

Chalcogenation Reactions of Overcrowded Doubly Bonded Systems between Heavier Group 15 Elements[#]

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Novel heterocyclic compounds containing chalcogen (S, Se, and Te) and pnictogen (P, Sb, and Bi) atoms were obtained by chalcogenation reactions of the doubly bonded systems between heavier group 15 elements (dipnictenes) kinetically stabilized by 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) groups. Whereas the sulfurization reaction of BbtP=PBbt (1) with elemental sulfur (S₈) gave the Bbt-substituted thiadiphosphirane, i.e., the three-membered ring compound of P–S–P, those of BbtSb=SbBbt (2) and BbtBi=BiBbt (3) afforded the corresponding five-membered ring compounds, i.e., the 1,2,4,3,5-trithiadistibolane and 1,2,4,3,5-trithiadibismolane, as the main products, respectively. From each selenization reaction of dipnictenes 1-3 using elemental selenium, the corresponding three-membered ring compounds (selenadipnictiranes) were obtained as stable compounds. On the other hand, the tellurization reactions of distibene 2 and dibismuthene 3 using $(n-Bu)_3P=Te$ gave the corresponding telluradipnic-tiranes as in the case of their selenization reactions, though diphosphene 1 underwent no tellurization when $(n-Bu)_3P=Te$ or elemental tellurium was used as a tellurium source.

The chemistry of low-coordinated compounds of heavier main group elements has been one of the most attractive areas¹ since the first isolation of distance $Dis_2Sn=SnDis_2$ [Dis = $CH(SiMe_3)_2]$,² disilene Mes₂Si=SiMes₂ (Mes = mesityl),³ and diphosphene $Mes^*P=PMes^*$ ($Mes^* = 2,4,6$ -tri-t-butylphenyl)⁴ by taking advantage of kinetic stabilization. Doubly bonded systems of heavier group 14 (dimetallenes) and 15 elements (dipnictenes) are possible even in the case of the heaviest element, bismuth, when they are kinetically well stabilized. Recently, much more attention has been paid to the elucidation of their reactivity. Above all, the cycloaddition reactions of such heavier π -bond systems have been found to be convenient routes to obtain novel heterocyclic systems. For example, the oxidation and chalcogenation reactions of disilenes, digermenes, and distannenes are known to give the corresponding three- or four-membered ring heterocyclic compounds containing oxygen or chalcogen (S, Se, or Te) atoms.⁵ Indeed, Mes₂Si=SiMes₂ can be oxidized by atmospheric oxygen to give the corresponding 1,3,2,4-dioxadisiletane derivative, although most alkenes do not react with triplet oxygen $(^{3}O_{2})$ under ambient conditions. In addition, the Mes-substituted oxadisilirane, thiadisilirane, selenadisilirane, and telluradisilirane derivatives have been obtained as stable compounds by the oxidation and chalcogenation reactions of Mes₂Si= SiMes₂ using N₂O⁶, S₈⁷, Se⁸, and Te⁸, respectively.

In contrast to the systematic studies on the oxidation and chalcogenation reactions of dimetallenes (or metallylenes), the reactivities of dipnictenes have been concealed except for the case of the kinetically stabilized diphosphene and diarsenes due to the lack of stable examples of a distibene and dibismuthene until our successful isolation of the first stable distibene⁹ and dibismuthene,¹⁰ TbtE=ETbt (E = Sb and Bi, Tbt = 2,4,6-tris[bis(trimethylsily1)methyl]phenyl), by taking advantage of an efficient steric protecting group, Tbt. Although

it has been found that the unique oxidation reactions of TbtSb=SbTbt and TbtBi=BiTbt proceed in the crystalline state to give the corresponding 1,3,2,4-dioxadistibetane⁹ and 1,3,2,4-dioxadibismetane¹¹ derivatives, further elucidation of the reactivities of TbtE=ETbt (E = Sb and Bi) has been hampered by their extremely low solubility in common organic solvents. We have developed another type of a bulky aromatic substituent, 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (denoted as Bbt) group, which is expected to be a potentially useful steric protecting group as well as the Tbt group. We have reported the successful application of Bbt group to the kinetic stabilization of the diphosphene,¹² distibute,^{11,13} and dibismuthene¹¹ (BbtE=EBbt, E = P, Sb, and Bi) together with the first stable stibabismuthene14 and phosphabismuthene,¹⁵ BbtSb=BiBbt and BbtBi=PMes*. These heavier dipnictenes have sufficient solubility in organic solvents. We have preliminarily reported that the sulfurization and selenization reactions of diphosphene 1 (BbtP=PBbt) with elemental sulfur and selenium affords the corresponding thiaand selenadiphosphirane derivatives, respectively.¹² Taking into account that the thia- and selenadiphosphirane derivatives are obtained as final products by the sulfurization and selenization reactions of $Mes^*P=PMes^*$ (4) as in the case of 1,¹⁶ the reactivity of Bbt-substituted dipnictenes should be investigated to examine the generality as compared with those of a diphosphene. Thus, we investigated the chalcogenation reactions of BbtSb=SbBbt (2) and BbtBi=BiBbt (3). We present here the details of the studies on the chalcogenation reactions of 2 and 3 together with systematic comparison with those of 1 (Scheme 1).

Results and Discussion

Sulfurization Reactions of the Dipnictenes. The sulfurization reaction of **1** proceeded under severe conditions



Scheme 2.

(Scheme 2), that is, heating of **1** with elemental sulfur (S₈, 4 equiv as S) at 120 °C in C₆D₆ for 162 h affords a mixture of the starting material **1**, thiadiphosphirane **5**, and dithioxophosphorane **6** in the ratio of 6:5:4 as judged by ¹H NMR spectrum.¹² On the other hand, the reaction of **1** with elemental sulfur (S₈, 10 equiv as S) in the presence of Et₃N (10 equiv) at 120 °C in C₆D₆ for 40 h results in the exclusive formation of thiadiphosphirane **5** (88%) as in the case of sulfurization of Mes*P=PMes* (**4**) with elemental sulfur.^{16a,b}

In view of these results, we examined the sulfurization reactions of distibene 2 and dibismuthene 3 (Scheme 3). Treatment of the benzene solutions of 2 and 3, which were easily prepared by the reductive coupling reaction of $BbtEBr_2$ (E = Sb and Bi) with magnesium metal in almost quantitative yields,¹¹ with an excess amount of elemental sulfur (S_8) at room temperature afforded the corresponding heterocycles containing sulfur and pnictogen (Sb and Bi) atoms, respectively.¹⁷ In contrast to the case of diphosphene 1, the heavier dipnictenes 2 and 3 readily underwent sulfurization reactions at room temperature, indicating their higher reactivity toward elemental sulfur than that of 1. Although 1,2,4,3,5-trithiadibismolane derivative 7 was obtained exclusively in the sulfurization of **3** using an excess amount of elemental sulfur (S_8) , treatment of 2 with an excess amount of S_8 under the same conditions afforded three types of antimony-containing cyclic polysulfides, i.e., 1,2,4,3,5-trithiadistibolane 8 (69%), 1,2,3,5,4,6tetrathiadistibinane 9 (17%), and 1,3,2,4-dithiadistibetane 10 (14%), without any other identifiable compound as judged by ¹HNMR spectroscopy. Since all of the obtained cyclic polysulfides gradually decomposed during the purification procedures, compounds 7 (22%), 8 (27%), 9 (4%), and 10 (9%) were isolated in relatively low yields.

Thus, it was found that the four-, five-, or six-membered





ring polysulfides were obtained from the sulfurization reactions of **2** and **3** in contrast to the case of the sulfurization reaction of **1**, where the three-membered ring compound (thiadiphosphirane) forms. When distibene **2** was treated with 1 molar amount (as S) of elemental sulfur (S₈) in the hope of obtaining Bbt-substituted thiadistibirane, the ¹H NMR spectrum showed that the reaction mixture contained unidentified compound **X** as a main product together with **2**, **8**, and **10**. Unfortunately, compound **X**¹⁸ could not be isolated because of its extreme sensitivity toward air and moisture. On the other hand, desulfurization of 1,3,2,4-dithiadistibetane **10** using triphenylphosphine at 60 °C in C₆D₆ did not occur, whereas 1,2,4,3,5trithiadistibolane **8** underwent desulfurization with triphenylphosphine under the same conditions leading to the quantitative formation of **10**.

Selenization Reactions of the Dipnictenes. The diphosphene, BbtP=PBbt (1), has been reported to react with elemental selenium to afford the corresponding selenadiphosphirane 11 together with diselenoxophosphorane 12 as well as the case of the selenization of $Mes^*P=PMes^*$ (4) (Scheme 4).^{16c}

We have preliminarily reported the unique selenium-transfer reaction from $(Me_2N)_3P=Se$ to the distibene **2** to form the corresponding three-membered ring compound, selenadistibirane **13**.^{11,13} On the other hand, the selenization reaction of **2** using elemental selenium in C₆D₆ in a sealed tube at high temperature proceeded very slowly to afford a mixture of distibene **2** and selenadistibirane **13** in a 1:2 ratio after heating for a long time (6 h at 80 °C, 14 h at 100 °C, 40 h at 120 °C, and 30 h at 130 °C, monitored by ¹H NMR spectroscopy). It was found that the addition of 3 molar amount of Et₃N promoted the selenization reaction of **2**. Indeed, heating of the C₆D₆ solution of **2** with elemental selenium (grey Se, 3 molar amount) in the presence of Et₃N (3 molar amount) at 60 °C for 100 h afforded selenadistibirane **13** quantitatively as judged by the ¹H NMR spectra (isolated yield; 50%) (Scheme 5).

The selenization reactions of 2 were attempted under much





Scheme	6.

severer conditions in the expectation of the formation of other cyclic polyselenides, such as diselenadistibetanes and/or triselenadistibolanes. However, an unexpected product, triselenide BbtSe₃Bbt (**14**), was obtained (53%) as a stable product, when **2** was treated with elemental selenium (10 molar amount) in the presence of Et₃N (10 molar amount) at 80 °C for 12 h. Although the formation mechanism for triselenide **14** is unclear at present, it can be interpreted in terms of the intermediacy of **13** in the selenization reaction of **2**. It was supported by the fact that selenadistibirane **13** underwent further selenization using elemental selenium (10 molar amount, in toluene-*d*₈, in an sealed tube, at 130 °C, for 2 h) to form BbtSe₃Bbt in 78% yield (Scheme 6).

The selenization reaction using elemental selenium in the presence of Et₃N was found to be applicable to the synthesis of the corresponding selenadibismirane. Heating dibismuthene **3** with elemental selenium (2.6 molar amount) in the presence of Et₃N (3.1 molar amount) in C₆D₆ at 80 °C for 10 h afforded selenadibismirane 15 quantitatively, determined from the ¹HNMR spectra (isolated yield; 58%). This result indicates that dibismuthene 3 should be more reactive toward elemental selenium than distibene 2. Thus, three-membered ring compounds 13 and 15 were obtained by the selenization reactions of 2 and 3, respectively, in contrast to the sulfurization reactions of 2 and 3, where the corresponding four-, five-, and sixmembered ring compounds were obtained without the corresponding thiadipnictirane derivatives. Although diselenoxophosphorane 12 formed in the selenization reaction of diphosphene 1,12 no diselenoxostiborane and diselenoxobismorane





derivatives were observed in the selenization reactions of 2 and 3 (Scheme 7).

Tellurization Reactions of the Dipnictenes. The successful synthesis of selenadipnictiranes 11, 13, and 15 naturally prompted us to examine the tellurization reactions of dipnictenes 1–3 in the expectation of obtaining unique three-membered ring systems, i.e., telluradipnictiranes,¹⁹ since to our knowledge no example of an isolated telluradipnictirane has been reported, except for only one report on the spectroscopic observation of a telluradiphosphirane derivative.²⁰

In contrast to the case of selenization reactions of the dipnictenes, however, tellurization reaction of diphosphene 1 using elemental tellurium or phosphine telluride, which is known to be a good tellurization reagent,²¹ does not occur even on heating at 120-150 °C in C₆D₆ in a sealed tube. On the other hand, the thermal reaction of distibene 2 with elemental tellurium (10 molar amount) in C_6D_6 in a sealed tube at 120 °C for 2 days afforded the corresponding telluradistibirane 17 as a stable compound in 15% yield. The relatively low yield of 17 is most likely due to the decomposition of the resulting products under the severe reaction conditions, which were indispensable due to the extremely low solubility of elemental tellurium. The tellurization reaction of dibismuthene 3 under the same conditions gave ditelluride 18, instead of telluradibismirane 19. However, we found that a phosphinetelluride, such as $(n-Bu)_3P=Te$, could be used as a good tellurization reagent toward distibene 2 and dibismuthene 3 under mild conditions. That is, treatment of distibene 2 and dibismuthene 3 with $(n-Bu)_3P=Te$ in benzene at room temperature for 2 h gave the corresponding telluradipnictiranes 17 (50%) and 19 (43%), respectively.²² Tellurabismirane 19 is the "heaviest" example among stable three-membered heterocyclic compounds isolated as stable compounds so far (Scheme 8).

Telluradistibirane 17 was found to be thermally stable in C_6D_6 solution at 140 °C in a sealed tube. In addition, it was

revealed that 17 is inert not only toward phosphine reagents, such as PPh₃ (at 100 °C), P(NMe₂)₃ (at 120 °C), and P(n-Bu)₃ (at 35 °C), in C_6D_6 in a sealed tube under heating conditions, but also toward photo-irradiation of the C₆D₆ solution using 100 W medium pressure Hg lamp at 60 °C in a Pyrex sealed tube. On the other hand, heating a C₆D₆ solution of telluradibismirane 19 at 80 °C for 1 h afforded a trace amount of ditelluride 18, though 19 was stable in solution under ambient conditions. After the solution was heated at 100 °C for 1 h. 19, 3, and 18 were observed in a ratio of 1:0.2:0.1. Additional heating of the solution at 110 °C for 1 h gave an unidentified compound Y together with dibismuthene 3 and ditelluride 18 as the final products in a ratio of Y:3:18 = 1:2:2 as determined from the ¹H NMR spectra. Unfortunately, the reaction mechanism and the structure of the final product for the decomposition process of 19 are still unclear at present due to the instability of compound Y during the purification procedure.

Structures of the Obtained Heterocycles. The molecular structures of the new heterocyclic compounds obtained by the chalcogenation reactions of dipnictenes 1-3 were determined by using X-ray crystallographic analyses. As shown in Fig. 1, all the chalcogenadipnictiranes, 5,¹² 11,¹² 13,¹³ 15, 17,¹⁹ and 19,¹⁹ showed isomorphous structures with an isosceles triangles of the E-Ch-E atoms (E = P, Sb, Bi; Ch = S, Se, Te). Their E-E bond lengths in the chalcogenadipnictiranes are within the range of the corresponding single-bond lengths and slightly longer (by ca. 0.002 nm) than those of the corresponding tetraphenyldipnictanes (for example: Ph₂P-PPh₂,²³ 0.2217 nm; Ph₂Sb–SbPh₂,²⁴ 0.2837 nm; Ph₂Bi–BiPh₂,²⁵ 0.2990 nm) (Table 1). Their E-Ch bond lengths are similar to or slightly shorter than those of the corresponding single-bond compounds (for examples: P–S in $(Mes^*PS)_{3}$,²⁶ 0.2113–0.2143 nm; P–Se in Se[PPh₂Cr(CO)₅]₂,²⁷ 0.2272 nm; Sb–Se in $(\text{DisSbSe})_2[W(\text{CO})_5]_2^{28}$ [Dis = CH(SiMe_3)_2], 0.2557–0.2559 nm; Sb–Te in some inorganic cluster,²⁹ ca. 0.28 nm; Bi–Se in (Mes₂Bi)₂Se,³⁰ 0.2651 nm; Bi-Te in (Dis₂Bi)₂Te,²⁸ 0.2872-0.2889 nm). These structural features observed in the chalcogenadipnictiranes can be interpreted in terms of the tendency



Fig. 1. ORTEP drawings of chalcogenadipnictiranes (50% probability). Hydrogen atoms, solvent molecules, and the minor part of the disordered moieties were omitted for clarity.

Table 1. Observed Structural Parameters of Chalcogenadipnictiranes 5, 11, 13, 17, 15, and 19

Bbt	Bond lengths/Å ^{a)}		Bond angles/degree			Ref.	
E1—E2 Ch Bbt	E1–E2	E1–Ch	Ch–E2	Ch-E1-E2	Ch-E2-E1	E1–Ch–E2	
5 : E = P	2.2349(12)	2.1083(13)	2.1285(12)	58.61(4)	57.72(4)	63.67(4)	12
Ch = S							
11: $E = P$	2.250(3)	2.250(3)	2.270(3)	60.59(9)	59.71(9)	59.70(8)	12
Ch = Se	0.050(0)	2.5(2(2))	0.565(1)	56 95(4)	56 15(4)		10
13: $E = Sb$	2.852(2)	2.562(2)	2.565(1)	56.25(4)	56.15(4)	67.60(5)	13
Ch = Se 17: E - Sh	2 8833(6)	2 7607(7)	2 7710(6)	58 781(16)	58 402(17)	62 817(16)	19
17. L = 30 Ch = Te	2.8855(0)	2.7007(7)	2.7719(0)	58.781(10)	38.402(17)	02.817(10)	10
15 : $E = Bi$	3.0105(4)	2.6492(9)	2.6649(8)	55.741(19)	55.25(2)	69.01(2)	This
Ch = Se							work
19 : E = Bi	3.0388(3)	2.8546(4)	2.8648(4)	58.068(9)	57.742(9)	64.190(9)	18
Ch = Te							
a) $1 \text{ Å} = 0.1 \text{ nm}$							

a) 1 A = 0.1 nm.



Fig. 2. Depiction of bonding properties for (a) a thiadiphosphirane and (b) a thiadisilirane.



of heavy atoms to maintain the $(ns)^2(np)^3$ valence electron configuration rather than to form a hybridized orbital. That is, the two pnictogen atoms (P, Sb, and Bi) form a threemembered ring with one chalcogen atom (S, Se, and Te) using three valence bonds with non-hybridized p-orbital, making a slightly longer E–E bond than the corresponding acyclic single bond with sp³-character, and the slightly shorter E–Ch bond observed in the chalcogenadipnictiranes than the corresponding E–Ch single bonds may be due to so-called "bananabonds" (Fig. 2).³¹ In addition, the E–E–C(Bbt) angles (104– 116°) less than 120° also indicate the E–C(Bbt) bond with non-hybridized p-orbital character, though the extreme steric hindrance of the Bbt group causes the bond angle to be larger than 90°.

The bonding properties of the chalcogenadipnictiranes were supported by NBO calculations. NBO calculations for parent thiadiphosphirane 20 and parent diphosphane 21 (Scheme 9) showed that the hybridization of P-P and P-S bonds in **20** should be $\sigma_{PP} = 0.5(sp^{11.93})P + 0.5(sp^{11.93})P$ and $\sigma_{PS} =$ $0.6367(sp^{12.63})P + 0.7711(sp^{10.84})S$, respectively, indicating slightly higher p-characters than that for 21, where the hybridization of the P–P bond should be $\sigma_{\rm PP} = 0.5({\rm sp}^{8.22}){\rm P} +$ 0.5(sp^{8.22})P. In contrast to the case of chalcogenadipnictiranes, which possess a concrete three-membered ring character (A) (Fig. 3) as described above, chalcogenadisiliranes 22, which have been reported to be obtained from the reaction of $Mes_2Si=SiMes_2$ with elemental chalcogens (S₈, Se, and Te),^{7,8} has a π -complex character (**B**) rather than the three-membered ring character (A).8 Thus, it should be noted that the bonding properties of chalcogenadipnictiranes³² differ from those of chalcogenadisiliranes,³³ which should consist of π -bonding



Fig. 3. Structures of chalcogenadipnictiranes and chalcogenadisiliranes.

from the disilene unit to the chalcogen atom and the π -back donating from the chalcogen atom to the disilene unit as shown in Fig. 2.

In ³¹P, ⁷⁷Se, ¹²⁵Te NMR spectra for chalcogenadipnictiranes 5, ¹² 11, ¹² 13, ¹³ 15, and 17, ¹⁹ characteristic signals corresponding to the atoms in the three-membered ring systems were observed upfield ($\delta_P = -71.3$ for 5; $\delta_P = -55.3$, $\delta_{Se} = 14.6$ (t, ¹ $J_{SeP} = 126$ Hz) for 11, $\delta_{Se} = -182.0$ for 13, $\delta_{Se} = -136.6$ (brs) for 15, $\delta_{Te} = -622.3$ for 17) from those of normal acyclic compounds probably due to the shielding effects of heavy atoms and paramagnetic term of the corresponding n– σ^* electron transitions. Such up-fielded chemical shifts should be characteristic of the three-membered ring skeletons.³⁴ Unfortunately, no signal was observed in the ¹²⁵Te NMR spectrum of telluradibismirane 17, probably due to the considerable peak broadening caused by the two adjacent bismuth atoms having nuclear spins of 9/2.

The molecular structures of cyclic sulfides 7-10 were also determined by using X-ray crystallographic analyses as shown in Fig. 4.¹⁷ To the best of our knowledge, polysulfides 7-9 are the first examples of 1,2,4,3,5-trithiadibismolane, 1,2,4,3,5-trithiadistibolane, and 1,2,3,5,4,6-tetrathiadistibinane ring systems, respectively. The five-membered ring skeletons of 1,2,4,3,5-trithiadipnictolanes 7 and 8 were found to be isomorphous with the half-chair geometries. Their Sb-S [0.24349(8), 0.24806(7), 0.24398(7), and 0.24833(7) nm] and Bi-S [0.2507(3), 0.2585(2), 0.2505(3), and 0.2582(2) nm] bond lengths are similar to those observed for the acyclic compounds with Sb-S [0.2444 nm in Ph₂SbS(8-quinolyl)³⁵] and Bi–S $[0.2572, 0.2557 \text{ nm in } S(BiDis_2)_2^{28}]$, respectively. 1,2,4,3,5-Trithiadibismolane 7 was found to possess a halfchair geometry for the central ring skeleton as in the case of 1,2,4,3,5-trithiadistibolane 8 (Fig. 5). On the other hand, one can see the chair-conformation for the central 1.2.3.5.4.6tetrathiadistibinane ring of 9 (Fig. 6). It was found that the 1,2,3,5,4,6-tetrathiadistibinane ring was disordered (78:22) due to the flipping of the six-membered ring. In both cases

of the two types of chair-conformations, two Bbt groups on the antimony atoms are in equatorial positions. 1,3,2,4-Dithiadistibetane **10** was found to have an almost planar squared ring with typical Sb–S single-bond lengths [0.24557(10) and 0.24630(9) nm] and a center of symmetry in the center of the four-membered ring, showing the structural resemblance to *cyclo*-Dis₂Sb₂S₂ [Sb–S: 0.2425(1) and 0.2428(1) nm].³⁶

Conclusion

In summary, several types of chalcogenacycles containing two pnictogen atoms were obtained by the reactions of kinetically stabilized heavier dipnictenes 1-3 with elemental chalcogens (S₈, Se, and Te) or phosphine chalcogenides [(Me₂N)₃P= Se or (*n*-Bu)₃P=Te]. It was found that the doubly bonded systems between heavier group 15 elements are good precursors for the unique heterocycles containing pnictogen atoms. The



Fig. 4. ORTEP drawings of cyclic polysulfides **7–10** (50% probability). Hydrogen atoms and solvent molecules were omitted for clarity.

obtained heterocyclic compounds are summarized in Table 2. The molecular structures of the obtained heterocyclic compounds were revealed by spectroscopic and X-ray crystallographic analyses. Especially, to our knowledge compounds 13, 15, 17, and 19 were the first examples of chalcogenadistibiranes and chalcogenadibismiranes. It should be of great importance that the three-membered heterocycles, chalcogenadipnictiranes 5, 11, 13, 15, 17, and 19, could be isolated as stable crystalline compounds, though three-membered ring compounds of heavier elements are known to be too reactive and difficult to isolate due to their highly strained structures.



Fig. 5. The structure of the central ring skeleton of 1,2,4,3,5-trithiadibismolane **7**.



Fig. 6. Disordered structure of the central ring skeleton of 1,2,3,5,4,6-tetrathiadistibinane **9**.

Table 2. Obtained Heterocycles by the Chalcogenation Reactions of Heavier Dipnictenes 1-3

	Sulfurization (S ₈)	Selenization (Se)	Tellurization [(<i>n</i> -Bu) ₃ P=Te]
BbtP=PBbt (1)	Bbt P S Bbt	Bbt P Se Bbt	_
BbtSb=SbBbt (2)	Bbt-Sb Sb-Bbt S_n	Bbt Sb—Sb Se Bbt	Bbt Sb—Sb Te Bbt
BbtBi=BiBbt (3)	n = 1, 2, 3 $Bbt Bi'S Bi'Bbt S-S'$	Bbt Bi Se Bbt	Bbt Bi-Bi Te Bbt

Experimental

General Procedure. All experiments were performed under an argon atmosphere unless otherwise noted. All solvents were dried by standard methods and were freshly distilled prior to use. The ¹HNMR (400 or 300 MHz) and ¹³C NMR (100 or 75 MHz) spectra were measured in CDCl₃ or C₆D₆ on a JEOL AL-400 or AL-300 spectrometer using CHCl₃ (7.25 ppm) or C₆D₅H (7.15 ppm) as an internal standard for ¹H NMR spectrometry, and using CDCl₃ (77.0 ppm) or C₆D₆ (128.0 ppm) as the standard for ¹³C NMR spectrometry. The ³¹P (121 MHz), ⁷⁷Se (75 or 57 MHz), and ¹²⁵Te NMR (125 or 94 MHz) spectra were measured in benzene- d_6 or toluene- d_8 with a JEOL AL-400 or AL-300 spectrometer using 85% H₃PO₄ in H₂O (0 ppm), diphenyldiselenide (460 ppm), diphenylditelluride (450 ppm) as external standards, respectively. High-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer. Gel permeation liquid chromatography (GPLC) was performed on an LC-918 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: chloroform or toluene). Preparative thin-layer chromatography (PTLC) was performed with Merck Kieselgel 60 PF254. Electronic spectra were recorded on a JASCO Ubest V-570. High- and low-resolution mass spectral data were recorded on a JEOL JMS-700 spectrometer. All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. Bbt₂Sb₂ (2),¹¹ Bbt₂Bi₂ (3),¹¹ and $(n-Bu)_3$ PTe³⁷ were prepared according to the reported procedures.

Reaction of 1,2-Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl}distibene (BbtSb=SbBbt, 2) with an Excess Amount of Elemental Sulfur (S_8) . To a benzene solution (2 mL) of Bbt₂Sb₂ (2, 60.0 mg, 0.04 mmol) was added elemental sulfur (S₈, 12.0 mg, 0.67 mmol, 10 molar amount as S). After stirring at room temperature for 7 h, the solvent was evaporated under reduced pressure. The ¹H NMR spectra of the reaction mixture showed signals corresponding to 1,3,2,4-dithiadistibetane 10 (14%), 1,2,4,3,5-trithiadistibolane 8 (69%), 1,2,3,5,4,6-tetrathiadistibinane 9 (17%). Purification of the reaction mixture by GPLC and PTLC afforded 10 (5.6 mg, 9%), 8 (17.4 mg, 27%), and **9** (2.8 mg, 4%). **10**: orange crystals, mp 152 °C (dec.); ¹H NMR $(300 \text{ MHz}, \text{ rt}, \text{ C}_6\text{D}_6) \delta 0.35 \text{ (s, 72H)}, 0.37 \text{ (s, 54H)}, 2.77 \text{ (s, 4H)},$ 7.02 (s, 4H). HRMS (FAB) Found: m/z 1554.4786 ([M]⁺). Calcd for $C_{60}H_{134}S_2^{121}Sb^{123}SbSi_{14}$ 1554.4777 ([M]⁺). Anal. Calcd for C₆₀H₁₃₄S₂Sb₂Si₁₄: C, 46.30; H, 8.68%. Found: C, 46.75; H, 8.70%. 8: yellow crystals, mp 186–187 °C (dec.); ¹H NMR (300 MHz, rt, C_6D_6) δ 0.34 (s, 126H), 2.59 (s, 4H), 7.04 (s, 4H); 13 C NMR (75 MHz, rt, C₆D₆) δ 1.70 (q), 1.89 (q), 5.60 (q), 22.74 (s), 34.84 (d), 128.12 (d), 147.61 (s), 147.94 (s), 151.12 (s). HRMS (FAB) Found: m/z 1589.4515 ([M + H]⁺). Calcd for $C_{60}H_{135}S_3^{123}Sb_2Si_{14}$ 1589.4586 ([M + H]⁺). Anal. Calcd for C₆₀H₁₃₄S₃Sb₂Si₁₄•C₆H₁₄: C, 47.65; H, 8.95%. Found: C, 47.66; H, 9.00%. 9: yellow crystals, mp 147 °C (dec.); ¹H NMR (300 MHz, rt, C₆D₆) δ 0.33 (s, 72H), 0.34 (s, 54H), 2.72 (s, 4H), 6.99 (s, 4H). HRMS (FAB) Found: *m*/*z* 1617.4316 ([M + H]⁺). Calcd for $C_{60}H_{135}S_4^{121}Sb_2Si_{14}$ 1617.4292 ([M + H]⁺). Anal. Calcd for C₆₀H₁₃₄S₄Sb₂Si₁₄•C₆H₁₄: C, 46.44; H, 8.74%. Found: C, 46.07; H, 8.57%.

Reaction of 1,2-Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl}distibene (BbtSb=SbBbt, 2) with 1 Molar Amount of Elemental Sulfur (S₈). To a benzene solution (2 mL) of Bbt₂Sb₂ (2, 149.0 mg, 0.10 mmol) was added elemental sulfur (S₈, 3.3 mg, 0.10 mmol, 1 molar amount as S). After stirring at room temperature for 7 h, the solvent was evaporated under reduced pressure. The ¹H NMR spectra of the reaction mixture showed signals corresponding to compound **X** as a main product together with distibene **2**, 1,3,2,4-dithiadistibetane **10**, and 1,2,4,3,5-trithiadistibolane **8**. The reaction mixture was subjected to GPLC (toluene) and PTLC to afford complicated mixture containing BbtH. Compound **X**: ¹H NMR (300 MHz, rt, C₆D₆) δ 0.32 (s, 126H), 2.96 (s, 4H), 6.94 (s, 4H).

Reaction of 3,5-Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl}-1,2,4,3,5-trithiadistibolane (8) with Triphenylphosphine. To a benzene- d_6 suspension (0.7 mL) of Bbt₂Sb₂S₃ (8, 5.0 mg, 3.1 µmol) was added triphenylphosphine (5.0 mg, 19 µmol). The reaction mixture was degassed and sealed in a 5 ϕ NMR tube. After heating at 60 °C for 9 h, the signals for 8 disappeared, and those for 10 and triphenylphosphine sulfide were observed without any other product in the ¹H NMR spectrum.

Reaction of 1,2-Bis{2,6-bis[bis(trimethylsily1)methyl]-4-[tris-(trimethylsily1)methyl]phenyl}dibismuthene (BbtBi=BiBbt, 3) with Elemental Sulfur (S₈). To a benzene solution (2 mL) of Bbt₂Bi₂ (3, 101 mg, 60.6 µmol) was added elemental sulfur (S₈, 19.0 mg, 0.606 mmol, 10 molar amount as S). After stirring at room temperature for 1 h, the solvent was evaporated under reduced pressure. Purification of the reaction mixture by GPLC afforded 1,2,4,3,5-trithiadibismolane 7 (23.3 mg, 22%). 7: dark brown crystals, mp 138–141 °C (dec.); ¹HNMR (300 MHz, rt, C₆D₆) δ 0.35 (s, 126H), 2.17 (s, 4H), 7.54 (s, 4H); ¹³C NMR (75 MHz, rt, C₆D₆) δ 1.61 (q), 1.86 (q), 5.61 (q), 22.76 (s), 37.53 (d), 128.28 (d), 131.57 (s), 145.53 (s), 151.73 (s). HRMS (FAB) Found: *m/z* 1761.6051 ([M + H]⁺). Calcd for C₆₀H₁₃₅Bi₂S₃Si₁₄ 1761.6103 ([M + H]⁺). Anal. Calcd for C₆₀H₁₃₄S₃Bi₂Si₁₄ •C₆H₁₄: C, 42.87; H, 8.07%. Found: C, 43.08; H, 8.24%.

Reaction of 1,2-Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl}distibene (BbtSb=SbBbt, 2) with an Excess Amount of Elemental Selenium. To a benzene- d_6 solution (0.6 mL) of Bbt₂Sb₂ (2, 30.0 mg, 0.02 mmol) was added elemental selenium (gray Se, 4.7 mg, 0.06 mmol, 3 molar amount) and Et₃N (8.4 µL, 0.06 mmol, 3 molar amount). The reaction mixture was degassed and sealed in a 5 ϕ NMR tube. After the suspension was heated at 60 °C for 4 days, recrystallization of the reaction mixture from hexane afforded selenadistibirane 13 (15.8 mg, 0.01 mmol, 50%). The product was identified according to the chemical data shown in Ref. 11.

Reaction of 1,2-Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl}distibene (BbtSb=SbBbt, 2) with an Excess Amount of Elemental Selenium. To a benzene- d_6 solution (0.6 mL) of Bbt₂Sb₂ (2, 71.6 mg, 0.048 mmol) was added elemental selenium (gray Se, 11 mg, 0.14 mmol, 10 molar amount) and Et₃N (20 µL, 0.14 mmol, 10 molar amount). The reaction mixture was degassed and sealed in a 5 ϕ NMR tube. After the suspension was heated at 80 °C for 24 h, recrystallization of the reaction mixture from hexane afforded BbtSe₃Bbt (14, 38 mg, 0.026 mmol, 53%). 14: orange crystal, mp 244 °C (dec.); ¹H NMR (300 MHz, rt, C₆D₆) δ 0.31 (s, 72H), 0.34 (s, 54H), 3.52 (s, 4H), 7.07 (s, 4H); ¹³C NMR (75 MHz, rt, C₆D₆) δ 1.69 (q), 5.60 (q), 22.74 (s), 32.64 (d), 126.85 (d), 133.78 (s), 147.24 (s), 150.87 (s). ⁷⁷Se NMR (57 MHz, rt, C₆D₆) δ 764, 455. HRMS (FAB) Found: m/z 1486.4751 ([M]⁺). Calcd for C₆₀H₁₃₄Se₃Si₁₄ 1486.4751 ([M]⁺).

Reaction of 2,3-Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl}selenadistibirane (13) with an Excess Amount of Elemental Selenium. To a toluene-*d*₈ solution (0.6 mL) of Bbt₂Sb₂Se (13, 34.8 mg, 0.022 mmol) was added elemental selenium (gray Se, 18.5 mg, 0.23 mmol, 10 molar amount). The reaction mixture was degassed and sealed in a 5ϕ NMR tube. After the suspension was heated at 130 °C for 2 h, the sealed tube was opened. After filtration through Celite[®], the filtrate was purified by GPLC (eluent: CHCl₃) to give BbtSe₃Bbt (14, 25.7 mg, 0.017 mmol, 78%).

Reaction of 1.2-Bis{2.6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl}dibismuthene (BbtBi=BiBbt, 3) with Elemental Selenium. To a benzene- d_6 solution (0.7 mL) of Bbt₂Bi₂ (3, 16 mg, 9.6 µmol) was added elemental selenium (gray Se, 2.0 mg, 0.025 mmol, 2.6 molar amount) and Et_3N (4.2 µL, 0.03 mmol, 3.1 equiv). The reaction mixture was degassed and sealed in a 5 ϕ NMR tube. After the suspension was heated at 80 °C for 10h, recrystallization of the reaction mixture from hexane afforded selenadibismirane 15 (9.8 mg, 5.6 µmol, 58%). 15: dark red crystals, mp 125–126 °C (dec.); ¹H NMR (400 MHz, rt, C₆D₆) δ 0.32 (s. 36H), 0.33 (s. 54H), 0.34 (s. 36H), 2.53 (s. 4H), 7.24 (s, 4H); 13 C NMR (100 MHz, rt, C₆D₆) δ 2.16 (q), 2.29 (q), 5.66 (q), 22.25 (s), 41.66 (d), 128.58 (d), 145.14 (s), 151.94 (s), 172.03 (brs); 77 Se NMR (75 MHz, rt, C₆D₆) δ -136.64. HRMS (FAB) Found: m/z 1745.6084 ([M + H]⁺). Calcd for C₆₀H₁₃₅Bi₂SeSi₁₄ 1745.6106 ([M + H]⁺).

Reaction of 1,2-Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl}distibene (BbtSb=SbBbt, 2) with **Elemental Tellurium.** To a benzene- d_6 solution (0.6 mL) of Bbt₂Sb₂ (2, 30.0 mg, 0.02 mmol) was added elemental tellurium (26.0 mg, 0.20 mmol, 10 equiv). The reaction mixture was degassed and sealed in a 5 ϕ NMR tube. After the suspension was heated at 120 °C for 2 days, the sealed tube was opened. The reaction mixture was purified by GPLC (eluent: toluene) to afford telluradistibirane 17 (4.7 mg, 2.9 µmol, 15%). 17: orange crystals, mp 161 °C (dec.); ¹H NMR (300 MHz, rt, C_6D_6) δ 0.33 (s, 54H), 0.36 (s, 36H), 0.37 (s, 36H), 2.87 (s, 4H), 6.96 (s, 4H); ¹³C NMR (75 MHz, rt, C₆D₆) δ 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 (s); ¹²⁵Te NMR (94 MHz, rt, toluene- d_8) δ -622.3. HRMS (FAB) Found: m/z 1619.4440 ([M + H]⁺). Calcd for C₆₀H₁₃₅¹²¹Sb₂Si₁₄¹³⁰Te 1619.4472 ($[M + H]^+$). UV-vis (hexane) λ_{max} (\mathcal{E}) = 458 (680), 390 (3100), 346 (8500) nm. Anal. Calcd for C₆₀H₁₃₄Sb₂Si₁₄Te: C, 44.48; H, 8.34%. Found: C, 44.23; H, 8.23%.

Reaction of 1,2-Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl}distibene (BbtSb=SbBbt, 2) with $(n-Bu)_3P=Te$. To a benzene solution (0.6 mL) of Bbt₂Sb₂ (2, 70.4 mg, 0.05 mmol) was added $(n-Bu)_3PTe$ (33 mg, 0.10 mmol, 2.0 equiv) at room temperature. After standing the solution for 2 h, filteration of the precipitated orange powder and purification of the filtrate by GPLC afforded telluradistibirane **17** (40.0 mg, 0.025 mmol, 50%).

Reaction of 2,3-Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl}telluradistibirane (17) with Triphenylphosphine. To a benzene- d_6 suspension (0.7 mL) of Bbt₂Sb₂Te (17, 13.0 mg, 8.0 µmol) was added triphenylphosphine (10.5 mg, 40µmol). The reaction mixture was degassed and sealed in a 5ϕ NMR tube. After heating of the solution at 60 °C for 24 h, at 70 °C for 24 h, at 80 °C for 24 h, and 100 °C for 120 h, no change was observed in the ¹H and ³¹P NMR spectra.

Reaction of 2,3-Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl}telluradistibirane (17) with (Me₂N)₃P. To a benzene- d_6 suspension (0.7 mL) of Bbt₂Sb₂Te (17, 13.0 mg, 8.0 µmol) was added (Me₂N)₃P (5.6 µL, 40 µmol). The reaction mixture was degassed and sealed in a 5 ϕ NMR tube. After heating of the solution at 40 °C for 24 h and at 120 °C for

7 h, no change was observed in the ¹H and ³¹P NMR spectra.

Reaction of 2,3-Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl}telluradistibirane (17) with (*n*-Bu)₃P. To a benzene- d_6 suspension (0.7 mL) of Bbt₂Sb₂Te (17, 10.0 mg, 6.2 µmol) was added (*n*-Bu)₃P (7.7 µL, 31 µmol). The reaction mixture was degassed and sealed in a 5 ϕ NMR tube. After heating of the solution at 35 °C for 2 days, no change was observed in the ¹H and ³¹P NMR spectra.

Reaction of 1,2-Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl}dibismuthene (BbtBi=BiBbt, 3) with Elemental Tellurium. To a benzene- d_6 solution (0.7 mL) of Bbt₂Bi₂ (3, 30 mg, 0.02 mmol) was added elemental tellurium (26 mg, 0.20 mmol, 10 equiv). The reaction mixture was degassed and sealed in a 5 ϕ NMR tube. After heating of the solution at 80 °C for 48 h, the sealed tube was opened. The reaction mixture was separated by GPLC (eluent: toluene) to afford ditelluride 18 (Bbt₂Te₂, 12.6 mg, 8.4 umol, 42%). **18**: dark green crystals, mp 239–240 °C (dec.); ¹H NMR (300 MHz, rt, C₆D₆) δ 0.34 (s, 72H), 0.35 (s, 54H), 3.05 (s, 4H), 7.05 (s, 4H); ¹³CNMR (75 MHz, rt, C₆D₆) δ 2.03 (q), 5.55 (q), 22.16 (s), 39.96 (d), 122.24 (d), 125.59 (s), 146.01 (s), 152.48 (s); 125 Te NMR (94 MHz, rt, C₆D₆) δ 328.71. HRMS (FAB) Found: *m*/*z* 1505.5448 ([M + H]⁺). Calcd for $C_{60}H_{135}Si_{14}^{128}Te^{130}Te$ 1505.5443 ([M + H]⁺). Anal. Calcd for C60H134Si14Te2: C, 47.91; H, 8.98%. Found: C, 48.20; H, 9.05%.

Reaction of 1,2-Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris-(trimethylsilyl)methyl]phenyl}dibismuthene (BbtBi=BiBbt, 3) with (*n*-Bu)₃P=Te. To a benzene solution (2.0 mL) of Bbt₂Bi₂ (3, 49.0 mg, 0.03 mmol) was added (*n*-Bu)₃PTe 23 mg, 0.06 mmol, 2.0 equiv) at room temperature. After standing the solution for 2 h, reprecipitation of the reaction mixture gave telluradibismirane **19** (23.3 mg, 0.013 mmol, 43%). **19**: dark brown crystals, mp 156 °C (dec.); ¹HNMR (400 MHz, rt, C₆D₆) δ 0.33 (s, 36H), 0.34 (s, 54H), 0.36 (s, 36H), 2.29 (s, 4H), 7.20 (s, 4H); ¹³C NMR (100 MHz, rt, C₆D₆) δ 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 (s). HRMS (FAB) Found: *m/z* 1795.6004 ([M + H]⁺). Calcd for C₆₀H₁₃₅Bi₂Si₁₄-¹³⁰Te 1795.6004 ([M + H]⁺). UV–vis (hexane) λ_{max} (\mathcal{E}) = 521 (2100), 450 (3200), 338 (18700) nm. Anal. Calcd for C₆₀H₁₃₄-Bi₂Si₁₄Te: C, 40.16; H, 7.53%. Found: C, 40.12; H, 7.48%.

Theoretical Calculations. All theoretical calculations were carried out using the Gaussian 98 program³⁸ with density function theory at the B3LYP method. The 6-311+G(2d,p) basis sets were used for structural optimization and NBO calculations. It was confirmed that the optimized structures have minimum energies by using frequency calculations.

X-ray Crystallographic Analyses of 7, 10, 14, 15, and 18. Crystal data of 5,¹² 8,¹⁷ 9,¹⁷ 11,¹² 13,¹³ 17,¹⁹ and 19¹⁹ have previously been reported. Single crystals of 7, 10, 14, 15, and 18 suitable for X-ray analysis were obtained by slow recrystallization from hexane (for 7, 14, and 15), benzene (for 10), and toluene (for 18) at room temperature (Fig. 7). The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71069$ Å, 1 Å = 0.1 nm) at $-170 \,^{\circ}\text{C}$ to $2\theta_{\text{max}} = 51^{\circ}$. The structures were solved by direct methods (SIR9739 or SHELXS-9740,41) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97⁴¹). All hydrogens were placed using AFIX instructions. Crystal data for [7-(C₆H₁₄)] (C₆₆H₁₄₈Bi₂- S_3Si_{14}): $M_r = 1849.24$, T = 103(2) K, triclinic, P1 (No. 2), a = 12.9780(3) Å, b = 18.1816(3) Å, c = 21.9077(6) Å, $\alpha =$ $69.9214(9)^{\circ}, \quad \beta = 73.7562(15)^{\circ}, \quad \gamma = 87.8865(10)^{\circ},$ V =



Fig. 7. Molecular structures of (a) triselenide 7 and (b) ditelluride 18 (thermal ellipsoid plots, 50% probability). Solvent molecules are omitted for clarity. Selected structural parameters: (a) C1–Se1, 0.1927(4) nm; Se1–Se2, 0.23344(6) nm; Se2–Se3, 0.23432(5) nm; Se3–C2, 0.1938(4) nm; C1–Se1–Se2, 100.23(10)°; Se1–Se2–Se3, 105.547(19)°; Se2–Se3–C2, 99.90(9)°; C1–Se1–Se2–Se3, 112.87(10)°; Se1–Se2–Se3–C2, 111.03(12)°. (b) C1–Te1, 0.21492(19) nm; Te1–Te2, 0.274016(19) nm; Te2–C2, 0.21469(18) nm; C1–Te1–Te2, 110.22(5)°; Te1–Te2–C2, 112.50(5)°; C1–Te1–Te2–C2, 116.83(8)°.

4651.32(18) Å³, Z = 2, $D_{calcd} = 1.320 \text{ g cm}^{-3}$, $\mu = 4.059 \text{ mm}^{-1}$, $\lambda = 0.71070$ Å, $2\theta_{\text{max}} = 51.0$, 40686 measured reflections, 17155 independent reflections [$R_{int} = 0.0250$], 803 refined parameters, GOF = 1.091, $R_1 = 0.0635$ and $wR_2 = 0.1852$ [$I > 2\sigma(I)$], $R_1 =$ 0.0751 and $wR_2 = 0.1926$ [for all data], largest diff. peak and hole 6.708 and $-3.421 \text{ e}\text{\AA}^{-3}$ (around Bi and S atoms). Crystal data for $[10 \cdot 2(C_6H_6)]$ (C₇₂H₁₄₆S₂Sb₂Si₁₄): $M_r = 1712.77$, T = 103(2) K, monoclinic, $P2_1/n$ (No. 14), a = 18.358(5) Å, b = 9.307(3) Å, $c = 27.865(8) \text{ Å}, \quad \beta = 101.429(3)^{\circ}, \quad V = 4667(2) \text{ Å}^3, \quad Z = 2,$ $D_{\text{calcd}} = 1.219 \,\text{g cm}^{-3}, \, \mu = 0.838 \,\text{mm}^{-1}, \, \lambda = 0.71070 \,\text{\AA}, \, 2\theta_{\text{max}} =$ 51.0, 33091 measured reflections, 7970 independent reflections $[R_{int} = 0.0395], 464$ refined parameters, GOF = 1.102, $R_1 =$ 0.0393 and $wR_2 = 0.0843$ [$I > 2\sigma(I)$], $R_1 = 0.0452$ and $wR_2 =$ 0.0452 [for all data], largest diff. peak and hole 0.679 and $-0.489 \text{ e}^{\text{\AA}-3}$. Crystal data for [14-0.5(C₆H₁₄)] (C₆₃H₁₄₁Se₃Si₁₄): $M_{\rm r} = 1528.90, T = 103(2) \,{\rm K}, \text{ triclinic}, P\bar{1}$ (No. 2), a =12.8566(5) Å, b = 18.9679(4) Å, c = 20.4422(6) Å, $\alpha =$ $62.2726(9)^{\circ}, \beta = 86.4864(10)^{\circ}, \gamma = 89.985(3)^{\circ}, V = 4402.1(2)$ Å³, Z = 2, $D_{\text{calcd}} = 1.153 \,\text{g cm}^{-3}$, $\mu = 1.476 \,\text{mm}^{-1}$, $\lambda =$ $0.71070 \text{ Å}, 2\theta_{\text{max}} = 50.0, 29344 \text{ measured reflections}, 15173$ independent reflections $[R_{int} = 0.0453]$, 845 refined parameters, GOF = 1.117, $R_1 = 0.0463$ and $wR_2 = 0.0780 [I > 2\sigma(I)]$, $R_1 =$ 0.0914 and $wR_2 = 0.0844$ [for all data], largest diff. peak and hole 0.991 and $-0.923 \text{ e}\text{\AA}^{-3}$. Crystal data for 15 (C₆₀H₁₃₄Bi₂-SeSi₁₄): $M_r = 1745.85$, T = 103(2) K, triclinic, P1 (No. 1), a =9.2258(4) Å, b = 12.5904(11) Å, c = 18.9877(13) Å, $\alpha =$ 86.747(4)°, $\beta = 84.096(3)°$, $\gamma = 73.881(3)°$, $V = 2106.7(3) Å^3$, $Z = 1, D_{\text{calcd}} = 1.376 \,\text{g cm}^{-3}, \ \mu = 4.833 \,\text{mm}^{-1}, \ \lambda = 0.71070 \,\text{\AA},$ $2\theta_{\text{max}} = 51.0, 18339$ measured reflections, 13681 independent reflections $[R_{int} = 0.0270]$, 737 refined parameters, GOF = 1.011, $R_1 = 0.0359$ and $wR_2 = 0.0858 [I > 2\sigma(I)]$, $R_1 = 0.0402$ and $wR_2 = 0.0874$ [for all data], largest diff. peak and hole 2.743 and $-1.490 \text{ e}\text{\AA}^{-3}$ (around Bi and Se atoms). Crystal data for $[18 \cdot (C_7 H_8)]$ (C₆₇H₁₄₂Te₂Si₁₄): $M_r = 1596.27$, T = 103(2) K, triclinic, $P\bar{1}$ (No. 2), a = 12.9377(5) Å, b = 18.2581(4) Å, c =18.9927(6) Å, $\alpha = 91.8263(9)^{\circ}$, $\beta = 99.1205(12)^{\circ}$, $\gamma =$ 89.899(3)°, $V = 4427.4(2) \text{ Å}^3$, Z = 2, $D_{\text{calcd}} = 1.197 \text{ g cm}^{-3}$, $\mu = 0.882 \,\mathrm{mm^{-1}}, \ \lambda = 0.71070 \,\mathrm{\AA}, \ 2\theta_{\mathrm{max}} = 51.0, \ 30658 \ \mathrm{mea-1}$ sured reflections, 16091 independent reflections $[R_{int} = 0.0289]$, 891 refined parameters, GOF = 1.029, $R_1 = 0.0264$ and $wR_2 =$ $0.0682 [I > 2\sigma(I)], R_1 = 0.0329$ and $wR_2 = 0.0707$ [for all data], largest diff. peak and hole 0.849 and -0.591 eÅ⁻³. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 650122 (for 7), 650123 (for 10), 650124 (for 14), 650125 (for 15), and 650126 (for 18). Copies of the data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; E-mail: deposit@ccdc. cam.ac.uk) or http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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