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Synthesis and Characterization of Group 14 Dialkylmetal Chalcogenones $R^{N}{}_{2}M{=}E$ [$R^{N} =$ $CH(SiMe_3)C_9H_6N$-8 or $CPh(SiMe_3)C_5H_4N$-2; M = Ge or Sn; E = S, Se, or Te]

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Treatment of group 14 metal dialkyl $MR^{N}{}_{2}$ (M = Ge or Sn) with elemental chalcogens (sulfur, selenium, or tellurium) in THF afforded the corresponding chalcogenones $R^{N}{}_{2}M{=}E$ [$R^{N} = CPh(SiMe_3)C_5H_4N$-2; M = Ge; E = S (**4**), Se (**5**), Te (**6**); M = Sn; E = S (**7**), Se (**8**); $R^{N} = CH(SiMe_3)C_9H_6N$-8, M = Sn; E = Se (**10**), Te (**11**)]. In contrast, a sulfido-bridged dimer $[R^{N}{}_{2}Sn(\mu\text{-}S)]_2$ (**9**) was obtained from similar reaction of $SnR^{N}{}_{2}$ [$R^{N} = CH(SiMe_3)C_9H_6N$-8] with elemental sulfur. These chalcogenones have been characterized by elemental analysis, ^{1}H, ^{13}C, ^{119}Sn, ^{77}Se, and ^{125}Te NMR, and mass spectroscopy. X-ray structure of **5**, **8**, **9**, **10**, and **11** have been determined. It was revealed that compounds **5**, **8**, **10**, and **11** consist of a terminal metal−chalcogen bond with the ligands R^{N} acting in a C,N-chelate fashion, except for **9**, which is a sulfido-bridged dimer.

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Introduction

Compounds featuring a double bond between heavier main-group G14−16 elements were considered to be unstable due to the weak pπ−pπ bonding.[1] Nevertheless, thioketone analogues comprised of group 14 and group 16 congeners such as silanethione (Si=S),[2,3] silaneselone (Si=Se),[2] germanethione (Ge=S),[3−5] germaneselone (Ge=Se),[6,7] stannanethione (Sn=S), and stannaneselone (Sn=Se) have been isolated in the past few years.[8−11] These compounds were either base-stabilized[2,3] or stabilized by using a sterically hindered protecting group as in [Tip(Tbt)Ge=E] [E = S and Se; Tbt = 2,4,6-tris(bistrimethylsilyl)methyl]phenyl; Tip = 2,4,6-triisopropylmethylphenyl].[3,5,7,8,11] Tin(IV) and germanium(IV) complexes with terminal sulfido and selenido ligands supported by porphyrin type or macrocyclic octamethyldibenzotetraaza[14]annulene ligands (Me_8taa) have also been reported recently.[6,9,10] The heavier congeners, thermally stable dialkylstannanetellurone [$R_2Sn{=}Te$] in particular, are scarcely found. Dialkylstannanethiones such as [$Bu^{t}{}_{2}Sn{=}S$] and [$Ph_2Sn{=}S$] are known to exist as transient species which readily oligomerize to dimers and trimers.[12] Monomeric diarylstannanethione and -selone with sterically hindered groups have only been detected as intermediates and trapped by various reagents to form cycloaddition products. The stannanethione [Tip(Tbt)Sn=S][8] isolated was found to dimerize readily at temperatures above 90 °C, and the structures of [{Tip(Tbt)Sn(μ-E)}$_2$] (E = S, Se)[8,11] have been reported.

In our previous communication, we have reported the synthesis and characterization of dialkylstannanechalcogenones [$(R^{N})_2Sn{=}E$] [$R^{N} = CH(SiMe_3)C_9H_6N$-8; E = Se, Te].[13] A year later, Meller and co-workers reported a base-stabilized dialkylgermanechalcogenone [$\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2Ge{=}E$].[14] In this paper, we report the full details of the synthesis, structures, and multinuclear NMR spectroscopic data of dialkylgermane- and dialkylstannanechalcogenones bearing *N*-functionalized alkyl ligands $[CH(SiMe_3)C_9H_6N\text{-}8]^{-}$ (R^1) and $[CPh(SiMe_3)C_5H_4N\text{-}2]^{-}$ (R^2).

Results and Discussion

Synthesis of Dialkylgermane- and Dialkylstannanechalcogenones. The reactions of germanium(II) and tin(II) dialkyls MR_2 ($R = R^1$ or R^2) with elemental chalcogens E (E = S, Se, and Te) are summarized in

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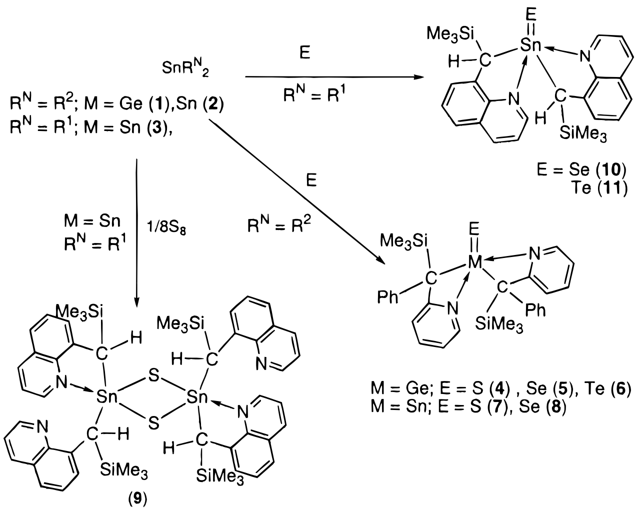
Scheme 1



Scheme 1. Treating germanium(II) dialkyl [Ge(R^2)$_2$] (**1**) with elemental chalcogens in THF afforded the corresponding thermally stable dialkylgermanethione (**4**), -selone (**5**), and -tellurone (**6**) were obtained, respectively. The reaction between **1** and tellurium powder was carried out in the absence of light, as compound **6** was found to be light-sensitive and turns black on exposure to light. Similar reactions of tin(II) dialkyl [Sn(R^2)$_2$] (**2**) with sulfur and selenium gave corresponding thermally stable dialkylstannanethione (**7**) and -selone (**8**). The reaction of tellurium powder with **2** gave a thermally unstable product, which decomposed to form tellurium powder at temperatures exceeding −30 °C. This result suggests that the Sn−Te interaction in [$(R^2)_2Sn{=}Te$] is weaker than the corresponding Ge−Te interaction in [$(R^2)_2Ge{=}Te$] (**6**). Indeed, terminal tellurido derivatives are rare for other elements due to their lower bond energy. This is also due to the fact that the ability of the main group elements to take part in multiple bonding is reduced for the heavier congener. The π-bond energy associated with the Sn=S bond has been calculated to be considerably lower than the corresponding values for C=S, Si=S, and Ge=S.[11] The first example of a terminal tellurido complex of a transition metal, namely [W(PMe$_3$)$_4$(Te)$_2$], has been reported.[15] More recently, bis[(2−pyridyl)bis(trimethylsilyl)methyl-*C*,*N*]germanethione, -selone, and -tellurone have also been structurally characterized.[14]

The reaction of [Sn(R^1)$_2$] (**3**) with stoichiometric amounts of elemental selenium and tellurium in THF afforded the corresponding thermally stable dialkylstannaneselone (**10**) and -tellurone (**11**) in good yields. These thermally stable chalcogenones have been isolated as THF or toluene solvates. In contrast, similar reaction of [Sn(R^1)$_2$] with sulfur afforded compound **9**, which was found to be a sulfido-bridged dimer, as confirmed by X-ray structural analysis. The structure of **9** is similar to that of [(Tip)(Tbt)Sn(μ-S)]$_2$, which was dimerized from the thermally unstable monomer [(Tip)(Tbt)Sn=S)]. To our knowledge, compound **11** is the first example of a compound having a terminal Sn=Te bond to be unequivocally characterized from spectroscopic and crystallographic data. Related work on the direct reaction of metal amides [M{N(SiMe$_3$)$_2$}$_2$] (M = Ge, Sn) with chalcogens yielded the appropriate metal(IV) oxidation products [M{N(SiMe$_3$)$_2$}$_2$(μ-E)]$_n$ (E = S, Se, Te).[16] It was found that the heavier chalcogen congeners are less stable, as shown by the behavior of the Sn−Te compound, which is thermally and particularly photochemically unstable, as it gradually decomposes to the tin amide and tellurium metal.[15] The present method provides a direct synthetic route from germylene and stannylene via oxidative addition to germane- and stannanechalcogenones. The thermal stability of compounds **4**−**8** is attributable to the steric crowding of the substituted α-carbon in ligands (R^1) and (R^2), *N*-coordination, and the quinolyl and pyridyl coordination.

Table 1. UV−Vis Absorption Data of Compounds 5, 7, 8, 9, 10, and 11 in THF

compound	λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})
[{CPh(SiMe$_3$)C$_5$H$_4$N-2}$_2$Ge=Se] (**5**)	294 (sh, 1910), 372 (1330)
[{CPh(SiMe$_3$)C$_5$H$_4$N-2}$_2$Sn=S] (**7**)	354 (5510)
[{CPh(SiMe$_3$)C$_5$H$_4$N-2}$_2$Sn=Se] (**8**)	324 (14750), 366 (sh, 7320)
[{CH(SiMe$_3$)C$_9$H$_6$N-8}$_2$Sn(μ−S)]$_2$ (**9**)	338 (16410), 412 (sh, 1230)
[{CH(SiMe$_3$)C$_9$H$_6$N-8}$_2$Sn=Se] (**10**)	310 (5920), 340 (sh, 5780), 414 (sh, 850)
[{CH(SiMe$_3$)C$_9$H$_6$N-8}$_2$Sn=Te] (**11**)	344 (8100), 416 (sh, 820)

Attempted reaction of Pb(II) compound Pb(R^1)$_2$ with Se and Te powder has led to the formation of black precipitates, suggesting that the cleavage of Pb−C bonds immediately occurred.

Spectroscopic Properties of Chalcogenones. Most of the chalcogenones prepared are less lipophilic than their parent compounds. They showed lower solubility toward toluene and ether and are soluble only in THF, except for compound **4**, which is soluble only in CHCl$_3$. The UV−vis spectral data of the metal chalcogenones are summarized in Table 1. The colors of compounds **4**−**6** [from white (**4**), through pale yellow (**5**), to orange (**6**)], compounds **9**−**11** [from pale yellow (**9**), through yellow-orange (**10**), to red (**11**)], and compounds **7** and **8** [from white (**7**) to yellow (**8**)] show changes with increasing atomic number of the chalcogen. These color trends are probably due to n → π^* transitions (transfer of lone-pair from E to a vacant metal-centered d orbital). Similar color trends have been reported for complexes [M{(NSiMe$_3$)$_2$}$_2$(μ-E)]$_n$ (M = Ge, Sn; E = S, Se, Te).[16]

Mass spectra of compounds **4**, **5**, and **8**−**10** all showed the presence of the parent peaks [M]$^+$, suggesting that compounds **4**, **5**, and **8**−**10** are monomeric in vapor phase. However, the mass spectrum of **9** did not show a peak at 1160 due to the parent peak [M]$^+$ of the dimerized species **9**, but a peak at 580 was found which was assignable to [M/2]$^+$, suggesting that compound **9** exists as a monomeric species in vapor phase.

The ^{1}H NMR spectra of **4**−**8** showed a similar pattern and displayed one set of signals due to the alkyl ligand R^2. The characteristic tin−proton coupling constants ($^2J_{Sn-H}$) of the methine protons due to alkyl ligands R^1 were observed in the ^{1}H NMR spectra of compounds **9**−**11**. The values of $^2J_{Sn-H}$ lie in the range 52.1−58.1 Hz, which are significantly small. The chemical shifts of **9**−**11** of methine protons (δ 1.02−1.64) are comparable to the value of δ 1.16 in the parent tin(II) compound [Sn(R^1)$_2$] (**3**), indicating the ambiguous oxida-

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Table 2. ^{119}Sn, ^{77}Se, and ^{125}Te NMR Spectroscopic Data for Some Metal−Chalcogenones

compound	^{119}Sn NMR^a δ, ppm	^{77}Se NMR^b δ, ppm	^{125}Te NMR^c δ, ppm
$[(R^2)_2Ge{=}Se]$ (**5**)	1097.08		
$[\{R^1(R^1)Sn(\mu\text{-}S)\}_2]$ (**9**)	−100.48		
$[(R^1)_2Sn{=}Se]$ (**10**)	−111.55 $^1J_{^{119}Sn-^{77}Se}$: 2951 Hz	−734.80 $^1J_{^{77}Se-^{117}Sn}$: 2818 Hz $^1J_{^{77}Se-^{119}Sn}$: 2966 Hz	
$[(R^1)_2Sn{=}Te]$ (**11**)	−350.34 $^1J_{^{119}Sn-^{125}Te}$: 7808 Hz		−2030.63 $^1J_{^{125}Te-^{117}Sn}$: 7641 Hz $^1J_{^{125}Te-^{119}Sn}$: 7808 Hz
$[(R^2)_2Sn{=}S]$ (**7**)	−54.70		
$[(R^2)_2Sn{=}Se]$ (**8**)	−179.18 $^1J_{^{119}Sn-^{77}Se}$: 2684 Hz	−531.95 $^1J_{^{77}Se-^{117}Sn}$: 2567 Hz $^1J_{^{77}Se-^{119}Sn}$: 2682 Hz	

[a] Recorded in THF/C_6D_6, referenced to external $SnMe_4$, 186.50 MHz. [b] Recorded in THF/C_6D_6, referenced to external Se_2Me_2, 95.41 MHz. [c] Recorded in THF/C_6D_6, referenced to external $Te(S_2CEt)_2$, 157.92 MHz.

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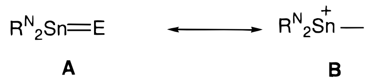
tion state of double-bonded tin in compounds **4**−**8**. The $^{13}C\{^1H\}$ NMR spectra of compounds **4**−**8** are not so significant.

The ^{77}Se, ^{119}Sn, and ^{125}Te NMR spectroscopic data of the metal chalcogenones are shown in Table 2. The ^{119}Sn signals lie in the range δ −54.70 to −350.34 ppm from S to Te. These values are comparatively different from the value of δ 2208 for stannanethione [(Tbt)(Tip)Sn=S],[8] but are comparable to the values of δ −301 and δ −444 ($^1J_{^{119}Sn-^{77}Se}$ = 3450 Hz) for stannanethione and -selone [(η^4-Me$_8$taa)Sn=E] (X = S, Se), respectively.[10] The singlet signals of **8**, **10,** and **11** display satellite signals due to coupling of ^{119}Sn−^{77}Se ($I = 1/2$, 7.6%) in **8** and **10** and ^{119}Sn to ^{125}Te ($I = 1/2$, 7.1%) in **11**. The large coupling constants, $^1J_{^{119}Sn-^{77}Se}$ (2951 Hz **10**, 2684 Hz **8**) and $^1J_{^{119}Sn-^{125}Te}$ (7808 Hz **11**) are consistent with directly bonded terminal Sn=Se and Sn=Te moieties. In contrast, the corresponding coupling constants for $[Sn\{N(SiMe_3)_2\}_2(\mu\text{-}E)]_n$ (E = Se, Te) are 1128 and 2700 Hz, respectively.[20]

The ^{77}Se NMR spectra of **10** and **8** display a singlet at δ −734.80 and δ −531.95, with doublet satellites due to coupling of ^{77}Se−^{117}Sn (2818 Hz **10**, 2567 Hz **8**) and ^{77}Se−^{119}Sn (2966 Hz **10**, 2682 Hz **8**), respectively, which are consistent with the values found in ^{119}Sn NMR spectra of **10** and **8**. The ^{77}Se NMR spectrum of **5** displays a singlet at δ 1097.08, which is quite different from the value of its tin analogue of compound **8**, but comparable to the value of δ 940.6 for germaneselone [(Tbt)(Tip)Ge=Se] (**18**).[7]

The ^{125}Te NMR spectrum of **11** displayed a singlet at δ −2030.63 with satellites due to the coupling constants $^1J_{^{125}Te-^{117}Sn}$ (7641 Hz) and $^1J_{^{125}Te-^{119}Sn}$ (7808 Hz), respectively, which are also consistent with the values found in the ^{119}Sn NMR spectrum of **11**.

X-ray Structures. Compound **5** and **8** are isostructural to each. The molecular structures with the atom-numbering schemes for compounds **5** and **8** are shown in Figures 2 and 3, respectively. Selected bond distances (Å) and angles (deg) of **5** and **8** are listed in Table 3.



$$\underset{\mathbf{A}}{R^N{}_2Sn{=}E} \longleftrightarrow \underset{\mathbf{B}}{R^N{}_2\overset{+}{Sn}-\overset{-}{E}}$$

Figure 1.

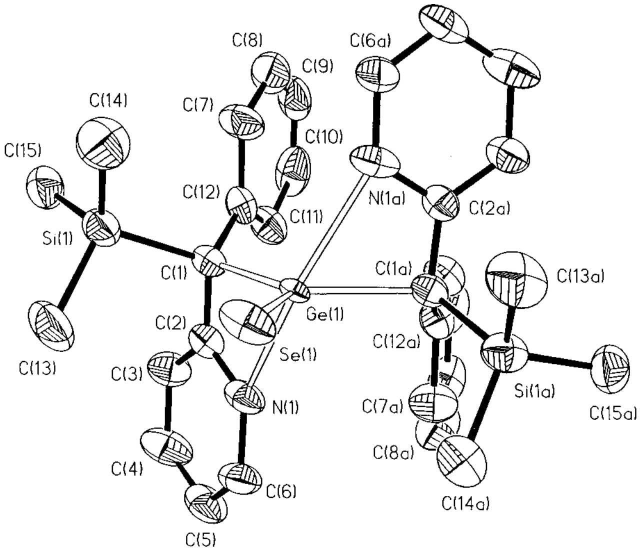


Figure 2. Crystal structure of **5** with atomic labeling scheme.

Dialkylgermaneselone **5** and -stannaneselone **8** both crystallize in a monoclinic *C*2 (No. 5) space group and were obtained as THF solvates. The two alkyl ligands R^2 are bonded to the central metal atom in a trans *C*,*N*-chelating fashion, and the metal centers display square pyramidal geometry with selenium atoms occupying the axial positions of the pyramidals. The values of N(1)−M−N(2) angles [M = Ge 143.8(2)°; Sn 145.9(2)°] are too small to describe as a distorted trigonal bipyramidal geometry. Both the structures of **5** and **8** lie on 2-fold rotation axes, so that the other half of the structures are identical to the original half when it is rotated along the 2-fold axis by 180°.

Four coordination atoms make a least-squares base plane, from which deviation of C(6), C(6a), N(1), and N(1a) atoms in **5** and **8** are about ±0.2766 and ±0.2772 Å, respectively. The Ge and Sn atoms occupy the apexes and are 1.0156 and 0.9675 Å departed from the base plane and lie 0.0325 and 00569 Å out of the $C_5H_4N(1,1a)$, respectively. The sums of the bond angles involving the basal ligand atoms are 317.0° and 320.6°, respectively. The two dihedral angles between the two phenyl planes of **5** and **8** are 11.4° and 10.9°, respectively.

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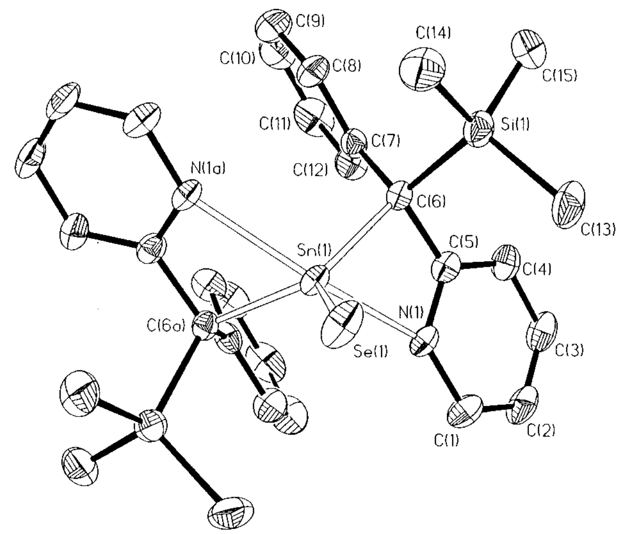

Figure 3. Crystal structure of **8** with atomic labeling scheme.

In compound **5**, the Ge−Se bond distance is 2.426(2) Å and is relatively longer than the Ge−Se distances in [(Tbt)(Tip)Ge=Se][7] [2.180(2) Å] and [(η^4-Me_8taa)Ge=Se][6] [2.247(1) Å], but slightly shorter than the distance in [{$C(SiMe_3)_2C_5H_4N$-2}$_2$Ge=Se][14] [2.2472(7) Å]. Surprisingly, the Ge−Se bond distance in **5** is slightly longer than the sum of the covalent radii of Ge (1.22 Å) and Se (1.16 Å). This suggests the resonance structure **B** in Figure 1 contributes more than the resonance structure **A**. The average Ge−C and Ge−N distances are 2.283 and 2.379 Å, respectively, which are larger than the values of 2.214 and 2.299 Å in the parent compound **1** unexpectedly. The C−Ge−C angle of **5** [111.1(2)°] is close to the value of 111.3(2)° in **1**. The average bite distance C···N and the bite angle C−Ge−N are 2.332 Å and 60.0°, respectively, which are comparable to the values of 2.350 Å and 64.2° in **1**.

In compound **8**, the Sn−Se bond distance is 2.418(1) Å, which is slightly longer than the value of 2.394(1) Å of the related compound [(η^4-Me_8taa)Sn=Se].[10] The calculated values of Sn=Se and Sn−Se are 2.37 and 2.57 Å.[17] The Sn−Se bond distance lies between the calculated values of Sn−Se single and double bonds and is quite different from the Ge−Se bonding in **5,** suggesting the type of Sn−Se bonding in **8** lies between the resonance structure **A** and **B** in Figure 1. The average Sn−C and Sn−N distances are 2.240 and 2.358 Å, respectively, which are significantly shorter than the values of 2.331 and 2.432 Å in the parent compound **2**. The decrease in these distances can be explained by the consequence of the change in oxidation state from Sn(II) to Sn(IV). The contrary findings in **5** may partly be explained by the difference in the covalent and ionic nature of tin and germanium. Also the steric congestion around Ge, which has a smaller size than Sn, also accounts for this contrast. The average bite distance C···N and bite angle C−Sn−N are 2.370 Å and 62.0°, respectively, which are comparable to the values of 2.383 Å and 60.0° in **2**.

Since the germanium and tin atoms adopt distorted square pyramidal geometry and are chiral respectively in **5** and **8**, they should have eight possible diastereoisomers with the combination of the two chiral α-carbons in the alkyl ligand R^2. From the unit cell lattice packing diagram of **5** and **8**, only one of the *rac*-isomers is observed with configuration (*R*,*A*,*R*). Therefore, the space groups of compound **5** and **8** are both chiral (*C*2). Similarly, there should exist another type of crystal that is packed by molecules with (*S*,*C*,*S*) configuration, and the formation of other diastereoisomers is believed to be unfavorable as proposed before. The X-ray structures of **5** and **8** (Figures 2 and 3) show the molecules of **5** and **8**, respectively, with (*R*,*A*,*R*) configuration.

Compound **9** crystallizes in a monoclinic *C*2/*c* (No. 15) space group and is obtained as THF solvates. X-ray crystallographic analysis established the dimeric structure of **9** (see ref 13), and selected bond distances (Å) and bond angles (deg) are shown in Table 4. The structure of **9** possesses an inversion center *i*, so that half of the structure is centrosymmetric to the other half. As a consequence of steric congestion around Sn, one of the *N*-functionalized alkyl ligands R^1 bonded to the metal center behaves as a monodentate C-centered ligand, while the other ligand is bonded to the tin in a chelate fashion. The two C-centered alkyl ligands and the two bidentate ligands are trans to each other, respectively. The five-coordinate Sn displays a distorted trigonal planar geometry with S(1a) and N(2) occupying the axial positions trans to each other. The S(1a)−Sn(1)−N(2) angle is 168.6(1)°, though it is slightly deviated from the value of 180° in the ideal trigonal planar geometry. The Sn atom is 0.2911 Å departed from the trigonal plane described by C(10), C(23), S(1). The other trigonal plane described by C(10a), C(23a), N(2a) is parallel to the previous trigonal plane as expected and in staggered configuration with a twist angle of 56.7°, 58.1° and 65.2°, respectively. The atoms Sn(1), Sn(1a), S(1), S(1a) form a four-membered ring, and this plane is nearly orthogonal (88.5°) to the trigonal planes described. The quinolyl plane $C_9H_6N(1)$ is nearly parallel to the other quinolyl plane $C_9H_6N(2)$, with a dihedral angle of 9.0°, which suggests the possibility of intramolecular π−π interaction between these two planes, while the planes $C_9H_6N(1)$ and $C_9H_6N(2)$ are coplanar to the planes of $C_9H_6N(1a)$ and $C_9H_6N(2a)$, respectively. The Sn(1) and Sn(1a) atoms both lie 0.6842 Å out of the chelated quinolyl planes $C_9H_6N(2)$ and $C_9H_6N(2a)$, respectively.

The average Sn−S distance of 2.47 Å in **9** is slightly longer than that [2.44 Å (av)] in [(Tbt)(Mes)Sn(μ-S)]$_2$.[18] The Sn−C(10) and Sn−C(23) distances of 2.198 and 2.203 Å in **9** are shorter than the value of 2.263 Å (av) in the corresponding tin(II) compound **3**. Due to the ring strain in the five-membered ring in the chelated ligand R^1, the bite distance C(23)···N(2) (2.805 Å) is slightly shorter than the related distance C(10)···N(1) (2.796 Å) of the C-centered ligand R^1.

It is noteworthy that the stereochemistry for the molecule of **9** is quite complicated. The structure determination of **9** shows one of the diastereoisomers with a configuration of (*S*,*C*,*S*) at Sn(1) and (*R*,*A*,*R*) at Sn(1a); therefore, the space group for this molecule in the X-ray structure analysis is *C*2/*c*, which possesses a center of symmetry. In the unit cell lattice packing diagram of **9**, only one type of diastereoisomer with configuration (*S*,*C*,*S*, *R*,*A*,*R*) is observed. It is possible that the formation of other diastereoisomers such as (*S*,*C*,*R*, *S*,*A*,*R*) is not favorable due to the steric hindrance of

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Table 3. Selected Bonds Distances (Å) and Angles (deg) for Compounds 5 and 8

	M = Ge **5**	M = Sn **8**		M = Ge **5**	M = Sn **8**
		Bond Distances			
M–Se(1)	2.426(2)	2.418(1)	M–N(1)	2.379(5)	2.358(6)
M–C(1)	2.283(5)	2.240(6)	M–N(1a)	2.379(5)	2.358(6)
M–C(1a)	2.283(5)	2.240(6)	Si(1)–C(1)	1.936(5)	1.928(6)
C(1)–C(2)	1.417(7)	1.520(9)	C(2)–N(1)	1.369(5)	1.344(7)
		Bond Angles			
Se(1)–M–N(1)	108.1(1)	107.0(1)	Se(1)–M–C(1)	124.5(1)	123.7(1)
N(1)–M–C(1)	60.0(2)	62.0(2)	N(1)–M–N(1a)	143.8(2)	145.9(2)
C(1)–M–N(1a)	98.5(2)	98.3(2)	Se(1)–M–C(1a)	124.5(1)	123.7(1)
C(1)–M–C(1a)	111.1(2)	112.5(3)	M–C(1)–C(2)	94.4(2)	93.2(3)
C(1)–C(2)–N(1)	113.7(4)	111.6(6)	M–N(1)–C(2)	91.6(3)	93.1(4)

Table 4. Selected Bonds Distances (Å) and Angles (deg) for Compound 9

	Bond Distances		
Sn(1)–S(1)	2.420(3)	Sn(1a)–S(1a)	2.420(3)
Sn(1)–C(10)	2.198(4)	Sn(1)–C(23)	2.203(6)
Sn(1)–S(1a)	2.528(2)	Sn(1a)-S(1)	2.528(2)
Sn(1)–N(2)	2.483(3)	Si(1)–C(10)	1.886(5)
Si(2)–C(23)	1.895(5)	C(10)–C(8)	1.518(4)
C(8)–C(9)	1.418(8)	C(9)–N(1)	1.330(7)
C(23)–C(22)	1.467(6)	C(21)–C(23)	1.424(7)
C(21)–C(22)	1.464(5)	C(22)–N(2)	1.343(8)
	Bond Angles		
S(1)–Sn(1)–N(2)	84.4(1)	S(1)–Sn(1)–C(10)	112.2(2)
N(2)–Sn(1)–C(10)	91.9(1)	S(1)–Sn(1)–C(23)	124.8(1)
N(2)–Sn(1)–C(23)	73.0(1)	C(10)–Sn(1)–C(23)	118.2(2)
S(1)–Sn(1)–S(1a)	89.2(1)	N(2)–Sn(1)–S(1a)	168.6(1)
C(10)–Sn(1)–S(1a)	99.2(1)	C(23)–Sn(1)–S(1a)	103.4(1)
Sn(1)–S(1)–Sn(1a)	90.8(1)	Sn(1)–C(10)–C(8)	113.4(3)
C(10)–C(8)–C(9)	121.2(4)	C(8)–C(9)–N(1)	116.7(3)
Sn(1)–C(23)–C(21)	110.6(3)	C(23)–C(21)–C(22)	119.6(5)
C(21)–C(22)–N(2)	116.5(4)	Sn(1)–N(2)–C(22)	109.6(2)

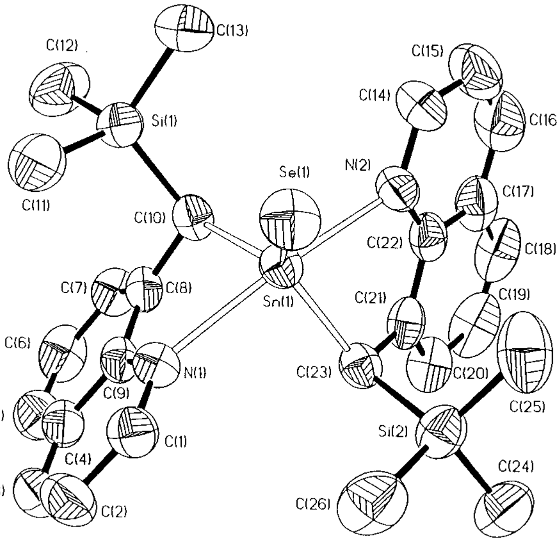

Figure 4. Crystal structure of **10** with atomic labeling scheme.

the bulky $SiMe_3$ groups. Moreover, in the solution state, some of the diastereoisomers may undergo a fast exchange process.

Compounds **10** and **11** are isostructural to each other with different terminal chalcogens (E = Se **10**, Te **11**). Compound **10** crystallizes in a monoclinic $P2_1/c$ (No. 14) space group and with 1 equiv of THF as the solvate, while compound **11** crystallizes in an orthorhombic *Pnna* space group. The structure of **10** with atom-numbering scheme is shown in Figure 4, and that of **11** has been reported in a previous communication.[13] Selected bond distances (Å) and bond angles (deg) of **10** and **11** are shown in Table 5. Similar to compounds **5** and **8**, the X-ray structures of **10** and **11** show the monomeric species with two alkyl ligands R^1 bonded to the tin center in a trans *C*,*N*-chelating fashion. The five-coordinate tin is bonded directly to the axial ligand Se and Te at 2.398(1) and 2.618(1) Å in **10** and **11**, respectively. The center tin atoms in **10** and **11** are both pentacoordinated, and they are better described as distorted trigonal bipyramidal since the values of key angles N(1)–M–N(2) of **10** and **11** are 158.0(2)° and 157.1(2)°, respectively.

The Sn–Se distance in **10** is significantly shorter than that in the selenium-bridged dimers [{Tbt)(Tip)Sn(μ-Se)]$_2$ [2.57 Å (av)] and [(Mes)(Tbt)Sn(μ-Se)]$_2$ (2.562 Å).[11] The 7% reduction in bond length is consistent with enhanced contribution of π-bonding between Sn and Se. The Sn–Se bond distance of **10** is comparable to the value of 2.394(1) Å in the related stannaneselone [(η^4-Me_8Taa)Sn=Se].[16] The Sn–Te bond distance of 2.618(1) Å in **11** is smaller than the sum of the covalent radii of Sn (1.40 Å) and Te (1.37 Å). The average Sn–C and Sn–N distances in **10** (2.187 and 2.376 Å) and **11** (2.174 and 2.382 Å) are shorter than the values of 2.263 and 2.506 Å, respectively. The decrease in the Sn–C and Sn–N distances is a consequence of the change in oxidation state from Sn(II) to Sn(IV). The average bite distance C···N and the bite angles C–Sn–N of alkyl ligands R^1 in **10** (2.798 Å, 75.5°) and **11** (2.785 Å, 75.2°) are quite different.

For compounds **10** and **11**, there exist two chiral α-carbons in the alkyl ligands R^1 and there are four possible diastereoisomers. However, only the *rac*-isomers with configuration (*R*,*R*) and (*S*,*S*) are observed in the unit cell lattice packing diagram of **10** and **11**. The formation of molecules with (*R*,*S*) and (*S*,*R*) configurations may be unfavorable due to the steric hindrance of the bulky $SiMe_3$ groups.

Experimental Section

General Procedures. All manipulations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques or in a dinitrogen glovebox. Solvents were dried over and distilled from CaH_2 (hexane) and/or Na (Et_2O). Sulfur, selenium, and tellurium powders were purchased from Aldrich Chemicals and used without further purification. Germanium(II) diaklyls **1** and tin(II) dialkyls **2** and **3** were prepared according to the literature.[19] The ^1H, ^{13}C, ^{119}Sn, ^{77}Se, and ^{125}Te NMR were recorded on Bruker WM-250 or ARX-500 instruments. All spectra were recorded in benzene-d_6, and the chemical shifts δ are relative to $SiMe_4$, $SnMe_4$, Me_2Se_2, and $Te(S_2CEt)_2$ for ^1H, ^{13}C, ^{119}Sn, ^{77}Se, and ^{125}Te NMR, respectively.

Synthesis of [{CPh($SiMe_3$)C_5H_4N-2}$_2$Ge=S] (4) [(R^2)$_2$Ge=S]. A solution of [Ge(R^2)$_2$] (**1**) (0.225 g, 0.407 mmol) in THF

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Table 5. Selected Bonds Distances (Å) and Angles (deg) for Compounds 10 and 11

	E = Se **10**	E = Te **11**		E = Se **10**	E = Te **11**
Bond Distances					
Sn(1)−E	2.398(1)	2.618(1)	Sn(1)−N(1)	2.361(4)	2.382(4)
Sn(1)−C(10)	2.190(6)	2.174(5)	Sn(1)−N(2)	2.390(4)	2.382(4)
Sn(1)−C(23)	2.283(5)	2.240(6)	N(1)−C(9)	1.372(9)	1.379(6)
C(9)−C(8)	1.436(8)	1.407(7)	C(8)−C(10)	1.487(8)	1.502(6)
N(2)−C(22)	1.371(9)	1.379(6)	C(22)−C(21)	1.430(8)	1.407(7)
C(21)−C(23)	1.493(8)	1.502(6)			
Bond Angles					
E−Sn(1)−N(1)	99.5(1)	101.5(1)	E−Sn(1)−C(10)	127.3(2)	127.3(1)
N(1)−Sn(1)−C(10)	75.9(2)	75.2(1)	E−Sn(1)−N(2)	102.5(1)	101.5(1)
N(1)−Sn(1)−N(2)	158.0(2)	157.1(2)	C(10)−Sn(1)−N(2)	91.0(2)	90.8(1)
E−Sn(1)−C(23)	125.4(2)	127.3(1)	N(1)−Sn(1)−C(23)	91.7(2)	90.8(1)
C(10)−Sn(1)−C(23)	107.3(2)	105.5(3)	N(2)−Sn(1)−C(23)	75.1(2)	75.2(1)
Sn(1)−N(1)−C(9)	109.5(3)	108.2(3)	N(1)−C(9)−C(8)	116.4(5)	117.3(4)
C(9)−C(8)−C(10)	120.2(6)	119.4(4)	Sn(1)−C(10)−C(8)	107.0(3)	107.7(3)
Sn(1)−N(2)−C(22)	109.7(3)	108.2(3)	N(2)−C(22)−C(21)	117.3(5)	117.3(4)
C(22)−C(21)−C(23)	119.0(6)	119.4(4)	Sn(1)−C(23)−C(21)	109.7(4)	107.7(3)

(20 mL) was added slowly to the colorless solution of powdered sulfur (13.0 mg 0.407 mmol) in THF (20 mL) at 0 °C. The orange color of **1** faded gradually when raised to ambient temperature. The pale yellow suspension was stirred for 18 h. The white solid was isolated, washed with pentane, and dried in vacuo, yielding 0.218 g, 91%. Mp: 245−248 °C (dec). EI-MS: *m/z* 586 $[M]^+$, 346 $[M - R^2]^+$, 240 $[R^2]^+$. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.21 (s, $SiMe_3$, 18H), 6.33(br, aryl H, 2H), 6.61−6.75 (m, aryl H, 6H), 7.08 (dd, J = 8.0, 1.0 Hz, aryl H, 2H), 7.32 (ddd, J = 7.4, 5.5, 1.0 Hz, aryl H, 2H), 7.73 (td, J = 7.7, 1.7 Hz, aryl H, 2H), 8.54 (dt, J = 5.1, 1.3 Hz, aryl H, 2H). ^{13}C NMR ($CDCl_3$, 62.90 MHz): δ 0.25 ($SiMe_3$), 61.58 ($CSiMe_3$), 122.22, 123.63, 124.77, 126.65, 127.66, 138.47, 140.41, 145.77, 164.76 (C_5H_4N and C_6H_5).

Synthesis of [{CPh(SiMe$_3$)C$_5$H$_4$N-2}$_2$Ge=Se] (5) [(R^2)$_2$-Ge=Se]. A solution of $[Ge(R^2)_2]$ (**1**) (0.178 g, 0.322 mmol) in THF (20 mL) was added slowly to the colorless solution of powdered sulfur (25.4 mg 0.322 mmol) in THF (20 mL) at 0 °C. The orange color of **1** faded gradually when raised to ambient temperature. The light yellow solution was stirred for 18 h. It was filtered, concentrated, and stored at −30 °C, yielding pale yellow crystals (0.111 g, 55%). Mp: 260−264 °C (dec). Anal. Found: C, 57.19; H, 6.30; N, 2.63. Calcd for $C_{30}H_{36}N_2Si_2GeSe{\cdot}THF$: C, 57.97; H, 6.30; N, 3.98. EI-MS: *m/z* 632 $[M]^+$, 392 $[M - R^2]^+$. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.23 (s, $SiMe_3$, 18H), 1.80−1.85 (m, THF, 4H), 3.69−3.74 (m, THF, 4H), 6.62−6.66 (m, aryl H, 4H), 6.70−6.75 (m, aryl H, 4H), 7.08 (dd, J = 8.0, 0.8 Hz, aryl H, 2H), 7.35 (ddd, J = 7.3, 5.5, 1.0 Hz, aryl H, 2H), 7.74 (td, J = 7.7, 1.5 Hz, aryl H, 2H), 8.54 (dt, J = 5.5, 1.2 Hz, aryl H, 2H). ^{13}C NMR ($CDCl_3$, 62.90 MHz): δ 0.37 ($SiMe_3$), 25.63 (THF), 60.02 ($CSiMe_3$), 67.94 (THF), 122.22, 123.42, 124.76, 126.20, 127.55, 138.26, 140.02, 145.48, 164.54 (C_5H_4N and C_6H_5). ^{77}Se NMR (THF/C_6D_6, 95.41 MHz, Me_2Se_2 (ext)): δ 1097.08 (s).

Synthesis of [{CPh(SiMe$_3$)C$_5$H$_4$N-2}$_2$Ge=Te] (6) [(R^2)$_2$-Ge=Te]. A solution of $[Ge(R^2)_2]$ (**1**) (0.509 g, 0.920 mmol) in THF (20 mL) was added slowly to the colorless solution of powdered tellurium (0.117 g, 0.920 mmol) in THF (20 mL) in the absence of light. The orange mixture was stirred for 18h. The unreacted tellerium powder was filtered off, the yellowish orange filtrate was concentrated and stored at −30 °C, yielding yellowish orange crystals of the title compound (0.300 g, 48%). Mp: 190−193 °C (dec). Anal. Found: C, 53.85; N, 5.81; N, 3.68. Calcd for $C_{30}H_{36}Si_2N_2GeTe{\cdot}THF$: C, 54.23; H, 5.89; N, 3.72. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.22 (s, $SiMe_3$, 18H), 1.78−1.83 (m, THF, 4H), 3.67−3.72 (m, THF, 4H), 5.74 (br, aryl H, 2 H), 6.59 (br, aryl H, 4H), 6.68−6.74 (m, aryl H, 4H), 7.05 (d, J = 8.1 Hz, aryl H, 2H), 7.38 (ddd, J = 7.3, 5.5, 1.0 Hz, aryl H, 2H), 7.74 (td, J = 7.8, 1.5 Hz, aryl H, 2H), 8.45−8.47 (m, aryl H, 2H). ^{13}C NMR ($CDCl_3$, 62.90 MHz): δ 0.72 ($SiMe_3$), 25.57 (THF), 57.00 ($CSiMe_3$), 67.88 (THF), 122.37, 123.24, 124.91, 125.45, 127.55, 138.17, 139.58, 145.16, 164.63 (C_5H_4N and C_6H_5).

Synthesis of [{CH(SiMe$_3$)C$_9$H$_6$N-8}{CH(SiMe$_3$)C$_9$H$_6$N-8}Sn(μ-S)]$_2$ (9), [(R^1)(R^1)Sn(μ-S)]$_2$. To a stirring solution of powdered sulfur (0.045 g, 1.42 mmol) in THF (20 mL) was added dropwise a solution of $[Sn(R^1)_2]$ (**3**) (0.77 g, 1.42 mmol) in THF (20 mL) at 0 °C. The resultant yellow solution was allowed to warm to room temperature and stirred for 18 h. The solution was concentrated and kept at −20 °C, affording a pale-yellow crystalline solid, which was washed with pentane and dried in vacuo. Yield: 0.74 g (90%). Mp: 216−220 °C (dec). Anal. Found: C, 54.19; H, 5.45; N, 3.86. Calcd. for $C_{52}H_{64}N_4Si_4Sn_2S_2{\cdot}THF$: C, 54.64; H, 5.89; N, 4.55. EI-MS: *m/z* 580 $[M/2]^+$. ^{1}H NMR ($CDCl_3$, 250 MHz): δ −0.49 (s, $SiMe_3$, 36H), 1.02 (s, $^2J_{H-Sn}$ = 58.1 Hz, CHSi, 4H), 6.79 (d, J = 7.1 Hz, quinolyl H, 4H), 7.07 (t, J = 7.7 Hz, quinolyl, 4H), 7.20−7.27 (m, quinolyl, 8H), 8.02 (dd, J = 8.3, 1.5 Hz, quinolyl, 4H), 8.82 (dd, J = 4.5, 1.5 Hz, quinolyl, 4H). ^{13}C NMR ($CDCl_3$, 62.90 MHz): δ −0.44 (s, $SiMe_3$), 26.22 (THF), 28.64 ($CSiMe_3$), 68.58 (THF), 121.99, 123.26, 128.42, 129.22, 130.65, 140.31, 142.78, 143.71, 147.74 (C_9H_6N). ^{119}Sn NMR (THF/C_6D_6, 186.50 Hz, $SnMe_4$(ext)): δ −100.48 (s).

Synthesis of [{CH(SiMe$_3$)C$_9$H$_6$N-8}$_2$Sn=Se] (10) [(R^1)$_2$-Sn=Se]. To a stirring solution of powdered selenium (87.5 mg, 1.11 mmol) in THF (20 mL) was added dropwise a solution of $[Sn(R^1)_2]$ (**3**) (0.606 g, 1.11 mmol) in THF (20 mL) at 0 °C. The resultant yellow solution was allowed to warm to room temperature and stirred for 18 h. Unreacted selenium powder was filtered off, and the filtrate was concentrated and stored at −20 °C. Orange crystals of **10** were obtained, washed with pentane, and dried in vacuo. Yield: 0.59 g (85%). Mp: 255−260 °C (dec). Anal. Found: C, 51.58; H, 5.64; N, 3.93. Calcd for $C_{26}H_{32}Si_2N_2SnSe{\cdot}THF$: C, 51.59; H, 5.77; N, 4.01. EI-MS: *m/z* 626 $[M]^+$, 554 $[M - Se]^+$, 412 $[M - R^1]^+$, 340 $[M - Se - R^1]^+$. ^{1}H NMR (CD_2Cl_2, 250 MHz): δ −0.16 (s, $SiMe_3$, 18H), 1.42 (s, $^2J_{H-Sn}$ = 56.6 Hz, CHSi, 2H), 1.77 (m, THF, 2H), 3.65 (m, THF, 2H), 7.12 (dd, J = 7.2, 3.7 Hz, quinolyl, 2H), 7.43 (t, J = 7.7 Hz, quinolyl, 2H), 7.58−7.65 (m, quinolyl, 2H), 8.43 (dd, J = 8.3, 1.6 Hz, quinolyl, 2H), 9.09 (dd, J = 4.6, 1.6 Hz, quinolyl, 2H). ^{13}C NMR (CD_2Cl_2, 125.76 MHz): δ −0.59 ($SiMe_3$), 26.41 (THF), 28.47 ($CSiMe_3$), 68.58 (THF), 122.07, 123.53, 128.59, 129.60, 130.87, 140.54, 143.47, 144.13, 147.58 (C_9H_6N). ^{77}Se NMR (THF/C_6D_6, 95.41 MHz, Me_2Se_2 (ext)): δ −734.84 (s, $^1J_{^{77}Se-^{119}Sn}$ = 2941.6 Hz, $^1J_{^{77}Se-^{117}Sn}$ = 2818.0 Hz). ^{119}Sn NMR (THF/C_6D_6, 186.50 MHz): δ −111.55 (s, $^1J_{Sn-Se}$ = 2950.5 Hz).

Synthesis of [{CH(SiMe$_3$)C$_9$H$_6$N-8}$_2$Sn=Te] (11) [(R^1)$_2$-Sn=Te]. To a stirring suspension of tellerium powder (0.117 g, 0.918 mmol) in THF (20 mL) was added dropwise a solution of $[Sn(R^1)_2]$ (**3**) (0.502 g, 0.918 mmol) in THF (20 mL). The

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Table 6. Selected Crystallographic and Data Collection Parameters for Compounds 5, 8, and 10

	5	**8**	**10**
molecular formula	$C_{30}H_{36}N_2Si_2GeSe.C_4H_{8O}$	$C_{35}H_{36}N_2Si_2SnSe$	$C_{30}H_{40}N_2OSi_2SnSe$
molecular weight	704.4	738.5	698.5
cryst size, mm	0.20 × 0.18 × 0.28	0.14 × 0.16 × 0.20	0.25 × 0.25 × 0.20
cryst syst	monoclinic	monoclinic	monoclinic
space group	C_2 (No. 5)	C_2	$P2_1/c$
a, Å	16.296(3)	16.302(2)	14.456(3)
b, Å	10.724(2)	10.7300(10)	10.700(2)
c, Å	12.071(2)	12.0620(10)	21.915(4)
V, Å^3	1803.05	1803.3(9)	3200.2(16)
Z	2	2	4
density, g cm^{-3}	1.298	1.360	1.450
abs coeff, mm^{-1}	not measured	1.808	2.035
scan type and rate	oscillation IP photos; 30 frames in total, $\phi = -30$ to 150°, $\Delta\phi = 6°$, 8 min per frame	oscillation IP photos; 60 frames in total, $\phi = -30$ to 150°, $\Delta\phi = 3°$, 6 min per frame	oscillation IP photos; 60 frames in total, $\phi = -40$ to 80°, $\Delta\phi = 2°$, 12 min per frame
background level	−70	−50	−40
collection range	$0 \leq h \leq 19$, $0 \leq k \leq 12$, $-14 \leq l \leq 12$	$-20 \leq h \leq 17$, $-13 \leq k \leq 13$, $0 \leq l \leq 15$	$-17 \leq h \leq 0$, $-12 \leq k \leq 13$, $-25 \leq l \leq 27$
no. of unique data (R_{int})	1682	3311	5205
no. of obsd data, n	1324	3212	3813
no. of variables, ρ	186	209	335
R^a	0.056	0.039	0.046
$R_w{}^b$	0.076	0.053	0.059
S	1.61	1.61	1.80
weighting scheme	$w = [\sigma^2\lvert F_o\rvert + 0.0008\lvert F_o\rvert^2]^{-1}$	$w = [\sigma^2\lvert F_o\rvert + 0.0006\lvert F_o\rvert^2]^{-1}$	$w = [\sigma^2\lvert F_o\rvert + 0.0006\lvert F_o\rvert^2]^{-1}$
largest and mean Δ/σ	0.012, 0.006	0.969, 0.057	0.000, 0.000
residual extrema in final diff map, e Å^{-3}	+0.50 to −0.57	1.21 to −0.73	0.77 to −1.22
extinction corr	$\chi = 0.0043$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$	$\chi = 0.0039(4)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$	$\chi = 0.00078(10)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$

resultant red solution was stirred for 18 h. Unreacted tellurium powder was removed by filtration, and the filtrate was concentrated and cooled at −20 °C. Red crystals of **11** were obtained, washed with pentane, and dried in vacuo. Yield: 0.55 g (88%). Mp: 135−140 °C (dec). Anal. Found: C, 49.13; H, 4.94; N, 3.88. Calcd for $C_{26}H_{32}Si_2N_2SnTe{\cdot}1/2C_7H_8$: C, 49.14; H, 5.03; N, 3.88. EI-MS: m/z 675 [M]$^+$, 461 [M − R^1]$^+$, 334 [M − R^1 − Te]$^+$. ^{1}H NMR (C_6D_6, 250 MHz): δ 0.09 (s, SiMe$_3$, 18H), 1.64 (s, $^2J_{H-Sn}$ = 52.1 Hz, CHSi, 2H), 6,69 (dd, J = 8.3, 4.5 Hz, quinolyl, 2H), 6.77 (dd, J = 6.1, 2.4 Hz, quinolyl, 2H), 6.95−7.02 (m, quinolyl, 2H), 7.40 (dd, J = 8.3, 1.6 Hz, quinolyl, 2H), 9.32 (dd, J = 4.5, 1.5 Hz, quinolyl, 2H). ^{13}C NMR (C_6D_6, 62.90 MHz): δ -0.67 (SiMe$_3$), 27.82 (CSiMe$_3$), 121.24, 122.67, 128.79, 129.29, 130.23, 139.22, 143.86, 144.55, 147.20 (C_9H_6N). ^{119}Sn NMR (THF/C_6D_6, 186.50 MHz, SnMe$_4$ (ext)): δ −350.34 (s, $^1J_{Sn-Te}$ = 7808.3 Hz). ^{125}Te NMR (THF/C_6D_6, 157.92 MHz, Te(S$_2$CEt)$_2$ (ext)): δ −2030.63 (s, $^1J_{^{125}Te-^{119}Sn}$ = 7793.4 Hz, $^1J_{^{125}Te-^{117}Sn}$ = 7490.2 Hz).

Synthesis of [{CPh(SiMe$_3$)C$_5$H$_4$N-2}$_2$Sn=S] (7) [(R^2)$_2$Sn=S]. A solution of [Sn(R^2)$_2$] (**2**) (0.675 g, 1.13 mmol) in THF (20 mL) was added slowly to the colorless solution of powdered sulfur (36.0 mg 1.13 mmol) in THF (20 mL) at 0 °C. The yellow color of **2** faded gradually when raised to ambient temperature. The mixture was stirred for 18 h. It was then filtered, concentrated, and stored at −20 °C. White solid was obtained (0.570 g, 66%). Mp: 171−174 °C (dec). Anal. Found: C, 56.39; H, 6.19; N, 3.97. Calcd for $C_{30}H_{36}N_2Si_2SnS$: C, 57.05; H, 5.75; N, 4.44. EI-MS: m/z 632 [M]$^+$. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 0.21 (s, SiMe$_3$, 1H), 1.78−1.84 (m, THF, 4H), 3.68−3.74 (m, THF, 4H), 6.31−6.35 (m, aryl H, 4H), 6.66−6.69 (m, aryl H, 6H), 7.07 (d, J = 8 Hz, aryl H, 2H), 7.25−7.30 (m, aryl H, 2H), 7.73 (dt, J = 7.7, 1.6 Hz, 2H), 8.39 (d, J = 5.4 Hz, 2H). ^{13}C NMR (CDCl$_3$, 62.90 MHz): δ 0.19 (SiMe$_3$), 25.80 (THF), 64.07 (CSiMe$_3$), 67.92 (THF), 122.05, 123.01, 125.53, 125.70, 127.72, 138.66, 141.43, 146.28, 165.33 (C_5H_4N and C_6H_5). ^{119}Sn NMR (THF/C_6D_6, 186.50 MHz, SnMe$_4$ (ext)): δ −54.70 (s).

Synthesis of [{CPh(SiMe$_3$)C$_5$H$_4$N-2}$_2$Sn=Se] (8) [(R^2)$_2$Sn=Se]. To a stirring suspension of selenium powder (0.140 g, 1.78 mmol) in THF (30 mL) was added dropwise a solution of [Sn(R^2)$_2$] (**2**) (1.07 g, 1.78 mmol) in THF (30 mL). The yellow color of **2** deepened, and the mixture was stirred for 18 h. Unreacted selenium powder was removed by filtration, and the filtrate was concentrated and cooled at −20 °C. Yellow crystals obtained were washed with pentane and dried in vacuo. Yield: 0.147 g (60%). Mp: 260−264 °C (dec). Anal. Found: C, 54.37; H, 5.88; N, 3.72. Calcd for $C_{30}H_{36}N_2Si_2SnSe{\cdot}$THF: C, 54.41; H, 5.91; N, 3.73. EI-MS: m/z 679 [M]$^+$, 664 [M − Me]$^+$. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 0.21 (s, SiMe$_3$, 18H), 1.77−1.83 (m, THF, 4H), 3.67−3.72 (m, THF, 4H), 6.31−6.33 (m, aryl H, 4H), 6.64−6.68 (m, aryl H, 6H), 7.05 (dt, J = 8.1, 1.0 Hz, aryl H, 2H), 7.28−7.31 (m, aryl H, 2H), 7.72 (dt, J = 7.9, 1.3 Hz, aryl H, 2H), 8.36 (dd, J = 5.5, 1.3 Hz, aryl H, 2H). ^{13}C NMR (CDCl$_3$, 62.90 MHz): δ 0.25 (SiMe$_3$), 25.54 (THF), 62.46 (CSiMe$_3$), 67.86 (THF), 122.07, 122.94, 125.38, 125.82, 127.55, 138.52, 141.26, 146.14, 165.42 (C_5H_4N and C_6H_5). ^{77}Se NMR (THF/C_6D_6, 95.41 MHz, Se$_2$Me$_2$ (ext)): δ −531.95 (s, $^1J_{^{77}Se-^{117}Sn}$ = 2566.5 Hz, $^1J_{^{77}Se-^{119}Sn}$ = 2681.9 Hz). ^{119}Sn NMR (THF/C_6D_6, 186.50 MHz, SnMe$_4$ (ext)): δ −179.18 (s, $^1J_{Sn-Se}$ = 2683.8 Hz).

X-ray Crystallography. Single crystals were sealed in 0.3 mm Lindemann glass capillaries under argon. X-ray data of **5**, **8**, **9**, **10**, and **11** were collected on a Rigaku R-AXIS II imaging plate using graphite-monochromatized Mo Kα radiation (l = 0.71073 Å) from a rotating-anode generator operating at 50 kV and 90 mA. Crystallogaphic data for compounds **9** and **11** have been published in a previous communication.[13] Crystal data for **5**, **8**, and **10** are summarized in Table 6.The structures were solved by direct phase determination using the computer program SHELXTL-PC[20] on a PC 486 and refined by full-matrix least squares with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were introduced in their idealized positions and included in structure factor calculations with assigned isotropic temperature factors. Full details of the crystallographic analysis of **5**, **8**, **9**, **10**, and **11** are given in the Supporting Information.

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Supporting Information Available: Details about the X-ray crystal structures, including ORTEP diagrams and tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **5**, **8**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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