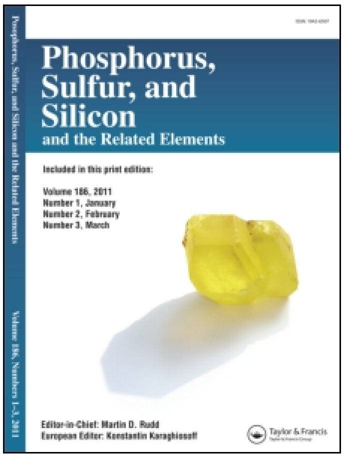

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New Aspects of Organoselenium Compounds Containing Group 14 Elements

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NEW ASPECTS OF ORGANOSELENIUM COMPOUNDS CONTAINING GROUP 14 ELEMENTS

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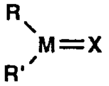
Abstract The synthesis and reactivities of double bond compounds between Group 14 and Group 16 elements have been reported. Specifically the chemistry of M=X type compounds (C=Se, Ge=S, Ge=Se, Sn=S, Sn=Se) are described.

INTRODUCTION

In recent years much attention has been paid to the chemistry of multiple bond compounds of Group 14-16 elements.[1]



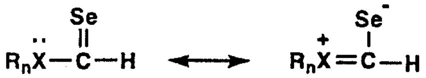
1

M = C, Si, Ge, Sn, Pb
X = O, S, Se, Te

Although, among these, the chemistry of carbonyl and thiocarbonyl compounds has been entensively studied, compounds of the other combinations (1) are highly reactive and much less studies have been carried out on their synthesis and reactivities, especially on the stable compounds of these types. In this paper we will describe our recent results on the chemistry of selenoaldehyde, germanethione, germaneselone, stannanethione, and stannaneselone.

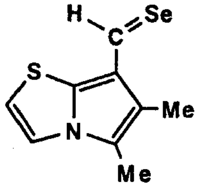
SELENOALDEHYDE

Although the first synthesis of stable selenoketone (selone) was reported in 1976 by Barton,[2] no example of a stable selenoaldehyde has been described (except some compounds stabilized by mesomeric effect due to heteroatoms, see below). There have been a considerable number of reports on spectroscopic detection of simple selenoaldehydes in the gas phase[1c] and some reactivities of transient selenoaldehydes in solution,[1c,3] whereas the examples of the isolation of compounds having a selenoformyl group have been restricted only to selenoamides and esters **2** (or their vinylogues such as **3**)[1c,4] which are strongly stabilized by the mesomeric effect due to heteroatoms such as nitrogen, oxygen and sulfur and hence the properties of the selenoformyl group are perturbed to such an extent that they cannot be rocognized as selenoaldehydes any more.



$$R_n\ddot{X}-\overset{\overset{Se}{\|}}{C}-H \longleftrightarrow R_n\overset{+}{X}=\overset{\overset{Se^-}{|}}{C}-H$$

2 (X = O, N)



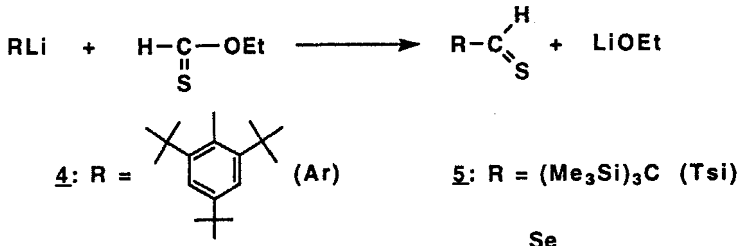
3

Some transition metal complexes of selenoaldehydes have been also reported.[1c]

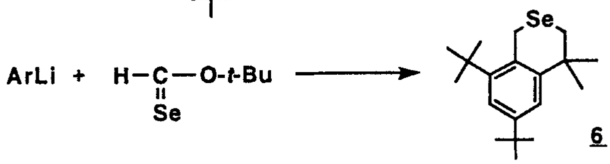
Synthesis

Since we were successful in the synthesis of stable aromatic[5] **4** and aliphatic[6] thioaldehyde **5** [Eq. (1)] by taking advantage of kinetic stabilization due to bulky groups, 2,4,6-tri-t-butylphenyl (denoted as Ar throughout this paper) and tris(trimethylsilyl)methyl (trisyl; abbreviated as Tsi), we first attempted similar approaches also in the synthesis of a selenoaldehyde.

However, the reactions of ArLi and TsiLi with t-butyl selenoformate resulted in the formation of bicyclic selenide 6[7] and vinyl ether 7, respectively [Eq. (2),(3)].



(1)



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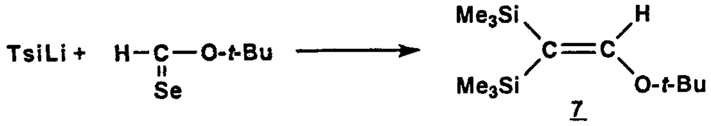
(2)



7

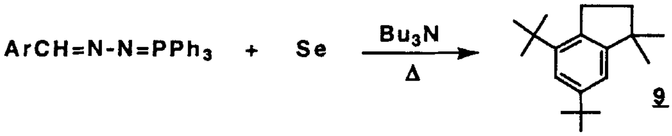
(3)

Although we previously reported a new preparative method for selenoketone using the reaction of hydrazones with diselenium dichloride,[8] application of this methodology to selenoaldehyde synthesis again met with failure since the product was diazo compound 8 in spite of attempts using various combinations of M and X in Eq. (4).

$$\mathrm{ArCH{=}NNM_2} + \mathrm{Se_2X_2} \longrightarrow \mathrm{ArCH{=}N_2} \qquad (4)$$

$$(\mathrm{M} = \mathrm{H},\ \mathrm{MgCl},\ \mathrm{SiMe_3};\ \mathrm{X} = \mathrm{Cl},\ \mathrm{Br}) \qquad \underline{8}$$

Application of the Barton's procedure[2] for selenoketone synthesis was also unsuccessful; the product was indane derivative 9 most likely produced via intermediary 8 [Eq. (5)].



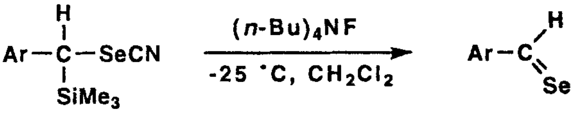
9

(5)

The Lwowski's method[9] can be successfully applied to thioaldehyde synthesis [Eq. (6)], but use of carbon diselenide instead of carbon disulfide gave only nitrile **10**.

$$\mathrm{ArCH{=}NLi} + \mathrm{CS_2} \longrightarrow \underset{\underline{4}\ (43\%)}{\mathrm{ArCHS}} + \underset{\underline{10}\ (40\%)}{\mathrm{ArCN}} \qquad (6)$$

After these unsuccessful attempts, we have finally succeeded in the synthesis of the first stable selenoaldehyde **11**[10] by using the Krafft's procedure,[11] i.e., fluoride induced elimination of cyanotrimethylsilane from selenocyanate **12** [Eq. (7)]. The reaction proceeded almost instantaneously at -25° C and the purification was

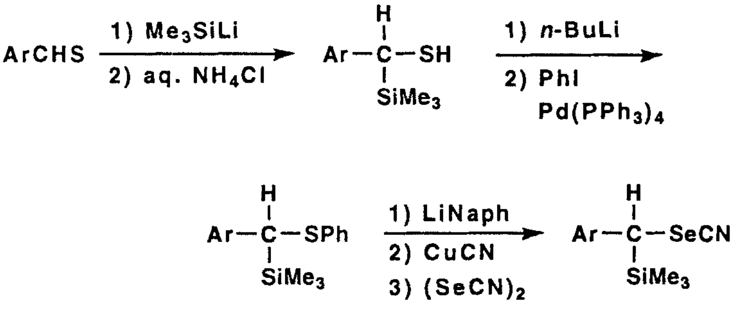


(7)

12

11 (44%)

carried out by flash chromatography at about -50° C. The selenoaldehyde **11** is a blue crystalline compound. Once purified it is stable at room temperature and can be handled with care although in solution it is quite sensitive to oxygen to give the corresponding aldehyde even at low temperatures. The starting selenocyanate can be synthesized from thioaldehyde **4** as shown in Scheme 1.



SCHEME 1

Physical and Chemical Properties

Some spectroscopic data of **11** are listed in Table 1 along with those of some related compounds.

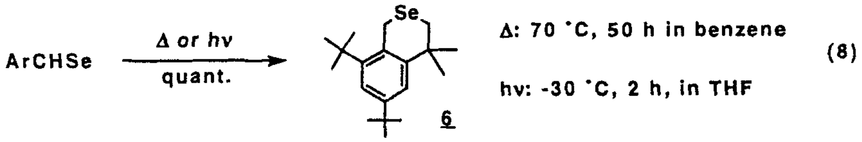
TABLE 1 Spectroscopic Data of Selenoaldehyde 11

	^{1}H-NMR/δ (H-C=X)	^{13}C-NMR/δ (H-C=X)	^{77}Se-NMR/δ	VIS/nm
ArCHO	11.11	202.7		
ArCHS	13.02	250.4		564[a] 552[b]
ArCHSe	17.38	258.2	2398	759[a] 739[b]
$(1\text{-Ad})_2C=Se$		293.9	2134	712[c]

[a] Hexane. [b] Ethanol. [c] Cyclohexane.

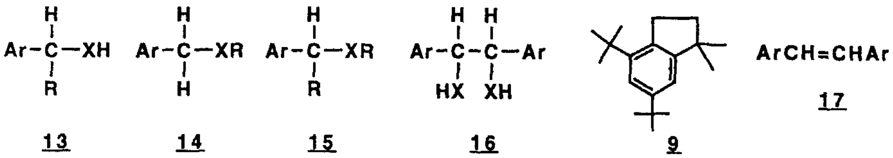
The most interesting data in Table 1 is a very low chemical shift value of the selenoformyl proton of 17.38 ppm. This suggests that the C=Se bond has a much higher anisotropic effect than the C=S bond. To our knowledge this is the lowest record for a proton attached to a neutral carbon. In contrast to this value of **11**, that of the heterocyclic selenoaldehyde prepared by Reid,[4] e.g., **3**, is 12.59, indicating the perturbation of the property of the C=Se bond by the mesomeric effect due to heteroatoms as described previously. The ^{77}Se NMR chemical shift of the selenoformyl group is also noticeable because this is again the lowest chemical shift value so far observed for organoselenium compounds.

The selenoaldehyde **11** is stable at room temperature but it undergoes isomerization involving the insertion of the C=Se bond into the o-t-butyl group to give bicyclic selenide **6** at 70° C [Eq. (8)]. Although a similar isomerization occurs also in the case of thioaldehyde **4**, it proceeds at about 200° C,[5] indicating the higher reactivity of the selenocarbonyl compound compared to the thiocarbonyl compound. The isomerization was induced also photochemically.



When **11** was reacted with organolithium reagents, selenophilic **14** and carbophilic product **13** were obtained along with stilbene derivative **17**. Table 2 summarizes these results together with those for thioaldehyde **4**. Although in both reactions the heterophilic product is a main one, there is a notable difference between the two reactions, that is, the products involving two molecules of the starting compound are stilbene **17** from **11**, but dithiol **16** from **4**.

TABLE 2 Reactions with Organolithium Reagents.

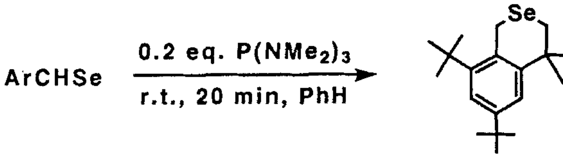


RLi	Substate	Products and Yield/%					
		13	14	15	16	9	17
MeLi	ArCHSe		52				12
	ArCHS		46		39		
t-BuLi	ArCHSe	26	26				
	ArCHS	7	23	11	12	24	
PhLi	ArCHSe		24				38
	ArCHS		97				

Reaction of **11** with butylamine proceeds rapidly even at 0° C to afford Schiff's base **18** and diselenide **19** [Eq. (9)], while the reaction of **4** with the same amine occurs only at about 70° C giving **18**. This fact again indicates the higher reactivity of **11**.

$$\mathrm{ArCHSe} + n\text{-}\mathrm{BuNH_2} \xrightarrow[\text{toluene-}d_8]{0\ ^\circ\mathrm{C},\ 45\ \mathrm{min}} \underset{\underline{18}\ (43\%)}{\mathrm{ArCH{=}N}(n\text{-}\mathrm{Bu})} + \underset{\underline{19}\ (42\%)}{(\mathrm{ArCHSe})_2} \qquad (9)$$

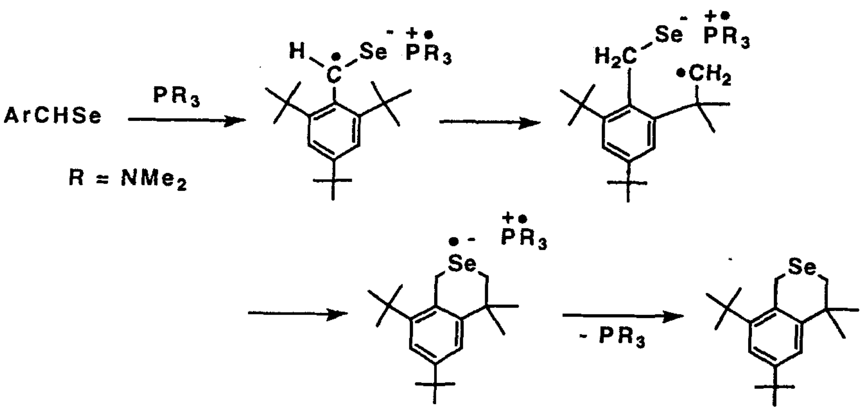
The isomerization to the selenide **6** is characteristic of **11**. In the presence of a catalytic amount of hexamethylphosphorous triamide, **11** undergoes fast isomerization to **6** even at room temperature. This stands in a sharp contrast with the fact that heating at 70° C for a long time (50 h) is required to promote the isomerization in the absence of the phosphorus reagent [Eq. (10)].



(10)

6 (96%)

Although a similar phosphine catalysed isomerization takes place also for thioaldehyde **4**, it requires refluxing for 7 h in benzene, again indicative of the higher reactivity of **11**. A plausible mechanism for the catalytic process is illustrated in Scheme 2.

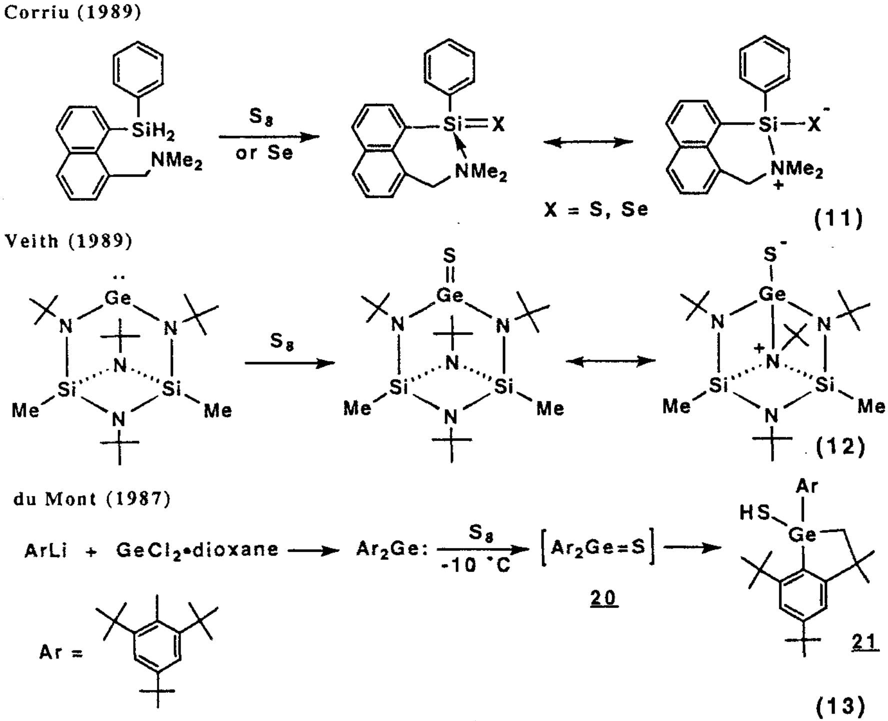


SCHEME 2

THIONE AND SELONE ANALOGUES OF GERMANIUM AND TIN

Although there are some reports on the transient species of $R_2M{=}X$ type (M=Si, Ge, Sn; X=S, Se),[1,12] very little has been known for stable compounds capable of existence at ambient temperature.

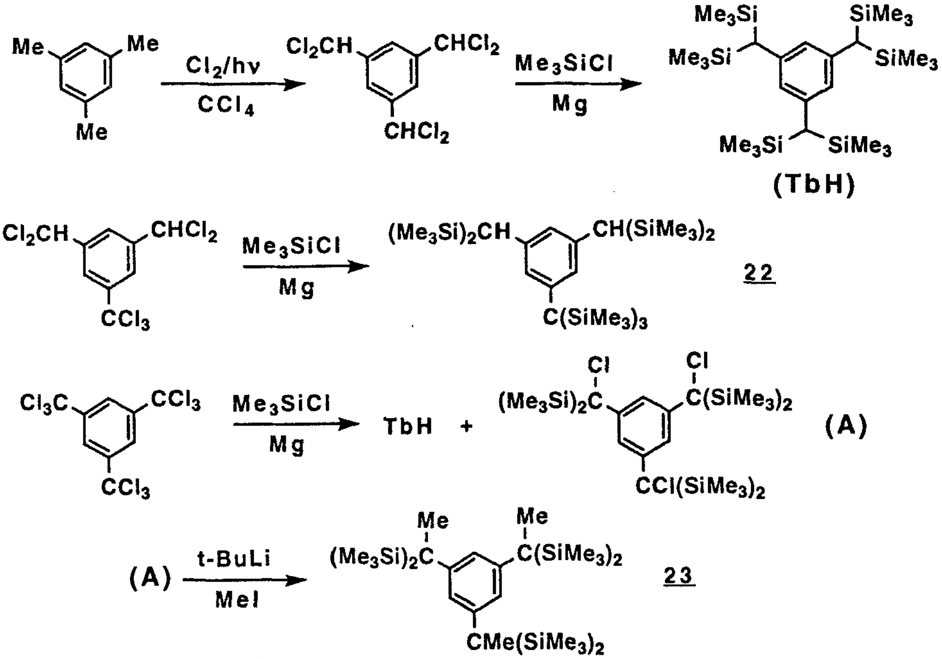
Corriu[13] has reported the isolation of silanethione and silaneselone [Eq. (11)], while Veith[14] has described the isolable germanethione [Eq. (12)]. These compounds, however, are stabilized by coordination of the amine nitrogen toward a silicon or germanium Lewis acid center resulting in great contribution of the zwitter ionic form as evidenced by X-ray structure analyses. du Mont[15] has reported the intermediary of an interesting germanethione **20** which undergoes intramolecular cyclization to **21** even at -10° C [Eq. (13)] (Scheme 3).



SCHEME 3

Development of a New Steric Protection Group

Although 2,4,6-tri-t-butylphenyl group is now recognized to be very useful for kinetic stabilization due to steric protection as shown, for example, by the successful isolation of stable thio- and selenoaldehydes **4**, **5**, **11** as described above, it has a serious drawback that its o-t-butyl group participates in intramolecular cyclization as shown in Eq. (13) or undergoes skeletal rearrangement in the reaction with electrophiles.[16] Therefore, we need to develop a new type of steric protection group which is expected to be bulkier than 2,4,6-tri-t-butylphenyl group. We have chosen 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (abbreviated as Tb) group. 1,3,5-Tris[bis(trimethylsilyl)methyl]benzene (TbH) can be easily prepared from mesitylene by chlorination and subsequent trimethylsilation[17] (Scheme 4). Similarly, even bulkier compounds such as **22** and **23** can be synthesized. In the following study we use TbH instead of **22** and **23** because of its easy accessibility.



SCHEME 4

The unique feature of Tb group can be seen from the ORTEP drawing shown in Figure 1.[18] The bis(trimethylsilyl)methyl group at the o-position is very bulky as a whole and protects effectively a reactive functional group at 1-position from, for example, dimerizaiton, but the presence of the hydrogen on the o-benzylic carbon makes the congestion at 1-position less severe, thus enabling easy functionalization at this position.

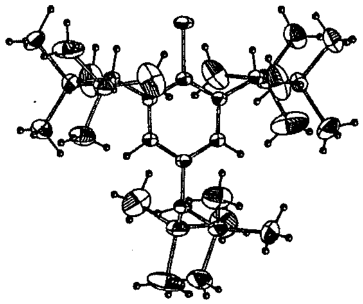
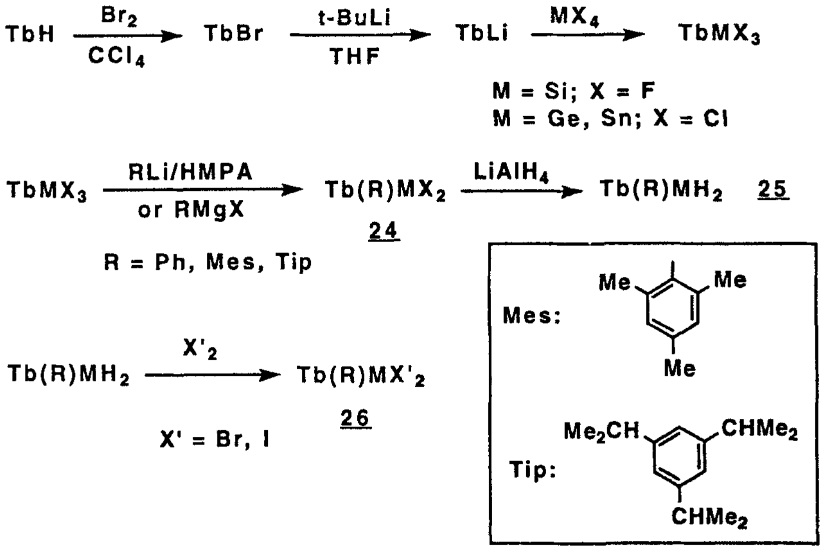


FIGURE 1 ORTEP Drawing of TbBr.

Synthesis and Structures of Tetrachalcogenametallolanes

TbH is easily converted to metal dihalides or dihydrides **24**-**26** (M=Si, Ge, Sn) having Tb and an aryl group (R=Ph, Mes, Tip) as shown in Scheme 5.



SCHEME 5

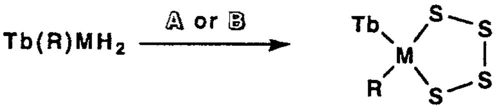
Reaction of **25** itself (method A) or its lithium salt (method B) with sulfur afforded 1,2,3,4,5-tetrathiametallolane **27** (M=Si, Ge, Sn) (Table 3). This makes a marked contrast to the results on the Corriu's dihydrosilane described in Eq. (11) where the product is a silanethione instead of a tetrathiasilolane. Similar reactions of **24** or **25** with selenium afforded again 1,2,3,4,5-tetraselenametallolanes **28** (M=Ge, Sn)(Table 4). The compounds **27** and **28** represent the first example of cyclic polychalcogenides of Group 14 elements in contrast to the fact that many known examples of similar polychalcogenides of transition metals.[19] The molecular structures obtained by X-ray structure analyses for some of these cyclic polychalcogenides are shown in Figures 2-4. Although they are similar to each other, tetrathiametalollanes take a half chair form while tetraselenometalolanes take an envelope form.

Reactions of Tetrachalcogenametallolanes

With these tetrachalcogenides in our hand, we submitted them to dechalcogenation reaction since they were considered to be a good precusor for double bond compounds between Group 14 and 16 elements. When **27** (M=Ge, R=Mes) was reacted with hexamethylphosphorous triamide **29**, cis-dithiadigermetane **30** and germanethiol **31** were obtained. Their formation can reasonably be explained in terms of intermediacy of germanethione **32**; dimerization and reaction with adventions water in the reaction system lead to **30** and **31**, respectively. Thermal reactions of **27** (M=Ge, R=Mes) and **28** (M=Ge, R=Mes) were carried out in the presence of 2,3-dimethylbutadiene in the hope of obtaining Diels-Alder adducts of possible intermediate **32**, but here again the products were cis-dimers (**30** and **33**) of **32** and its selenium counterpart (Scheme 6).

A similar deselenation reaction of **28** (M=Sn, R=Mes) with phosphine **29** gave two dimeric products of stannaneselone **36**, i.e., cis-(**34**) and trans-diselenadistannetanes (**35**) in contrast to the sole formation of cis-isomer in the reaction of **27** (M=Ge, R=Mes) described above. On the other hands, the reactions of bulkier **28**

TABLE 3 Synthesis of 27.

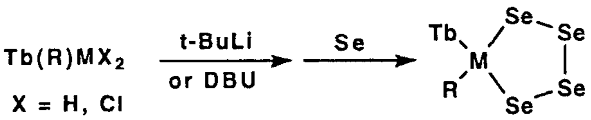


27

𝔸: S_8/Δ ; 𝔹: 1. *t*-BuLi/-78 °C/THF, 2. S_8/Δ

M	R	Conditions	Yield/%
Si	Mes	A, 230 °C	7
Ge	Mes	A, 150 °C	57
Ge	Mes	B, reflux	74
Sn	Mes	A, THF reflux	92
Sn	Mes	B, -78 °C~RT	33

TABLE 4 Synthesis of 28.



28

M	R	X	Conditions	Yield/%
Ge	Mes	H	*t*-Buli	22
Ge	Mes	Cl	*t*-BuLi	19
Ge	Tip	H	*t*-BuLi	13
Sn	Mes	H	*t*-BuLi	33
Sn	Mes	H	DBU	35
Sn	Mes	Cl	*t*-BuLi	27
Sn	Tip	H	DBU	89
Sn	Tip	Cl	*t*-BuLi	71

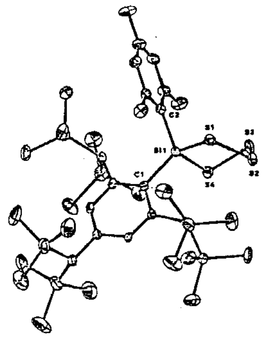


FIGURE 2 Molecular Structure of Tb(Mes)SiS_4.

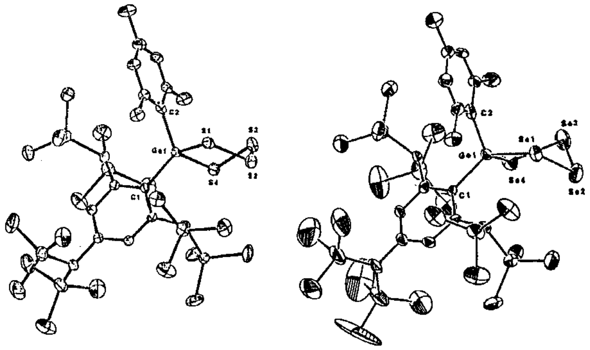


FIGURE 3 Molecular Structures of Tb(Mes)GeY_4 ($Y = S$, Se).

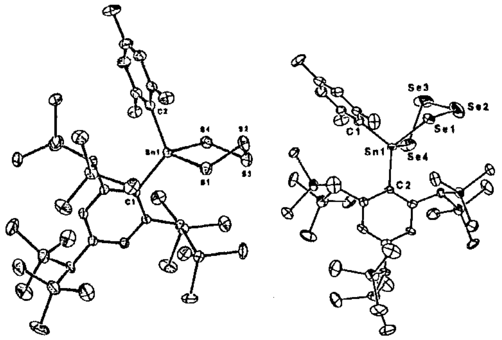
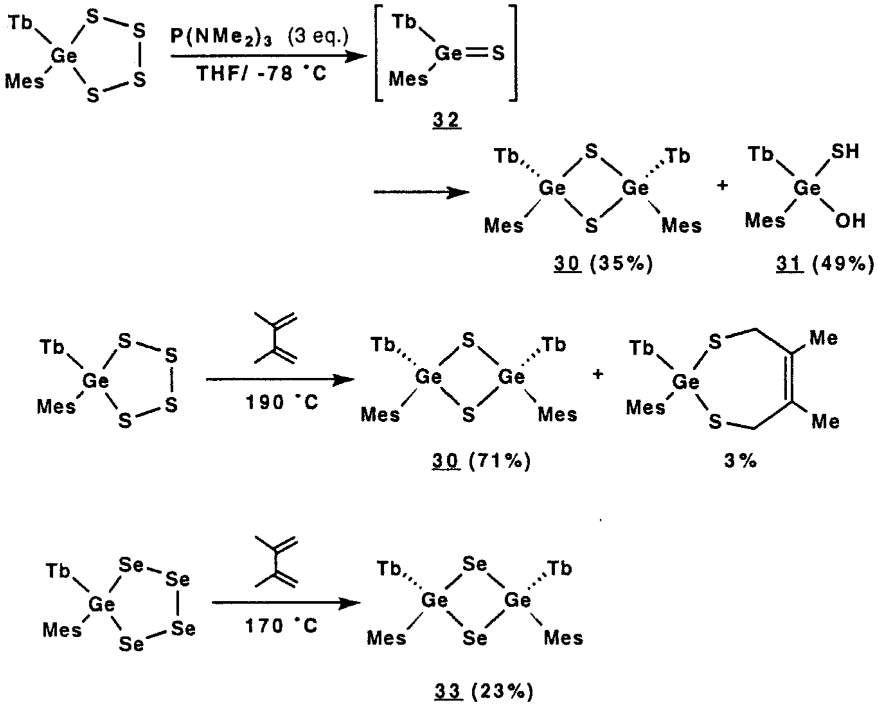
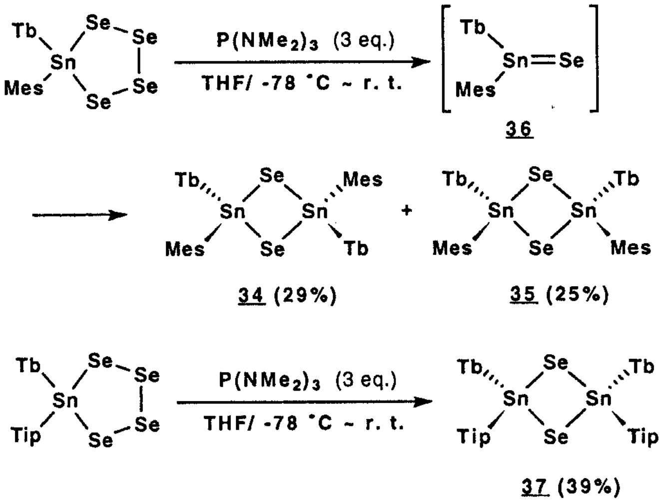


FIGURE 4 Molecular Structures of Tb(Mes)SnY_4 ($Y = S$, Se).

(M=Sn, R=Tip) produced only cis-isomer **37** (Scheme 7). These stereochemical outcomes are explicable in terms of steric congestion around these four-membered rings as revealed by X-ray structural analyses shown in Figures 5 and 6.



SCHEME 6



SCHEME 7

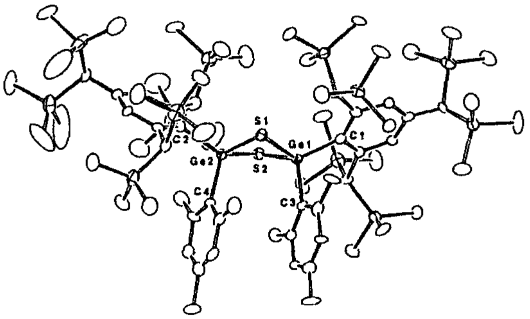


FIGURE 5 **Molecular Structure of** ***cis*****-[Tb(Mes)GeS]$_2$ (30)**

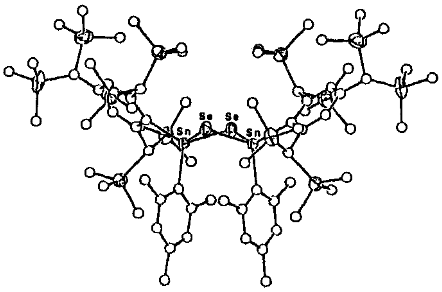
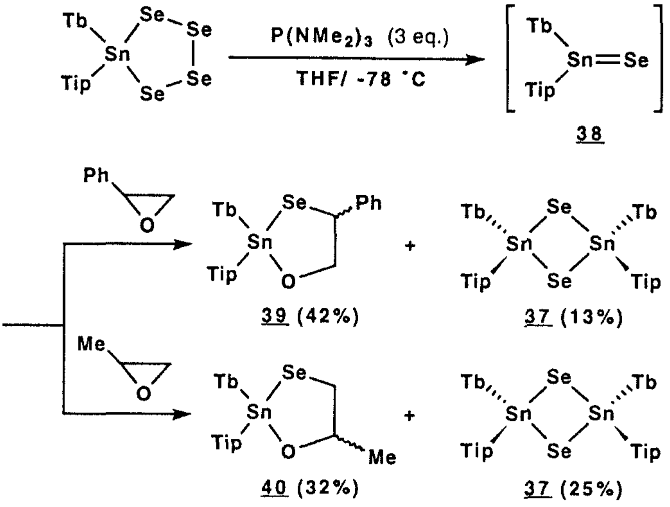


FIGURE 6 **Molecular Structure of** ***cis*****-[Tb(Mes)SnSe]$_2$ (35).**

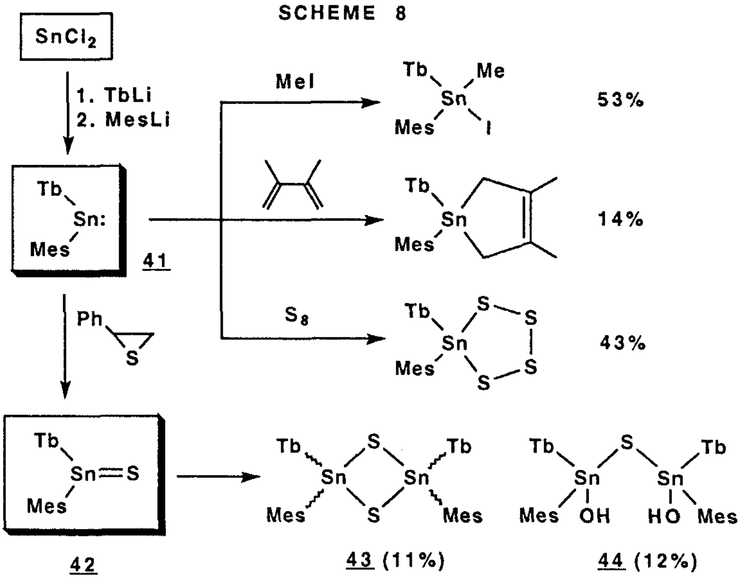
In the case of dithiadigermetanes, the trans-isomer cannot exist because of severe congestion by two Tb groups as revealed by inspection of the molecular model, whereas, in the case of diselenadistannetanes, both isomers are capable of existence because longer bond distances of C-Sn and Sn-Se compared to those of C-Ge and Ge-S mitigate the congestion by two Tb groups. It is interesting that the cis-isomers are folded while the trans-isomer is flat.

In order to trap an intermediary stannaneselone the deselenation reaction of **28** (M=Sn, R=Tip) with **29** was performed in the presence of styrene oxide and propylene oxide to give 1,3,2-oxaselenastannolanes **39** and **40**, respectively, in addition to the dimer **37** (Scheme 8).

Since it is desirable to develop a different approach to tin-containing double bonds, we attempted the sulfurization of a stannylene by an episulfide. Stannylene **41** was synthesized by the sequential reactions of tin dichloride with TbLi and mesityllithium and its formation was confirmed by the trapping reactions with methyl iodide, 1,3-dimethylbutadiene, and sulfur as shown in Scheme

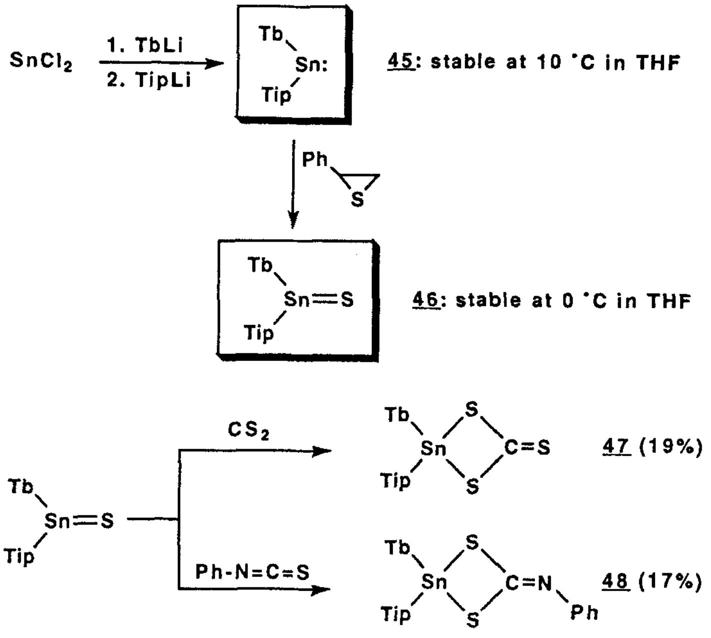


SCHEME 8



SCHEME 9

9. When styrene episulfide was added to the solution of **41**, the dimeric product **43** was obtained along with **44**, suggesting the intermediary formation of stannanethione **42**. In the hope of



SCHEME 10

increasing the stability of a stannanethione, we used bulkier stannylene **45** as a precursor. The stannylene **45** was found to be stable at 10° C in a THF solution for a long time. Stannanethione **46** obtained by the reaction with styrene episulfide was also found to be stable at 0° C in a THF solution, as evidenced by trapping with carbon disulfide and phenyl isothiocyanate giving new heterocycles **47** and **48** (Scheme 10). This is the first example of a stannanethione stable in solution and it is reasonably expected that stannaneselone might be also stable at least in solution. We are now making our effort toward the isolation of stable compounds of these species.

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