Main Group Chemistry

Telluradistibirane and Telluradibismirane: Three-Membered Heterocycles of Heavier Main Group Elements**

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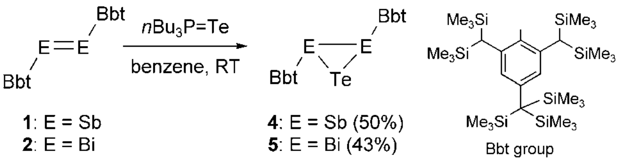
The chemistry of three-membered heterocycles has been widely explored in organic chemistry from the viewpoint of their unique structures and properties, which are attributed to their strained skeletons.[1,2] Although numerous papers have been published on the theory, preparation, and applications of three-membered heterocycles containing one heteroatom such as nitrogen, oxygen, or sulfur, only very few examples of three-membered ring compounds containing heavier chalcogen atoms such as selenium or tellurium have appeared to date.[3] In addition, three-membered ring systems composed of three heavier heteroatoms are also scarce, most likely owing to the instability of these systems. To synthesize such three-membered heterocycles that incorporate selenium or tellurium together with other heavier heteroatoms in their skeletons, one effective method should be the chalcogenation of highly reactive heavier double-bond compounds by formal [2+1] cycloaddition reactions. In the case of heavier Group 14 elements, selenadimetalliranes and telluradimetalliranes (Ch-M-M three-membered ring compounds; Ch = Se, Te, M = Si, Sn) have been successfully synthesized by chalcogenation reactions of the corresponding kinetically stabilized dimetallenes (M=M double-bond compounds) using elemental chalcogens.[4] There has also been much interest in doubly bonded compounds between heavier Group 15 elements, that is, heavier congeners of azo compounds. We synthesized a series of kinetically stabilized distibene (ArSb=SbAr)[5,6] and dibismuthene (ArBi=BiAr)[5,7] compounds by using 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) and 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) groups as effective steric protection groups. However, whereas no tellurirane containing two heavier Group 15 elements was obtained from the tellurization reaction of BbtP=PBbt using elemental Te or $(n\mathrm{Bu})_3\mathrm{P{=}Te}$,[8] selenadiphosphiranes[8,9] and a selenadistibirane[10] were synthesized by the selenization reaction of the corresponding diphosphene (Mes*P=PMes* (Mes* = 2,4,6-tri-*tert*-butylphenyl), BbtP=PBbt, etc.) and distibene (BbtSb=SbBbt), respectively. Herein, we report the tellurization reaction of the kinetically stabilized distibene BbtSb=SbBbt (**1**) and dibismuthene BbtBi=BiBbt (**2**), which led to the formation of novel three-membered heterocycles, that is, the first stable telluradistibirane and telluradibismirane, respectively.

The reaction of BbtBi=BiBbt (**2**, 30 mg, 0.02 mmol), which was readily prepared by reductive coupling of $\mathrm{BbtBiBr_2}$ with Mg in almost quantitative yield,[5] with an excess amount of elemental tellurium (26 mg, 10 equiv) in $[\mathrm{D_6}]$benzene solution was performed in the hope of generating a telluradibismirane derivative. After heating the mixture at 60 °C for 72 h, then at 80 °C for 72 h, and finally at 100 °C for 72 h, **2** disappeared completely as judged by the ^{1}H NMR spectra. However, not the desired telluradibismirane but only the ditelluride **3** (Bbt-Te-Te-Bbt) was obtained (12 mg, 42%) as green crystals after purification by GPLC. The structure of **3** was determined by spectroscopic data (^{1}H, ^{13}C, ^{125}Te NMR, FAB-MS) and X-ray crystallographic analysis.[11] Although mechanism for the formation of **3** is not clear at present, **3** was most likely generated by over-tellurization of **2** under severe conditions such as heating at 60–100 °C, which would be required to dissolving elemental tellurium in benzene.

Since $n\mathrm{Bu_3P{=}Te}$ has been known to function as a tellurization reagent under mild conditions,[12] we selected $n\mathrm{Bu_3P{=}Te}$ as an alternative tellurium source for the tellurization of **1** and **2**. When a solution of **2** (49 mg, 0.03 mmol) in benzene (2.0 mL) was mixed with two equivalents of $n\mathrm{Bu_3P{=}Te}$ (23 mg, 0.06 mmol) at room temperature, telluradibismirane **5**, in the form of an insoluble brown powder, precipitated from the reaction mixture (Scheme 1). After the suspension



Scheme 1. Synthesis of telluradipnictiranes.

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was left to stand for 2 h, **5** was isolated as a pure material by filtration followed by washing with hexane (23.3 mg, 0.013 mmol, 43 %). In this case, the tellurization reaction of **2** occurred at room temperature probably due to the fact that $n\mathrm{Bu_3P{=}Te}$ is more soluble than elemental tellurium. In addition, no ditelluride **3** was observed in the ^{1}H NMR spectrum of the crude mixture. Distibene **1** was also tellurized by this method, giving the corresponding telluradistibirane **4**. Treatment of **1** with $n\mathrm{Bu_3P{=}Te}$ under conditions similar to those applied to **2** afforded **4** as an orange powder in 50 % yield. Three-membered ring compounds were obtained by the tellurization reaction of **1** and **2**, in contrast to the case of sulfurization reactions of **1**, which resulted in the formation of corresponding four-, five-, and six-membered ring compounds.[13] The formation of **4** and **5** is worthy of note not only as the synthesis of new members of three-membered heterocycles, but also as a new finding on the reactivity of distibenes and dibismuthenes toward the tellurization reaction.

The telluradistibirane **4** was found to be thermally stable in [D$_6$]benzene solution up to 140 °C, and showed satisfactory ^{1}H and ^{13}C NMR spectral data. In addition, no change was observed in [D$_6$]benzene solution at 60 °C under photoirradiation with a 100-W high-pressure Hg lamp. Although the telluradibismirane **5** was stable under ambient conditions, heating a solution of **5** in [D$_6$]benzene at 80 °C for 1 h afforded a trace amount of ditelluride **3**. After the solution was heated at 100 °C for 1 h, **5**, **2**, and **3** were observed in the ratio of 1:0.2:0.1. Additional heating of the solution at 110 °C for 1 h gave an unidentified compound (**X**) together with **2** and **3** as the final products in a ratio of **X**:**2**:**3** = 1:2:2 as judged by ^{1}H NMR spectroscopy. Unfortunately, the reaction mechanism and the structure of the final product for the decomposition process of **5** are still unclear owing to the instability of compound **X** during the purification procedure. On the other hand, ^{125}Te NMR spectra of **4** measured in [D$_8$]toluene show a signal at $\delta = -622.3$ ppm within an upfield region, which is characteristic of such three-membered ring compounds. For example, some telluradisilirane ($\delta_{\mathrm{Te}} = -784$ ppm)[4a] and telluradistannirane ($\delta_{\mathrm{Te}} = -903$ ppm)[4b] derivatives were reported to show their ^{125}Te NMR signals in an up-field region, similar to the case of **4**. In addition, the ^{125}Te NMR chemical shift of dimesityltelluradistibirane (**6**), a model compound for **4**, was computed as $\delta = -700$ ppm by a GIAO calculation, which supports the experimentally observed chemical shift of **4**. Unfortunately, no signal was observed in the ^{125}Te NMR spectrum of **5** probably due to considerable peak broadening caused by the adjacent two bismuth atoms having nuclear spins of 9/2.

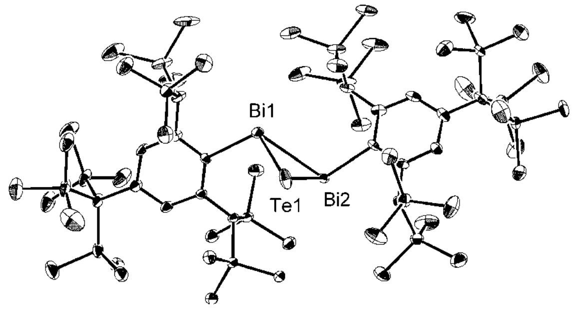


Figure 1. Molecular structure of **5** (ORTEP drawing; thermal ellipsoid plot (50 % probability)).

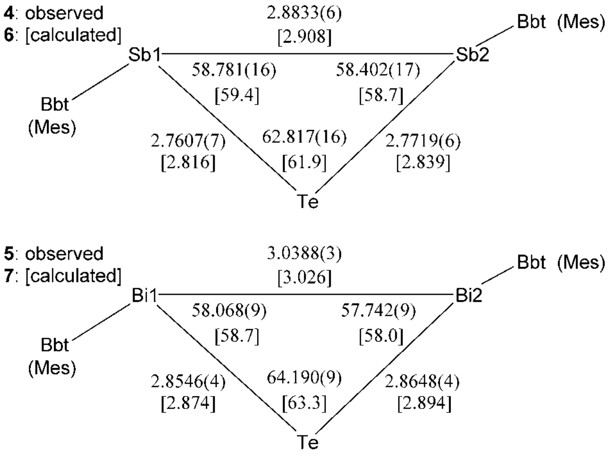
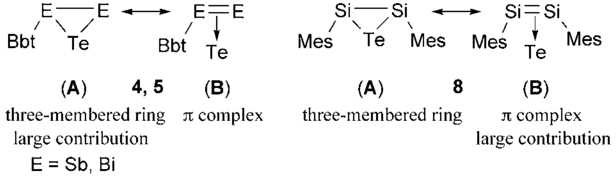


Figure 2. Selected bond lengths [Å] and bond angles [°] of **4** and **5**. Values in braces are calculated structural parameters for Mes-substituted model compounds **6** and **7**.

The molecular structures of **4** and **5** were determined by X-ray crystallographic analysis.[14] The structure of telluradibismirane **5** is shown in Figure 1 as a representative. The selected bond lengths and angles of **4** and **5** are depicted in Figure 2 together with the optimized structural parameters of model compounds, dimesityltelluradistibirane (**6**) and dimesityltelluradibismirane (**7**).[15] In both **4** and **5**, the two Bbt groups are oriented *trans* with regard to the central three-membered rings. The tellurirane skeletons of **4** and **5** are almost isosceles triangles with bond lengths (**4**: Sb–Sb 2.8833(6), Sb–Te 2.7607(7), 2.7719(6); **5**: Bi–Bi 3.0388(3), Bi–Te 2.8546(4), 2.8648(4) Å) that are comparable with previously reported values for the respective single bonds.[16] In addition, calculated structural parameters obtained by structural optimization (B3LYP) for the model compounds **6** and **7** supported the experimentally observed values obtained for the central three-membered-ring skeletons of **4** and **5**. These experimental and theoretical studies on the structures of **4** and **5** indicate that the telluradistibirane and telluradibismirane feature three-membered-ring character (**A**) rather than the π-complex character (**B**) as shown in Scheme 2. Interestingly, the telluradisilirane **8**, which is reported to be obtained by the reaction of $\mathrm{Mes_2Si{=}SiMes_2}$ with elemental tellurium, features π-complex character (**B**) rather than the three-membered-ring character (**A**).[4a] It should be noted



Scheme 2. Structures of telluriranes.

that the structural features of the corresponding tellurirane derivatives of heavier Group 15 elements differ from those of heavier group 14 elements.

In summary, we have synthesized the first stable telluradistibirane, **4**, and telluradibismirane, **5**, by a tellurization reaction of the reactive double-bond systems, BbtSb=SbBbt and BbtBi=BiBbt, by using (nBu)$_3$P=Te as a tellurization reagent. We have demonstrated here that telluradistibirane and telluradibismirane derivatives, which are three-membered ring compounds composed of much heavier elements, Sb, Bi, and Te, can be isolated without any oligomerization by using an appropriate steric protecting group and synthetic method. Further investigation of the physical and chemical properties of the newly obtained three-membered ring systems **4** and **5** is currently in progress.

Experimental Section

4: Addition of nBu$_3$P=Te (33 mg, 0.10 mmol) to a solution of **1** (70.4 mg, 0.05 mmol) in benzene (2 mL) at room temperature, led to the immediate precipitation of an orange powder. After the reaction mixture had been left to stand for 2 h, telluradistibirane **4** was separated by filtration, and then further purified by GPLC (40 mg, 0.025 mmol, 50 %). **4**: orange crystals, m.p. 161 °C (decomp); ^{1}H NMR (300 MHz, [D$_6$]benzene): $\delta = 0.33$ (s, 54H), 0.36 (s, 36H), 0.37 (s, 36H), 2.87 (s, 4H), 6.96 ppm (s, 4H); ^{13}C NMR (75 MHz, [D$_6$]benzene): $\delta = 2.09$ (q), 2.28 (q), 5.65 (q), 22.21 (s), 37.69 (d), 126.90 (d), 138.33 (s), 145.83 (s), 150.88 ppm (s); ^{125}Te NMR (94 MHz, [D$_8$]toluene): $\delta = -622.3$ ppm; UV/Vis (hexane): $\lambda_{\max}$ (ε) = 458 (680), 390 (3100), 346 nm (8500); HRMS (FAB): m/z: 1619.4440([M+H]$^+$), calcd for $C_{60}H_{135}{}^{121}Sb_2Si_{14}{}^{130}Te$ ([M+H]$^+$): 1619.4472; elemental analysis calcd (%) for $C_{60}H_{134}Sb_2Si_{14}Te$: C 44.48, H 8.34; found: C 44.23, H 8.23.

5: nBu$_3$P=Te (23 mg, 0.06 mmol) was added to a solution of **2** (49.0 mg, 0.03 mmol) in benzene (2 mL) at room temperature. The color of the reaction mixture immediately changed to dark brown. After the resulting suspension had been stirred for 2 h, the reaction mixture was filtered, and the residue was washed with hexane (20 mL) to afford brown crystals of telluradibismirane **5** (23.3 mg, 0.013 mmol, 43 %). **5**: brown crystals, m.p. 156 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]benzene): $\delta = 0.33$ (s, 36H), 0.34 (s, 54H), 0.36 (s, 36H), 2.29 (s, 4H), 7.20 ppm (s, 4H); ^{13}C NMR (100 MHz, [D$_6$]benzene): $\delta = 2.31$ (q), 2.41 (q), 5.65 (q), 22.10 (s), 43.15 (d), 126.54 (d), 145.08 (s), 151.68 (s), 161.38 ppm (s); UV/Vis (hexane): $\lambda_{\max}$ (ε) = 521 (2100), 450 (3200), 338 nm (18700); HRMS (FAB): m/z: 1795.6004 ([M+H]$^+$), calcd for $C_{60}H_{135}Bi_2Si_{14}{}^{130}Te$ ([M+H]$^+$): 1795.6004; elemental analysis calcd (%) for $C_{60}H_{134}Bi_2Si_{14}$ Te: C 40.16, H 7.53; found: C 40.12, H 7.48.

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[1] For a review of three-membered heterocycles, see: *Comprehensive Heterocyclic Chemistry II* (Eds.: A. R. Katritzky, C. W. Rees, E. F. Scriven), *Vol. 1A* (Ed.: A. Padwa), Pergamon, Oxford, **1996**.

[2] We have recently reported the synthesis and structures of the heavier analogues of a cyclopropabenzene, sila- and germa cyclopropabenzenes and bis(silacyclopropa)benzenes, unprecedented heavier congeners of cycloproparene derivatives, see: a) K. Hatano, N. Tokitoh, N. Takagi, S. Nagase, *J. Am. Chem. Soc.* **2000**, *122*, 4829; b) N. Tokitoh, K. Hatano, T. Sasaki, T. Sasamori, N. Takeda, N. Takagi, S. Nagase, *Organometallics* **2002**, *21*, 4309; c) T. Tajima, K. Hatano, T. Sasaki, T. Sasamori, N. Takeda, N. Tokitoh, *Chem. Lett.* **2003**, *32*, 220; d) T. Tajima, K. Hatano, T. Sasaki, T. Sasamori, N. Takeda, N. Tokitoh, N. Takagi, S. Nagase, *J. Organomet. Chem.* **2003**, *686*, 118. In addition, unique three-membered ring systems of heavier Group 14 elements have been reported as a review, see: A. Sekiguchi, V. Y. Lee, *Chem. Rev.* **2003**, *103*, 1429.

[3] For a review of selenirenes and tellurirenes, see: N. Tokitoh, W. Ando, N. Choi in *Comprehensive Heterocyclic Chemistry II* (Eds.: A. R. Katritzky, C. W. Rees, E. F. Scriven), *Vol. 1A* (Ed.: A. Padwa), Pergamon, Oxford, **1996**, pp. 173–240; N. Tokitoh, W. Ando in *Science of Synthesis, Houben-Weyl Methods of Molecular Transformations*, *Vol. 9* (Eds.: D. Bellus, S. V. Ley, R. Noyori, M. Regitz, E. Schaumann, I. Shinkai, E. J. Thomas, B. M. Trost, M. Regitz, G. Maas), Thieme, Stuttgart, **2001**, pp. 61–65.

[4] a) R. P. K. Tan, G. R. Gillette, D. R. Powell, R. West, *Organometallics* **1991**, *10*, 546; b) A. Schäfer, M. Weidenbruch, W. Saak, S. Pohl, H. Marsmann, *Angew. Chem. Int.* **1991**, *103*, 873; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 834; c) A. Schäfer, M. Weidenbruch, W. Saak, S. Pohl, H. Marsmann, *Angew. Chem.* **1991**, *103*, 978; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 962.

[5] T. Sasamori, Y. Arai, N. Takeda, R. Okazaki, Y. Furukawa, M. Kimura, S. Nagase, N. Tokitoh, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 661.

[6] N. Tokitoh, Y. Arai, T. Sasamori, R. Okazaki, S. Nagase, H. Uekusa, Y. Ohashi, *J. Am. Chem. Soc.* **1998**, *120*, 433.

[7] N. Tokitoh, Y. Arai, R. Okazaki, S. Nagase, *Science* **1997**, *277*, 78.

[8] T. Sasamori, N. Takeda, N. Tokitoh, *J. Phys. Org. Chem.* **2003**, *16*, 450.

[9] M. Yoshifuji, K. Shibayama, N. Inamoto, *Chem. Lett.* **1984**, 603.

[10] N. Tokitoh, T. Sasamori, R. Okazaki, *Chem. Lett.* **1998**, 725.

[11] **3**: dark-green crystals, m.p. 238.6–240.0 °C (decomp); ^{1}H NMR (300 MHz, [D$_6$]benzene): $\delta = 0.34$ (s, 72H), 0.35 (s, 54H), 3.05 (s, 4H), 7.05 ppm (s, 4H); ^{125}Te NMR (94 MHz, [D$_6$]benzene): $\delta = 328.7$ ppm; HRMS (FAB): m/z: 1505.5448 ([M+H]$^+$), calcd for $C_{60}H_{135}Si_{14}{}^{128}Te^{130}Te$ 1505.5443; elemental analysis calcd (%) for $C_{60}H_{134}Si_{14}Te_2$: C 47.91, H 8.98; found: C 48.20, H 9.05; the X-ray crystallographic analysis of **3** will be described elsewhere.

[12] For example, the synthesis of an alkylidenetelluragermirane derivative with tributylphosphine telluride has been reported; see: K. Kishikawa, N. Tokitoh, R. Okazaki, *Organometallics* **1997**, *16*, 5127.

[13] Treatment of **1** with S_8 in benzene afforded the corresponding 1,3,2,4-dithiadistibolane, 1,2,4,3,5-trithiadistibolane, and 1,2,3,5,4,6-tetrathiadistibinane derivatives; see: T. Sasamori, E. Mieda, N. Takeda, N. Tokitoh, *Chem. Lett.* **2004**, *33*, 104.

[14] Crystal data for **4** ($C_{60}H_{134}Sb_2Si_{14}Te$): $M_r = 1620.03$, $T = 103(2)$ K, monoclinic, $C2/c$ (no. 15), $a = 38.348(3)$, $b = 9.2753(5)$, $c = 47.689(3)$ Å, $\beta = 92.732(3)°$, $V = 16943.2(18)$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.270\ \mathrm{g\,cm^{-3}}$, $\mu = 1.205\ \mathrm{mm^{-1}}$, $\lambda = 0.71070$ Å, $2\theta_{\max} = 50.0$, 51832 measured reflections, 13961 independent reflections, 793 refined parameters, GOF = 1.159, $R_1 = 0.0658$ and w$R_2 = 0.1420$ [$I > 2\sigma(I)$], $R_1 = 0.0757$ and w$R_2 = 0.1480$ (for all data), largest difference peak and hole 3.312 and $-2.129\ \mathrm{e\,Å^{-3}}$, respectively, (around Sb and Te atoms); crystal data for **5** ($C_{60}H_{134}Bi_2Si_{14}Te$): $M_r = 1794.49$, $T = 103(2)$ K, monoclinic, $C2/c$ (no. 15), $a = 39.199(2)$, $b = 9.2798(3)$, $c = 47.120(2)$ Å, $\beta = 92.517(2)°$, $V = 17123.9(13)$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.392\ \mathrm{g\,cm^{-3}}$, $\mu = 4.666\ \mathrm{mm^{-1}}$, $\lambda = 0.71070$ Å, $2\theta_{\max} = 51.0$, 69668 measured reflections, 15682 independent reflections, 819 refined parameters, GOF = 1.121, $R_1 = 0.0381$ and w$R_2 = 0.0717$ [$I > 2\sigma(I)$], $R_1 = 0.0433$ and w$R_2 = 0.0736$ (for all data), largest difference peak and hole 2.230 and $-1.456\ \mathrm{e\,Å^{-3}}$, respectively, (around Bi and Te atoms). CCDC-

249239 (**4**) and -249238 (**5**) contains 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. The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).

[15] Structural optimization for **6** and **7** was carried out by using the Gaussian 98 program with density functional theory at the B3LYP level. The triple zeta basis sets ([3s3p]) for Sb and Bi, and double zeta basis sets ([2s2p]) for Te were used with effective core potentials; the 6-31G* basis set was used for C and H.

[16] Sb–Sb and Bi–Bi bond lengths are reported as 2.837 and 2.990 Å, respectively, in $Ph_2E{-}EPh_2$, see: H. Bürger, R. Eujen, G. Becker, O. Mundt, M. Westerhausen, C. Witthauer, *J. Mol. Struct.* **1983**, *98*, 265; F. Calderazzo, R. Poli, G. Pelizzi, *J. Chem. Soc. Dalton Trans.* **1984**, *11*, 2365; a few examples of compounds containing an E–Te bond (E = Sb, Bi) have been reported to date; Sb–Te bond lengths observed in a cluster compound are in the range of 2.75–72.78 Å, see: S. S. Dhingra, R. C. Haushalter, *J. Am. Chem. Soc.* **1994**, *116*, 3651; Bi–Te bond lengths observed in $(Dis_2Bi)_2Te$ ($Dis = CH(SiMe_3)_2$) are 2.872 and 2.889 Å, see: H. J. Breunig, I. Ghesner, E. Lork, *J. Organomet. Chem.* **2002**, *664*, 130.