Bull. Chem. Soc. Jpn. Vol. 80, No. 12, 2425–2435 (2007)

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

Takahiro Sasamori, Eiko Mieda, and Norihiro Tokitoh[*]

Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011

Received July 26, 2007; E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp

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 (S_8) 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 $(n\text{-Bu})_3P{=}Te$ gave the corresponding telluradipnictiranes as in the case of their selenization reactions, though diphosphene **1** underwent no tellurization when $(n\text{-Bu})_3P{=}Te$ or elemental tellurium was used as a tellurium source.

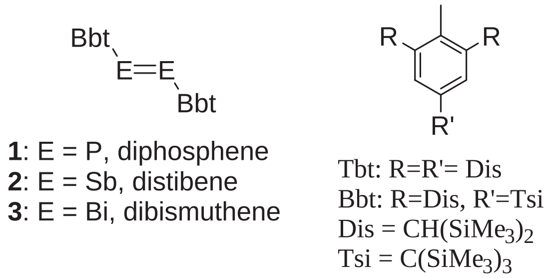
The chemistry of low-coordinated compounds of heavier main group elements has been one of the most attractive areas[1] since the first isolation of distannene $Dis_2Sn{=}SnDis_2$ [Dis = $CH(SiMe_3)_2$],[2] disilene $Mes_2Si{=}SiMes_2$ (Mes = mesityl),[3] and diphosphene Mes*P=PMes* (Mes* = 2,4,6-tri-*t*-butylphenyl)[4] 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, $Mes_2Si{=}SiMes_2$ 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 ($^3O_2$) 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 $Mes_2Si{=}SiMes_2$ using N_2O,[6] S_8,[7] Se,[8] and Te,[8] 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 distibene[9] and dibismuthene,[10] TbtE=ETbt (E = Sb and Bi, Tbt = 2,4,6-tris[bis(trimethylsilyl)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-dioxadistibetane[9] and 1,3,2,4-dioxadibismetane[11] 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] distibene,[11,13] and dibismuthene[11] (BbtE=EBbt, E = P, Sb, and Bi) together with the first stable stibabismuthene[14] 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 thia- and 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

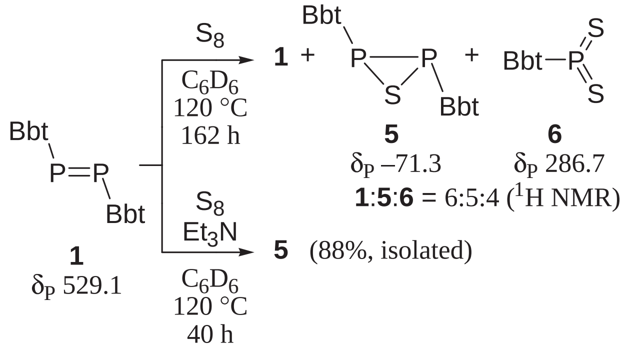
Published on the web December 13, 2007; doi:10.1246/bcsj.80.2425



1: E = P, diphosphene
2: E = Sb, distibene
3: E = Bi, dibismuthene

Tbt: R=R'= Dis
Bbt: R=Dis, R'=Tsi
Dis = $CH(SiMe_3)_2$
Tsi = $C(SiMe_3)_3$

Scheme 1.



1
δ_P 529.1

5
δ_P −71.3

6
δ_P 286.7

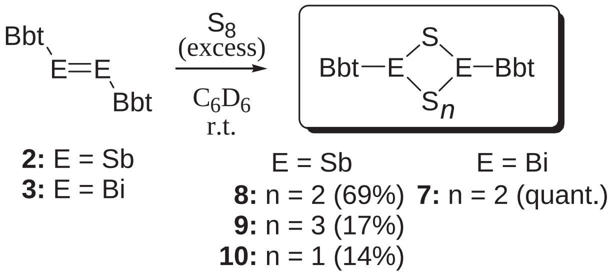
1:**5**:**6** = 6:5:4 (^{1}H NMR)

5 (88%, isolated)

Scheme 2.

(Scheme 2), that is, heating of **1** with elemental sulfur (S_8, 4 equiv as S) at 120 °C in C_6D_6 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 ^{1}H NMR spectrum.[12] On the other hand, the reaction of **1** with elemental sulfur (S_8, 10 equiv as S) in the presence of Et_3N (10 equiv) at 120 °C in C_6D_6 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%), 1,2,3,5,4,6-tetrathiadistibinane **9** (17%), and 1,3,2,4-dithiadistibetane **10** (14%), without any other identifiable compound as judged by ^{1}H NMR 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.

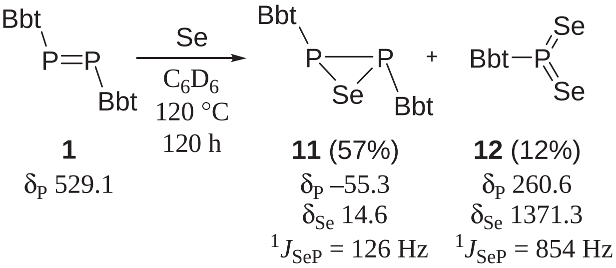


2: E = Sb
3: E = Bi

E = Sb
8: n = 2 (69%)
9: n = 3 (17%)
10: n = 1 (14%)

E = Bi
7: n = 2 (quant.)

Scheme 3.



1
δ_P 529.1

11 (57%)
δ_P −55.3
δ_{Se} 14.6
$^1J_{SeP}$ = 126 Hz

12 (12%)
δ_P 260.6
δ_{Se} 1371.3
$^1J_{SeP}$ = 854 Hz

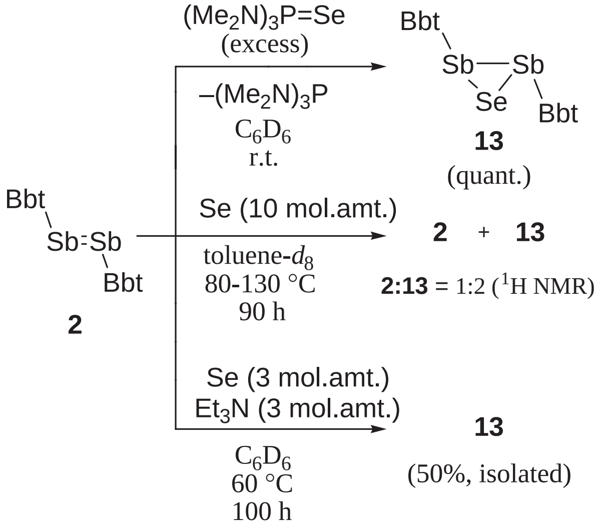
Scheme 4.

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 (S_8) in the hope of obtaining Bbt-substituted thiadistibirane, the ^{1}H 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 C_6D_6 did not occur, whereas 1,2,4,3,5-trithiadistibolane **8** underwent desulfurization with triphenylphosphine under the same conditions leading to the quantitative formation of **10**.

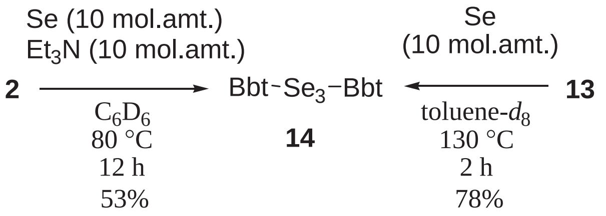
Selenization Reactions of the Dipnictenes. The diphosphene, BbtP=PBbt (**1**), has been reported to react with elemental selenium to afford the corresponding selenadiphosphirane **11** together with diselenoxophosphorane **12** as well as the case of the selenization of Mes*P=PMes* (**4**) (Scheme 4).[16c]

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 C_6D_6 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 ^{1}H NMR spectroscopy). It was found that the addition of 3 molar amount of Et_3N promoted the selenization reaction of **2**. Indeed, heating of the C_6D_6 solution of **2** with elemental selenium (grey Se, 3 molar amount) in the presence of Et_3N (3 molar amount) at 60 °C for 100 h afforded selenadistibirane **13** quantitatively as judged by the ^{1}H NMR spectra (isolated yield; 50%) (Scheme 5).

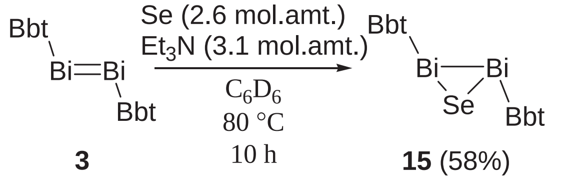
The selenization reactions of **2** were attempted under much



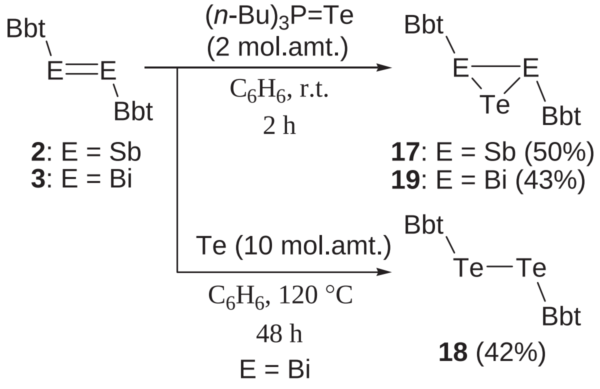
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

severer conditions in the expectation of the formation of other cyclic polyselenides, such as diselenadistibetanes and/or triselenadistibolanes. However, an unexpected product, triselenide $BbtSe_3Bbt$ (**14**), was obtained (53%) as a stable product, when **2** was treated with elemental selenium (10 molar amount) in the presence of Et_3N (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 $BbtSe_3Bbt$ in 78% yield (Scheme 6).

The selenization reaction using elemental selenium in the presence of Et_3N 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 Et_3N (3.1 molar amount) in C_6D_6 at 80 °C for 10 h afforded selenadibismirane **15** quantitatively, determined from the ^{1}H NMR 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 six-membered 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 C_6D_6 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 $(n\text{-Bu})_3P{=}Te$, 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 $(n\text{-Bu})_3P{=}Te$ 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 PPh_3 (at 100 °C), $P(NMe_2)_3$ (at 120 °C), and $P(\textit{n}\text{-Bu})_3$ (at 35 °C), in C_6D_6 in a sealed tube under heating conditions, but also toward photo-irradiation of the C_6D_6 solution using 100 W medium pressure Hg lamp at 60 °C in a Pyrex sealed tube. On the other hand, heating a C_6D_6 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: $Ph_2P–PPh_2$,[23] 0.2217 nm; $Ph_2Sb–SbPh_2$,[24] 0.2837 nm; $Ph_2Bi–BiPh_2$,[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 $Se[PPh_2Cr(CO)_5]_2$,[27] 0.2272 nm; Sb–Se in $(DisSbSe)_2[W(CO)_5]_2$[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 $(Mes_2Bi)_2Se$,[30] 0.2651 nm; Bi–Te in $(Dis_2Bi)_2Te$,[28] 0.2872–0.2889 nm). These structural features observed in the chalcogenadipnictiranes can be interpreted in terms of the tendency

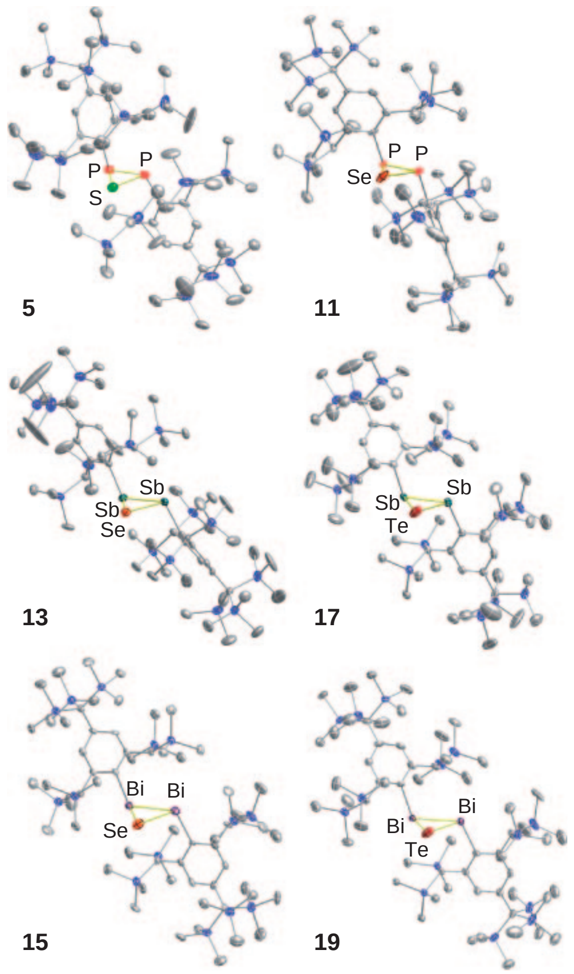
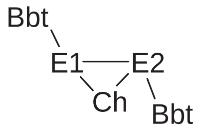


Fig. 1. ORTEP drawings of chalcogenadipnictiranes (50% probability). Hydrogen atoms, solvent molecules, and the minor part of the disordered moieties were omitted for clarity.

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

	Bond lengths/Å[a)]			Bond angles/degree			Ref.
	E1–E2	E1–Ch	Ch–E2	Ch–E1–E2	Ch–E2–E1	E1–Ch–E2	
5: E = P Ch = S	2.2349(12)	2.1083(13)	2.1285(12)	58.61(4)	57.72(4)	63.67(4)	12
11: E = P Ch = Se	2.250(3)	2.250(3)	2.270(3)	60.59(9)	59.71(9)	59.70(8)	12
13: E = Sb Ch = Se	2.852(2)	2.562(2)	2.565(1)	56.25(4)	56.15(4)	67.60(5)	13
17: E = Sb Ch = Te	2.8833(6)	2.7607(7)	2.7719(6)	58.781(16)	58.402(17)	62.817(16)	18
15: E = Bi Ch = Se	3.0105(4)	2.6492(9)	2.6649(8)	55.741(19)	55.25(2)	69.01(2)	This work
19: E = Bi Ch = Te	3.0388(3)	2.8546(4)	2.8648(4)	58.068(9)	57.742(9)	64.190(9)	18

a) 1 Å = 0.1 nm.

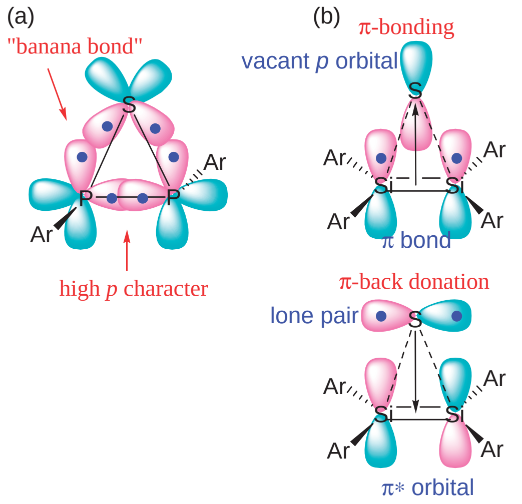
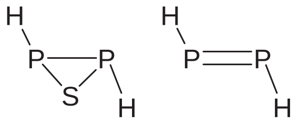


Fig. 2. Depiction of bonding properties for (a) a thiadiphosphirane and (b) a thiadisilirane.

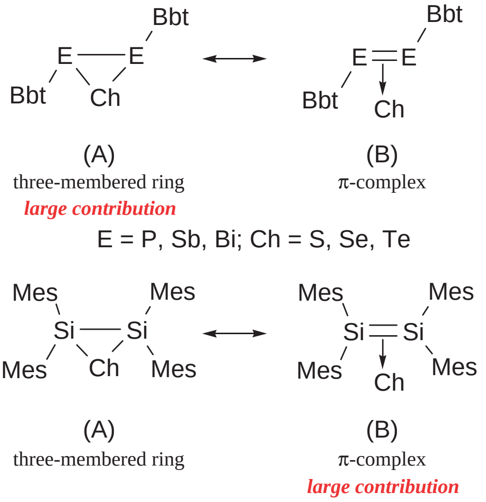


20 **21**

Scheme 9.

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 three-membered 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 sp^3-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 "banana-bonds" (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 $\sigma_{PP} = 0.5(sp^{8.22})P + 0.5(sp^{8.22})P$. 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 (S_8, 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 chalcogenadipnictiranes[32] differ from those of chalcogenadisiliranes,[33] which should consist of π-bonding 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.



22a (Ch = S)
22b (Ch = Se)
22c (Ch = Te)

Fig. 3. Structures of chalcogenadipnictiranes and chalcogenadisiliranes.

In ^{31}P, ^{77}Se, ^{125}Te 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, $^1J_{SeP} = 126$ 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 ^{125}Te 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 Ph_2SbS(8-quinolyl)[35]] and Bi–S [0.2572, 0.2557 nm in $S(BiDis_2)_2$[28]], respectively. 1,2,4,3,5-Trithiadibismolane **7** was found to possess a half-chair 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 1,2,3,5,4,6-tetrathiadistibinane 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*-$Dis_2Sb_2S_2$ [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 (S_8, Se, and Te) or phosphine chalcogenides [$(Me_2N)_3P{=}Se$ or $(n\text{-}Bu)_3P{=}Te$]. It was found that the doubly bonded systems between heavier group 15 elements are good precursors for the unique heterocycles containing pnictogen atoms. The 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.

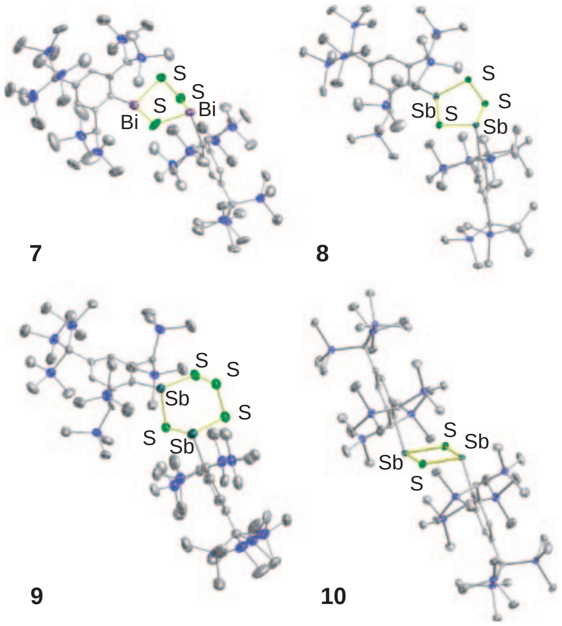


Fig. 4. ORTEP drawings of cyclic polysulfides **7**–**10** (50% probability). Hydrogen atoms and solvent molecules were omitted for clarity.

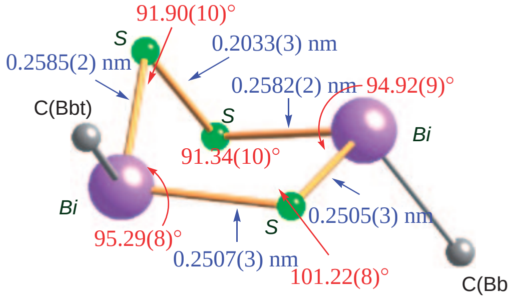


Fig. 5. The structure of the central ring skeleton of 1,2,4,3,5-trithiadibismolane **7**.

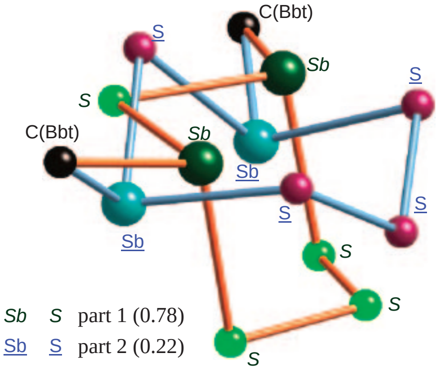
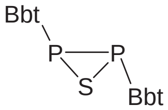
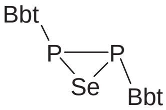
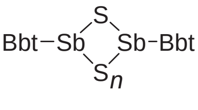
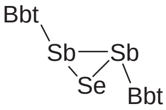
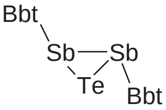
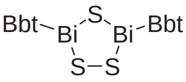
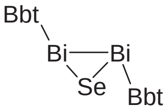
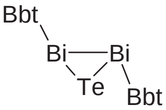


Fig. 6. Disordered structure of the central ring skeleton of 1,2,3,5,4,6-tetrathiadistibinane **9**.

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

	Sulfurization (S_8)	Selenization (Se)	Tellurization [$(n\text{-}Bu)_3P{=}Te$]
BbtP=PBbt (**1**)			—
BbtSb=SbBbt (**2**)	 n = 1, 2, 3		
BbtBi=BiBbt (**3**)			

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 ^{1}H NMR (400 or 300 MHz) and ^{13}C NMR (100 or 75 MHz) spectra were measured in $CDCl_3$ or C_6D_6 on a JEOL AL-400 or AL-300 spectrometer using $CHCl_3$ (7.25 ppm) or C_6D_5H (7.15 ppm) as an internal standard for ^{1}H NMR spectrometry, and using $CDCl_3$ (77.0 ppm) or C_6D_6 (128.0 ppm) as the standard for ^{13}C NMR spectrometry. The ^{31}P (121 MHz), ^{77}Se (75 or 57 MHz), and ^{125}Te 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% H_3PO_4 in H_2O (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. Bbt_2Sb_2 (**2**),[11] Bbt_2Bi_2 (**3**),[11] and $(n\text{-Bu})_3PTe$[37] 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 Bbt_2Sb_2 (**2**, 60.0 mg, 0.04 mmol) was added elemental sulfur (S_8, 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 ^{1}H 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.); ^{1}H NMR (300 MHz, rt, C_6D_6) δ 0.35 (s, 72H), 0.37 (s, 54H), 2.77 (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 $C_{60}H_{134}S_2Sb_2Si_{14}$: C, 46.30; H, 8.68%. Found: C, 46.75; H, 8.70%. **8**: yellow crystals, mp 186–187 °C (dec.); ^{1}H 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, C_6D_6) 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 $C_{60}H_{134}S_3Sb_2Si_{14}\cdot C_6H_{14}$: C, 47.65; H, 8.95%. Found: C, 47.66; H, 9.00%. **9**: yellow crystals, mp 147 °C (dec.); ^{1}H NMR (300 MHz, rt, C_6D_6) 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 $C_{60}H_{134}S_4Sb_2Si_{14}\cdot C_6H_{14}$: 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 (S_8). To a benzene solution (2 mL) of Bbt_2Sb_2 (**2**, 149.0 mg, 0.10 mmol) was added elemental sulfur (S_8, 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 ^{1}H 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**: ^{1}H NMR (300 MHz, rt, C_6D_6) 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 $Bbt_2Sb_2S_3$ (**8**, 5.0 mg, 3.1 μmol) was added triphenylphosphine (5.0 mg, 19 μmol). The reaction mixture was degassed and sealed in a 5ϕ 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 ^{1}H NMR spectrum.

Reaction of 1,2-Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}dibismuthene (BbtBi=BiBbt, 3) with Elemental Sulfur (S_8). To a benzene solution (2 mL) of Bbt_2Bi_2 (**3**, 101 mg, 60.6 μmol) was added elemental sulfur (S_8, 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.); ^{1}H NMR (300 MHz, rt, C_6D_6) δ 0.35 (s, 126H), 2.17 (s, 4H), 7.54 (s, 4H); ^{13}C NMR (75 MHz, rt, C_6D_6) 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 $C_{60}H_{135}Bi_2S_3Si_{14}$ 1761.6103 ($[M+H]^+$). Anal. Calcd for $C_{60}H_{134}S_3Bi_2Si_{14}\cdot C_6H_{14}$: 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 Bbt_2Sb_2 (**2**, 30.0 mg, 0.02 mmol) was added elemental selenium (gray Se, 4.7 mg, 0.06 mmol, 3 molar amount) and Et_3N (8.4 μL, 0.06 mmol, 3 molar amount). The reaction mixture was degassed and sealed in a 5ϕ 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 Bbt_2Sb_2 (**2**, 71.6 mg, 0.048 mmol) was added elemental selenium (gray Se, 11 mg, 0.14 mmol, 10 molar amount) and Et_3N (20 μL, 0.14 mmol, 10 molar amount). The reaction mixture was degassed and sealed in a 5ϕ NMR tube. After the suspension was heated at 80 °C for 24 h, recrystallization of the reaction mixture from hexane afforded $BbtSe_3Bbt$ (**14**, 38 mg, 0.026 mmol, 53%). **14**: orange crystal, mp 244 °C (dec.); ^{1}H NMR (300 MHz, rt, C_6D_6) δ 0.31 (s, 72H), 0.34 (s, 54H), 3.52 (s, 4H), 7.07 (s, 4H); ^{13}C NMR (75 MHz, rt, C_6D_6) 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). ^{77}Se NMR (57 MHz, rt, C_6D_6) δ 764, 455. HRMS (FAB) Found: m/z 1486.4751 ($[M]^+$). Calcd for $C_{60}H_{134}Se_3Si_{14}$ 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 Bbt_2Sb_2Se (**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: $CHCl_3$) to give $BbtSe_3Bbt$ (**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 Bbt_2Bi_2 (**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 5ϕ NMR tube. After the suspension was heated at 80 °C for 10 h, 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.); ^{1}H NMR (400 MHz, rt, C_6D_6) 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, C_6D_6) 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, C_6D_6) δ −136.64. HRMS (FAB) Found: m/z 1745.6084 ($[M + H]^+$). Calcd for $C_{60}H_{135}Bi_2SeSi_{14}$ 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 Bbt_2Sb_2 (**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 5ϕ 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.); ^{1}H 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); ^{13}C NMR (75 MHz, rt, C_6D_6) 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); ^{125}Te NMR (94 MHz, rt, toluene-d_8) δ −622.3. HRMS (FAB) Found: m/z 1619.4440 ($[M + H]^+$). Calcd for $C_{60}H_{135}{}^{121}Sb_2Si_{14}{}^{130}Te$ 1619.4472 ($[M + H]^+$). UV–vis (hexane) λ_{max} (ε) = 458 (680), 390 (3100), 346 (8500) nm. Anal. Calcd for $C_{60}H_{134}Sb_2Si_{14}Te$: 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$)_3$P=Te. To a benzene solution (0.6 mL) of Bbt_2Sb_2 (**2**, 70.4 mg, 0.05 mmol) was added (n-Bu)$_3$PTe (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 Bbt_2Sb_2Te (**17**, 13.0 mg, 8.0 µmol) was added triphenylphosphine (10.5 mg, 40 µmol). 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 ^{1}H and ^{31}P NMR spectra.

Reaction of 2,3-Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}telluradistibirane (17) with $(Me_2N)_3$P. To a benzene-d_6 suspension (0.7 mL) of Bbt_2Sb_2Te (**17**, 13.0 mg, 8.0 µmol) was added $(Me_2N)_3P$ (5.6 µL, 40 µmol). The reaction mixture was degassed and sealed in a 5ϕ 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 ^{1}H and ^{31}P NMR spectra.

Reaction of 2,3-Bis{2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}telluradistibirane (17) with (n-Bu)$_3$P. To a benzene-d_6 suspension (0.7 mL) of Bbt_2Sb_2Te (**17**, 10.0 mg, 6.2 µmol) was added (n-Bu)$_3$P (7.7 µL, 31 µmol). The reaction mixture was degassed and sealed in a 5ϕ NMR tube. After heating of the solution at 35 °C for 2 days, no change was observed in the ^{1}H and ^{31}P 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 Bbt_2Bi_2 (**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 5ϕ 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** (Bbt_2Te_2, 12.6 mg, 8.4 µmol, 42%). **18**: dark green crystals, mp 239–240 °C (dec.); ^{1}H NMR (300 MHz, rt, C_6D_6) δ 0.34 (s, 72H), 0.35 (s, 54H), 3.05 (s, 4H), 7.05 (s, 4H); ^{13}C NMR (75 MHz, rt, C_6D_6) 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, C_6D_6) 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 $C_{60}H_{134}Si_{14}Te_2$: 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)$_3$P=Te. To a benzene solution (2.0 mL) of Bbt_2Bi_2 (**3**, 49.0 mg, 0.03 mmol) was added (n-Bu)$_3$PTe 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.); ^{1}H NMR (400 MHz, rt, C_6D_6) δ 0.33 (s, 36H), 0.34 (s, 54H), 0.36 (s, 36H), 2.29 (s, 4H), 7.20 (s, 4H); ^{13}C NMR (100 MHz, rt, C_6D_6) 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 $C_{60}H_{135}Bi_2Si_{14}{}^{130}Te$ 1795.6004 ($[M + H]^+$). UV–vis (hexane) λ_{max} (ε) = 521 (2100), 450 (3200), 338 (18700) nm. Anal. Calcd for $C_{60}H_{134}Bi_2Si_{14}Te$: 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 program[38] 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 **19**[19] 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 Kα radiation ($\lambda = 0.71069$ Å, 1 Å = 0.1 nm) at −170 °C to $2\theta_{max} = 51°$. The structures were solved by direct methods (SIR97[39] or SHELXS-97[40,41]) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97[41]). All hydrogens were placed using AFIX instructions. Crystal data for **[7·(C$_6$H$_{14}$)]** ($C_{66}H_{148}Bi_2S_3Si_{14}$): $M_r = 1849.24$, $T = 103(2)$ K, triclinic, $P\bar{1}$ (No. 2), $a = 12.9780(3)$ Å, $b = 18.1816(3)$ Å, $c = 21.9077(6)$ Å, $\alpha = 69.9214(9)°$, $\beta = 73.7562(15)°$, $\gamma = 87.8865(10)°$, $V =$

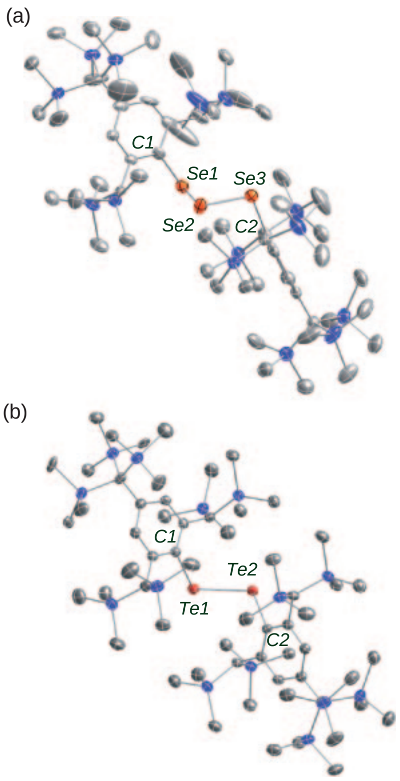


Fig. 7. Molecular structures of (a) triselenide **7** and (b) ditelluride **18** (thermal ellipsoid plots, 50% probability). Solvent molecules are omitted for clarity. Selected structural parameters: (a) C1–Se1, 0.1927(4) nm; Se1–Se2, 0.23344(6) nm; Se2–Se3, 0.23432(5) nm; Se3–C2, 0.1938(4) nm; C1–Se1–Se2, 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) Å^3, $Z = 2$, $D_{\text{calcd}} = 1.320\,\text{g cm}^{-3}$, $\mu = 4.059\,\text{mm}^{-1}$, $\lambda = 0.71070$ Å, $2\theta_{\max} = 51.0$, 40686 measured reflections, 17155 independent reflections [$R_{\text{int}} = 0.0250$], 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 eÅ^{-3} (around Bi and S atoms). Crystal data for **[10•2(C$_6$H$_6$)]** ($C_{72}H_{146}S_2Sb_2Si_{14}$): $M_r = 1712.77$, $T = 103(2)$ K, monoclinic, $P2_1/n$ (No. 14), $a = 18.358(5)$ Å, $b = 9.307(3)$ Å, $c = 27.865(8)$ Å, $\beta = 101.429(3)°$, $V = 4667(2)$ Å^3, $Z = 2$, $D_{\text{calcd}} = 1.219\,\text{g cm}^{-3}$, $\mu = 0.838\,\text{mm}^{-1}$, $\lambda = 0.71070$ Å, $2\theta_{\max} = 51.0$, 33091 measured reflections, 7970 independent reflections [$R_{\text{int}} = 0.0395$], 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 eÅ^{-3}. Crystal data for **[14•0.5(C$_6$H$_{14}$)]** ($C_{63}H_{141}Se_3Si_{14}$): $M_r = 1528.90$, $T = 103(2)$ K, triclinic, $P\bar{1}$ (No. 2), $a = 12.8566(5)$ Å, $b = 18.9679(4)$ Å, $c = 20.4422(6)$ Å, $\alpha = 62.2726(9)°$, $\beta = 86.4864(10)°$, $\gamma = 89.985(3)°$, $V = 4402.1(2)$ Å^3, $Z = 2$, $D_{\text{calcd}} = 1.153\,\text{g cm}^{-3}$, $\mu = 1.476\,\text{mm}^{-1}$, $\lambda = 0.71070$ Å, $2\theta_{\max} = 50.0$, 29344 measured reflections, 15173 independent reflections [$R_{\text{int}} = 0.0453$], 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 eÅ^{-3}. Crystal data for **15** ($C_{60}H_{134}Bi_2SeSi_{14}$): $M_r = 1745.85$, $T = 103(2)$ 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, $Z = 1$, $D_{\text{calcd}} = 1.376\,\text{g cm}^{-3}$, $\mu = 4.833\,\text{mm}^{-1}$, $\lambda = 0.71070$ Å, $2\theta_{\max} = 51.0$, 18339 measured reflections, 13681 independent reflections [$R_{\text{int}} = 0.0270$], 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 eÅ^{-3} (around Bi and Se atoms). Crystal data for **[18•(C$_7$H$_8$)]** ($C_{67}H_{142}Te_2Si_{14}$): $M_r = 1596.27$, $T = 103(2)$ K, triclinic, $P\bar{1}$ (No. 2), $a = 12.9377(5)$ Å, $b = 18.2581(4)$ Å, $c = 18.9927(6)$ Å, $\alpha = 91.8263(9)°$, $\beta = 99.1205(12)°$, $\gamma = 89.899(3)°$, $V = 4427.4(2)$ Å^3, $Z = 2$, $D_{\text{calcd}} = 1.197\,\text{g cm}^{-3}$, $\mu = 0.882\,\text{mm}^{-1}$, $\lambda = 0.71070$ Å, $2\theta_{\max} = 51.0$, 30658 measured reflections, 16091 independent reflections [$R_{\text{int}} = 0.0289$], 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.

This work was partially supported by Grants-in-Aid for Creative Scientific Research (No. 17GS0207), Science Research on Priority Areas (No. 19027024, "Synergy of Elements"), Young Scientist (B) (No. 18750030), and the 21st Century COE and the Global COE Programs, Kyoto University Alliance for Chemistry from Ministry of Education, Culture, Sports, Science and Technology, Japan. This manuscript was written at TU Braunschweig during the tenure of a von Humboldt Senior Research Award of one of the authors (Tokitoh), who is grateful to von Humboldt Stiftung for their generosity and to Professors Reinhard Schmutzler and Wolf-Walther du Mont for their warm hospitality.

References

Dedicated to Professor Renji Okazaki on the occasion of his 70th birthday.

1 For reviews, see: a) L. Weber, *Chem. Rev.* **1992**, *92*, 1839. b) G. Raabe, J. Michl, *Chem. Rev.* **1985**, *85*, 419. c) P. P. Power, *Chem. Rev.* **1999**, *99*, 3463. d) A. G. Brook, M. A. Brook, *Adv. Organomet. Chem.* **1996**, *39*, 71. e) N. Tokitoh, R. Okazaki, *Coord. Chem. Rev.* **2000**, *210*, 251. f) N. Tokitoh, *J. Organomet. Chem.* **2000**, *611*, 217. g) K. M. Baines, W. G. Stibbs, *Adv. Organomet. Chem.* **1996**, *39*, 275. h) T. Sasamori, N. Tokitoh, in *Encyclopedia of Inorganic Chemistry II*, ed. by R. Bruce King, John Wiley & Sons, Chichester, **2005**, pp. 1698–1740.

2 a) P. J. Davidson, M. F. Lappert, *J. Chem. Soc., Chem. Commun.* **1973**, 317. b) D. E. Goldberg, D. H. Harris, M. F. Lappert, K. M. Thomas, *J. Chem. Soc., Chem. Commun.* **1976**, 261. c) M. F. Lappert, *Adv. Chem. Ser.* **1976**, 256. d) D. E. Goldberg, P. B. Hitchcock, M. F. Lappert, K. M. Thomas, A. J. Thorne, T. Fjeldberg, A. Haaland, B. E. R. Schilling, *J. Chem. Soc., Dalton Trans.* **1986**, 2387.

3 R. West, M. Fink, J. Michl, *Science* **1981**, *214*, 1343.

4 M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* **1981**, *103*, 4587.

5 For examples: a) T. Tsumuraya, Y. Kabe, W. Ando, *J. Chem. Soc., Chem. Commun.* **1990**, 1159. b) T. Tsumuraya, S. Sato, W. Ando, *Organometallics* **1988**, *7*, 2015. c) N. Tokitoh, K. Kishikawa, R. Okazaki, T. Sasamori, N. Nakata, N. Takeda, *Polyhedron* **2002**, *21*, 563. d) M. Driess, S. Rell, H. Pritzkow, *J. Chem. Soc., Chem. Commun.* **1995**, 253. e) K. L. Mckillop, G. R. Gillette, D. R. Powell, R. West, *J. Am. Chem. Soc.* **1992**, *114*, 5203. f) M. J. Fink, K. J. Haller, R. West, J. Michl, *J. Am. Chem. Soc.* **1984**, *106*, 822. g) A. J. Millevolte, D. R. Powell, S. G. Johnson, R. West, *Organometallics* **1992**, *11*, 1091. h) A. Schäfer, M. Weidenbruch, W. Saak, S. Pohl, H. Marsmann, *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 962. i) A. Schäfer, M. Weidenbruch, W. Saak, S. Pohl, H. Marsmann, *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 834. j) H. Suzuki, N. Tokitoh, R. Okazaki, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2471. k) S. Masamune, S. A. Batcheller, J. Park, W. M. Davis, O. Yamashita, Y. Ohta, Y. Kabe, *J. Am. Chem. Soc.* **1989**, *111*, 1888.

6 H. B. Yokelson, A. J. Millevolte, G. R. Gillette, R. West, *J. Am. Chem. Soc.* **1987**, *109*, 6865.

7 R. West, D. J. Deyoung, K. J. Haller, *J. Am. Chem. Soc.* **1985**, *107*, 4942.

8 R. P.-K. Tan, G. R. Gillette, D. R. Powell, R. West, *Organometallics* **1991**, *10*, 546.

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

10 N. Tokitoh, Y. Arai, R. Okazaki, S. Nagase, *Science* **1997**, *277*, 78.

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

12 T. Sasamori, N. Takeda, N. Tokitoh, *J. Phys. Org. Chem.* **2003**, *16*, 450.

13 N. Tokitoh, T. Sasamori, R. Okazaki, *Chem. Lett.* **1998**, 725.

14 T. Sasamori, N. Takeda, N. Tokitoh, *Chem. Commun.* **2000**, 1353.

15 T. Sasamori, N. Takeda, M. Fujio, M. Kimura, S. Nagase, N. Tokitoh, *Angew. Chem., Int. Ed.* **2002**, *41*, 139.

16 In the sulfurization reaction of Mes*P=PMes*, the corresponding diphosphene-1-sulfide, Mes*P(S)=PMes*, was obtained as isolable intermediate. a) M. Yoshifuji, K. Shibayama, I. Shima, N. Inamoto, *Phosphorus Sulfur* **1983**, *18*, 11. b) M. Yoshifuji, K. Shibayama, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Chem. Soc., Chem. Commun.* **1983**, 862. c) M. Yoshifuji, K. Shibayama, N. Inamoto, *Chem. Lett.* **1984**, 603.

17 Sulfurization reaction of distibene **2** has already been reported as a preliminary communication, see: T. Sasamori, E. Mieda, N. Takeda, N. Tokitoh, *Chem. Lett.* **2004**, *33*, 104.

18 Compound **X** might be the corresponding thiadistibirane derivative, since it was formed only by using 1 equiv of elemental sulfur (S_8) or 1 equiv of stilbene sulfide as a sulfurization reagent of distibene **2**.

19 Tellurization reactions of distibene **2** and dibismuthene **3** have already been reported as a preliminary communication, see: T. Sasamori, E. Mieda, N. Takeda, N. Tokitoh, *Angew. Chem., Int. Ed.* **2005**, *44*, 3717.

20 a) W.-W. du Mont, T. Severengiz, *Z. Anorg. Allg. Chem.* **1993**, *619*, 1083. b) W.-W. du Mont, R. Hensel, T. Severengiz, *Phosphorus Sulfur* **1983**, *18*, 73.

21 Sometimes, the use of tributylphosphine telluride as a tellurium source promotes a tellurization reaction of a double-bond compound of heteroatoms giving a tellurium containing three-membered ring compound. For example, the synthesis of an alkylidenetelluragermirane derivative using tributylphosphine telluride as a tellurium source has been reported, see: K. Kishikawa, N. Tokitoh, R. Okazaki, *Organometallics* **1997**, *16*, 5127.

22 The relatively low yields of **17** and **18** are probably due to their gradual decomposition during recrystallization under the ambient light. Isolated **17** and **18** are somewhat sensitive to the light under the ambient conditions to afford unidentifiable black powder.

23 A. Dashti-Mommertz, B. Neumüller, *Z. Anorg. Allg. Chem.* **1999**, *625*, 954.

24 a) G. Becker, H. Freudenblum, C. Witthauer, *Z. Anorg. Allg. Chem.* **1982**, *492*, 37. b) K. von Deuten, D. Rehder, *Cryst. Struct. Commun.* **1980**, *9*, 167.

25 F. Calderazzo, R. Poli, G. Pelizzi, *J. Chem. Soc., Dalton Trans.* **1984**, 2365.

26 B. Cetinkaya, P. B. Hitchcock, M. F. Lappert, A. J. Thorne, H. Goldwhite, *J. Chem. Soc., Chem. Commun.* **1982**, 691.

27 K. Merzweiler, H. J. Kersten, *Z. Naturforsch., B: Chem. Sci.* **1991**, *46*, 1025.

28 H. J. Breunig, I. Ghesner, E. Lork, *J. Organomet. Chem.* **2002**, *664*, 130.

29 S. S. Dhingra, R. C. Haushalter, *J. Am. Chem. Soc.* **1994**, *116*, 3651.

30 H. J. Breunig, K. H. Ebert, R. E. Schulz, M. Wieber, I. Sauer, *Z. Naturforsch., B: Chem. Sci.* **1995**, *50*, 735.

31 K. B. Wiberg, *Acc. Chem. Res.* **1996**, *29*, 229.

32 There are a few reports on the theoretical studies on a thiadiphosphirane, see: a) T. Matsushita, K. Hirotsu, T. Higuchi, K. Nishimoto, M. Yoshifuji, K. Shibayama, N. Inamoto, *Tetrahedron Lett.* **1984**, *25*, 3321. b) R. Gleiter, W. Schäfer, M. Baudler, *J. Am. Chem. Soc.* **1985**, *107*, 8043.

33 The bonding properties of a thiadisilirane have been discussed based on theoretical studies. For examples, see: a) J. F. Liebman, P. N. Skancke, *Int. J. Quantum Chem.* **1996**, *58*, 707. b) J. A. Boatz, M. S. Gordon, *J. Phys. Chem.* **1989**, *93*, 3025. c) R. S. Grev, H. F. Schaefer, *J. Am. Chem. Soc.* **1987**, *109*, 6577. d) Y. Naruse, J. Ma, S. Inagaki, *J. Phys. Chem. A* **2003**, *107*, 2860. e) T. Kudo, S. Akiba, Y. Kondo, H. Watanabe, K. Morokuma, T. Vreven, *Organometallics* **2003**, *22*, 4721.

34 N. Tokitoh, N. Choi, W. Ando, in *Comprehensive Heterocyclic Chemistry II*, ed. by A. R. Katritzky, C, W. Rees, E. F. Scriven, Pergamon, Oxford, **1996**, Vol. 1A, pp. 457–468.

35 H. Preut, U. Praeckel, F. Huber, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *42*, 1138.

36 H. J. Breunig, L. Ghesner, E. Lork, *Appl. Organomet. Chem.* **2002**, *16*, 547.

37 R. A. Zingaro, *J. Organomet. Chem.* **1963**, *1*, 200.

38 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe,

P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98, Revision A.9*, Gaussian, Inc., Pittsburgh PA, **1998**.

39 A. Altomare, M. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115.

40 G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

41 G. M. Sheldrick, *SHELX-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**.