shown in their capacity to act as nucleophiles in conjunction with ditellurides in the formation of diboratellurirenium cations with telluride anions.

These reactions serve to highlight both the similarities and differences between boron–boron multiple bonds and their conventional unsaturated organic analogues. Both are capable of sequestering chalogen atoms into three-membered rings, but the specific chalcogens employed, and the mechanism of their insertion, depends on the relative electronegativities of the chalcogen in question and the choice of the multiple bonding system (boron or carbon). With this lesson learned, we continue to seek out reactions which fail with electron-poor alkenes in the hope that increasing the reductive power of the multiple bond may enable the chemistry of this area to flourish.

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Keywords: boron · heterocycles · multiple bonds · selenium · tellurium

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Angew. Chem. **2016**, *128*, 5697–5700

[1] For an abridged list of reviews on epoxidation of alkenes since 2000, see a) Y. Zhu, Q. Wang, R. G. Cornwall, Y. Shi, *Chem. Rev.* **2014**, *114*, 8199 – 8256; b) Q.-H. Xia, H.-Q. Ge, C.-P. Ye, Z.-M. Liu, K.-X. Su, *Chem. Rev.* **2005**, *105*, 1603 – 1662; c) Y. Shi, *Acc. Chem. Res.* **2004**, *37*, 488 – 496; d) G. De Faveri, G. Ilyashenko, M, Watkinson, *Chem. Soc. Rev.* **2011**, *40*, 1722 – 1760; e) K. M. Weiß, S. B. Tsogoeva, *Chem. Rec.* **2011**, *11*, 18 – 39; f) J. W. Kück, R. M. Reich, F. E. Kühn, *Chem. Rec.* **2016**, *16*, 349 – 364; g) M. J. Portera, J. Skidmore, *Chem. Commun.* **2000**, 1215 – 1225; h) G. Grigoropoulou, J. H. Clark, J. A. Elings, *Green Chem.* **2003**, *5*, 1 – 7.

[2] For reviews on the aziridination of alkenes, see a) L. Degennaro, P. Trinchera, R. Luisi, *Chem. Rev.* **2014**, *114*, 7881 – 7929; b) J. B. Sweeney, *Chem. Soc. Rev.* **2002**, *31*, 247 – 258; c) A. Padwa in *Comprehensive Heterocyclic Chemistry III*, (Eds. A. R. Katritzky, C. A. Ramsden, E. F. V. Scriven, R. J. K. Taylor), Elsevier, Amsterdam, **2008**, pp. 43 – 82; d) D. Tanner, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 599 – 619; *Angew. Chem.* **1994**, *106*, 625 – 646; e) T. G. Driver, *Org. Biomol. Chem.* **2010**, *8*, 3831 – 3846.

[3] a) W. Adam, R. M. Bargon, W. A. Schenk, *J. Am. Chem. Soc.* **2003**, *125*, 3871 – 3876; b) W. Adam, R. M. Bargon, *Chem. Commun.* **2001**, 1910 – 1911; c) M. M. T. Khan, M. R. H. Siddiqui, *Inorg. Chem.* **1991**, *30*, 1157 – 1159.

[4] a) M. Sander, *Chem. Rev.* **1966**, *66*, 297 – 339; b) W. Chew, D. N. Harpp, *Sulfur Rep.* **1993**, *15*, 1 – 39; c) L. Goodman, E. J. Reist in *The Chemistry of Organic Sulfur Compounds*, *Vol. 2* (Eds.: N. Kharash, C. Y. Meyers), Pergamon Press, Oxford, **1966**, pp. 93 – 114.

[5] a) E. M. Lown, H. S. Sandhu, H. E. Gunning, O. P. Strausz, *J. Am. Chem. Soc.* **1968**, *90*, 7164 – 7165; b) R. D. Adams, J. A. Queisser, J. H. Yamamoto, *J. Am. Chem. Soc.* **1996**, *118*, 10674 – 10675; c) W. Ando, N. Choi, N. Tokitoh in *Comprehensive Heterocyclic Chemistry II*, *Vol. 1A* (Eds.: A. R. Katritzky, C. W. Rees, E. F. Scriven), Pergamon, Oxford, **1996**.

[6] A. Ibdah, W. S. Jenks, J. H. Espenson, *Inorg. Chem.* **2006**, *45*, 5351 – 5357.

[7] a) D. Van Ende, A. Krief, *Tetrahedron Lett.* **1975**, *16*, 2709 – 2712; b) A. Zhou, M. Segi, T. Nakajima, *Tetrahedron Lett.* **2003**, *44*, 1179 – 1182; c) K. Okuma, G. Koda, S. Okumura, A. Ohno, *Chem. Lett.* **1996**, *8*, 609 – 610; d) T. H. Chan, J. R. Finkenbine, *Tetrahedron Lett.* **1974**, *15*, 2091 – 2094.

[8] a) W. Ando, Y. Kumamoto, N. Tokitoh, *J. Phys. Org. Chem.* **1988**, *1*, 317 – 322; b) W. Ando, Y. Kumamoto, N. Tokitoh, *Tetrahedron Lett.* **1987**, *28*, 2867 – 2870; c) S. Dolai, P. Dutta, B. B. Muhoberac, C. D. Irving, R. Sardar, *Chem. Mater.* **2015**, *27*, 1057 – 1070.

[9] H. Braunschweig, R. D. Dewhurst, *Organometallics* **2014**, *33*, 6271 – 6277.

[10] a) P. Bissinger, H. Braunschweig, A. Damme, C, Hörl, I. Krummenacher, T. Kupfer, *Angew. Chem. Int. Ed.* **2015**, *54*, 359 – 362; *Angew. Chem.* **2015**, *127*, 366 – 369; b) P. Bissinger, H. Braunschweig, A. Damme, T. Kupfer, A. Vargas, *Angew. Chem. Int. Ed.* **2012**, *51*, 9931 – 9934; *Angew. Chem.* **2012**, *124*, 10069 – 10073; c) P. Bissinger, H. Braunschweig, A. Damme, T. Kupfer, I. Krummenacher, A. Vargas, *Angew. Chem. Int. Ed.* **2014**, *53*, 5689 – 5693; *Angew. Chem.* **2014**, *126*, 5797 – 5801.

[11] H. Braunschweig, T. Dellermann, W. C. Ewing, T. Kramer, C. Schneider, S. Ullrich, *Angew. Chem. Int. Ed.* **2015**, *54*, 10271 – 10275; *Angew. Chem.* **2015**, *127*, 10409 – 10413.

[12] The calculated frontier molecular orbitals of compounds **2**, **3**, and **5** are given in Figures S1 and S2 of the Supporting Information.

[13] a) Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2007**, *129*, 12412 – 12413; b) J. Böhnke, H. Braunschweig, T. Dellermann, W. C. Ewing, T. Kramer, I. Krummenacher, A. Vargas, *Angew. Chem. Int. Ed.* **2015**, *54*, 4469 – 4473; *Angew. Chem.* **2015**, *127*, 4551 – 4555.

[14] J. Böhnke, H. Braunschweig, W. C. Ewing, C. Hörl, T. Kramer, I. Krummenacher, J. Mies, A. Vargas, *Angew. Chem. Int. Ed.* **2014**, *53*, 9082 – 9085; *Angew. Chem.* **2014**, *126*, 9228 – 9231.

[15] P. Luger, C. Zaki, J. Buschmann, R. Rudert, *Angew. Chem.* **1986**, *98*, 254 – 255.

[16] G. J. H. Van Nes, A. Vos, *Acta Crystallogr. Sect. B* **1978**, *34*, 1947 – 1956.

[17] G. J. H. Van Nes, A. Vos, *Acta Crystallogr. Sect. B* **1978**, *34*, 2593 – 2601.

[18] F. H. Allen, *Tetrahedron* **1982**, *38*, 2843 – 2853.

[19] H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki, A. Vargas, *Science* **2012**, *336*, 1420 – 1422.

[20] H. Braunschweig, T. Dellermann, R. D. Dewhurst, W. C. Ewing, K. Hammond, J. O. C. Jimenez-Halla, T. Kramer, I. Krummenacher, J. Mies, A. K. Phukan, A. Vargas, *Nat. Chem.* **2013**, *5*, 1025 – 1028.

[21] a) H. Poleschner, K. Seppelt, *Angew. Chem. Int. Ed.* **2008**, *47*, 6461 – 6464; *Angew. Chem.* **2008**, *120*, 6561 – 6564; b) H. Poleschner, K. Seppelt, *Angew. Chem. Int. Ed.* **2013**, *52*, 12838 – 12842; *Angew. Chem.* **2013**, *125*, 13072 – 13077.

[22] a) P. D. Bartlett, *Rec. Chem. Prog.* **1950**, *11*, 47 – 50; b) H. Shi, Z. Zhang, Y. Wang, *J. Mol. Catal. A* **2005**, *238*, 13 – 25.

[23] a) A. Rybina, C. Lang, M. Wirtz, K. Grußmayer, A. Kurz, F. Maier, A. Schmitt, O. Trapp, G. Jung, D.-P. Herten, *Angew. Chem. Int. Ed.* **2013**, *52*, 6322 – 6325; *Angew. Chem.* **2013**, *125*, 6445 – 6449; b) D. I. Metelitsa, *Russ. Chem. Rev.* **1972**, *41*, 807 – 821.

[24] R. Boese, D. Bläser, R. Latz, A. Bäumen, *Acta Crystallogr. Sect. C* **1999**, *55*, IUC990001.

[25] *Table of interatomic distances and configuration in molecules and ions* (Ed.: L. E. Sutton), Supplement 1956 – 1959, Special publication No. 18, Chemical Society, London, UK, **1965**.

[26] It may be noted that the willingness of Te to act in either an aromatic or antiaromatic capacity within heterocycles has historically been called into question, and has been studied in comparison to this capacity in the other chalcogens. For additional literature, see a) F. Fringuelli, G. Marino, A. Taticchi, G. Grandolini, *J. Chem. Soc. Perkin Trans. 2* **1974**, 332 – 337; b) T. M. Krygowski, H. Szatylowicz, O. A. Stasyuk, J. Dominikowska, M. Palusiak, *Chem. Rev.* **2014**, *114*, 6383 – 6422; c) H. Karabıyık, R. Sevinçek, H. Karabıyık, *J. Phys. Org. Chem.* **2015**, *28*, 490 – 496; d) F. Fringuelli, G. Marino, G. Savelli, A. Taticchi, *J. Chem. Soc. D* **1971**, 1441.

[27] J. Böhnke, H. Braunschweig, P. Constantinidis, T. Dellermann, W. C. Ewing, I. Fischer, K. Hammond, F. Hupp, J. Mies, H.-C. Schmitt, A. Vargas, *J. Am. Chem. Soc.* **2015**, *137*, 1766 – 1769.

[28] CCDC 1451405 (**2**), 1451406 (**3**), 1451407 (**5**) and 1451408 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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